INJECTION-COMPRESSION AND CO-INJECTION
MOLDINGS OF AMORPHOUS POLYMERS:
VISCOELASTIC SIMULATION AND EXPERIMENT

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INJECTION-COMPRESSION AND CO-INJECTION
MOLDINGS OF AMORPHOUS POLYMERS:
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Dissertation

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Injection-compression molding (ICM) and co-injection molding have gained increasing importance in manufacturing of polymer products. Scientific understanding of these processes is presently limited and no attempts have been made to simulate co-injection molding using a viscoelastic model. In addressing this issue, the present study provides results of comprehensive viscoelastic simulations and experimental investigations of the residual stresses and birefringence in center-gated disk moldings of amorphous polymers obtained by ICM and sequential co-injection molding (SCIM) at various processing conditions. The governing equations for viscoelastic simulation of ICM and SCIM processes were derived using a nonlinear viscoelastic model. The equations were solved using a hybrid control volume/finite element/finite difference method.

In general, residual stresses and birefringence in moldings arise from the flow- and thermally-induced contributions. To consider the thermal contribution, simulations and experimental study of birefringence in freely quenched multi-layered plates were carried out. The flow- and thermally-induced stresses were simulated using nonlinear and linear viscoelastic theories, respectively. The overall residual birefringence in moldings was obtained by summation of the flow- and thermally-induced birefringence contributions calculated using the stress-optical rule and photoviscoelastic constitutive equation, respectively. The numerical results were found to be in fair agreement with experimental data on the distribution of residual birefringence, $\Delta n$, and average
transverse birefringence, $<n_{ss} - n_{60}>$, of the ICM made from polycarbonate (PC) and polystyrene (PS). It was found that the melt temperature and compression stroke strongly affected the residual birefringence in ICM, while the mold temperature had less effect. The numerical and experimental results of the gapwise distribution of the residual birefringence, $\Delta n$, and interface of the SCIM were obtained at various processing conditions and various combinations of multi-layers of PC, PS and PMMA. It was found that the melt temperature strongly affected the birefringence and interface distribution, while the mold temperature had less effect. In addition, the interface was strongly affected by the volume of injected skin melt. Numerical results were found to be in a fair agreement with experimental data.
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CHAPTER I
INTRODUCTION

During polymer processing operations such as conventional injection molding (CIM), injection-compression molding (ICM) and co-injection molding, the polymers undergo simultaneous rapid nonisothermal cooling and transformation from the rubbery state to glassy states. This results in inhomogeneous densification of the polymer melts and viscoelastic properties. As a result of the nonisothermal cavity filling under the high strain rates flow residual stresses are generated by high shear stresses, and the first and second normal stress differences. The latter is due to the viscoelastic nature of polymer melts having large relaxation times. In particular, the relaxation of the flow stresses is hampered due to the fact that the relaxation time of the melt rapidly increases with time prior to the occurrence of vitrification. Accordingly, the flow stresses become locked into the molding. Since the flow stresses give rise to the molecular orientation, the measurement of frozen-in molecular orientation in terms of residual birefringence is an indirect indication of the residual flow stresses. As the cooling progresses, thermal stresses and birefringence develop and become residual when the polymer melts vitrifies. Therefore, the residual stresses, molecular orientation, and birefringence can be attributed to two main sources. The first is due to the shear and normal stresses that develop during nonisothermal flow. Then stresses get frozen-in due to the occurrence of crystallization or solidification arising from the subsequent rapid cooling. Residual stresses and
birefringence strongly affect warpage, shrinkage, dimensional stability and end-use mechanical performance of the polymeric products. The optical performance of a molded product is also affected. Thus, it would be desirable to be able to control the residual stresses that affect the warpage and shrinkage and to minimize birefringence for the optical quality control. In reality, however, it has not been easy to predict the residual stresses and birefringence because of lack of complete understanding of complicated behavior of polymeric materials during the entire co-injection molding and ICM as well as CIM processes. For instance, nonlinear viscoelastic behavior, nonequilibrium thermodynamics and volume relaxation phenomena during the filling, packing and cooling stages and photoviscoelastic effect during the solidification, linear viscoelastic behavior after ejection and the nonisothermal crystallization kinetics become important.

This dissertation consists of three relatively independent but closely related topics: ICM, co-injection molding and residual birefringence in freely quenched multilayer plates. Each topic is described in two chapters. One includes theoretical modeling and mathematical formulation and second includes simulation and experimental study. The research deals with accurate predictions of the flow-induced and thermally-induced residual stresses and birefringence through nonlinear viscoelastic simulation of ICM including filling, compression, packing and cooling stages and co-injection molding process including filling, packing and cooling stage for amorphous polymers by solving the transport equations of mass, momentum and energy simultaneously with a nonlinear viscoelastic constitutive equation for flow-induced residual stresseses and birefringence. For thermally-induced residual stress and birefringence, linear viscoelastic constitutive equation and linear photoviscoelastic
models with a first order rate equation for the volume relaxation behavior were used with the strain-optical coefficient and a Young’s modulus from a tensile stress relaxation experiment. To verify the numerical simulation, several amorphous polymers were used. In particular, polystyrene (PS), polycarbonate (PC) and polymethyl methacrylate (PMMA) were chosen as representative polymers for the study. The frozen-in molecular orientation in terms of total residual birefringence resulting from the flow-induced and thermally-induced contributions for co-injection molding experiment was measured at a variety of processing conditions, such as packing pressure, packing time, melt temperature, mold temperature, injection speed and volume of first injected melt. Also thermally-induced residual birefringence for multilayer plates obtained in free quenching experiment was measured. For ICM, polystyrene (PS) and polycarbonate (PC) were used. Total residual birefringence in ICM products stemming from the flow-induced and thermally-induced contributions was measured.

The outline of the dissertation which summarized this research is given as follows. Chapter II gives an up-to-date review of the existing experimental studies and simulation models for residual stress and birefringence in co-injection molding and ICM. The current knowledge on co-injection molding regarding the interface development and the interrelations among processing conditions, material properties (mainly concerned with rheological properties), and material combination is described. The diverse methodologies for the two-dimensional or three-dimensional process simulation of co-injection molding with interface treatment are presented with relevant comments. In the case of ICM, the current state of knowledge on experiment and simulation is described with relevant comments regarding the processing characteristics including compression
speed, switch time from injection to compression, compression stroke, as well as melt temperature and mold temperature. Finally, earlier experimental and simulation studies on the flow-induced and thermally-induced residual stresses and birefringence in CIM are reviewed.

Chapter III is mainly concerned with the physical modeling and the corresponding numerical simulation of a precision ICM. Simulations of flow and thermal birefringence developed during the filling, compression, packing, and cooling stages of the ICM of a center-gated disk mold are considered by using a hybrid control volume finite element and finite difference method (CV/FE/FD). The compressible nonlinear viscoelastic model was used to calculate the flow stresses. The flow birefringence was calculated through a linear stress-optical rule. Linear viscoelasticity, photoviscoelasticity and free volume theory used to take into account the density relaxation phenomenon were considered to predict the thermally-induced birefringence. The total residual birefringence is taken to be the sum of the flow birefringence related to the flow stresses through the stress-optical rule, and the thermal birefringence related to the thermal stresses through the photoviscoelastic constitutive equation.

In Chapter IV, a methodology is developed to calculate the transient and frozen-in thermal birefringence from mechanical and optical material functions for the multilayer plates. The residual birefringence and stresses in the freely quenching multilayer plates are simulated and predicted based on stress relaxation experiments over a wide range of temperature with simultaneous measurements of Young’s modulus and the strain-optical coefficient \( C_\varepsilon \) conducted on polystyrene (PS) and polycarbonate (PC).
and master curves of $C_\varepsilon$, the stress-optical coefficient ($C_\sigma$), and Young’s relaxation modulus obtained in the reference [1,2].

In Chapter V, a physical modeling and a two-dimensional numerical simulation of the sequential co-injection molding of a center-gated disk cavity by using a hybrid control volume finite element and finite difference method (CV/FE/FD) on the modeling of interface evolution, encapsulation phenomenon and flow-induced residual stress and birefringence under various processing conditions and material combinations are presented. Three stages of the sequential co-injection cycle-filling, packing, and cooling-are included. A physical model of multilayer flow, which is based on the kinematics and dynamics of the interface development and Hele-Shaw type of flow, is proposed. The total residual stresses are taken to be a sum of the flow stresses calculated using a compressible nonlinear viscoelastic constitutive equation and the thermal stresses calculated using a linear viscoelastic constitutive equation. The total residual birefringence is taken to be the sum of the flow birefringence related to the flow stresses through the stress-optical rule, and the thermal birefringence related to the thermal stresses through the photoviscoelastic constitutive equation. The Tait equation is used to describe the P-V-T relationship especially for the packing stage.

To verify these physical models, and to test the capability of the process simulations and predictions of average transverse birefringence, flow-induced birefringence, thermally-induced birefringence, or interface development in the moldings, the models are applied for different molding processes in the following chapters. The results of numerical simulation are compared with data from the corresponding molding experiments. The effect of processing variables and rheology of the materials is
experimentally and theoretically evaluated. In Chapter VI, the model which was presented in Chapter III is utilized to analyze the ICM of different amorphous polymers to describe the effects of process condition on the average transverse birefringence and total residual birefringence distribution. In Chapter VII, the free quenching experiments were carried out under various quenching conditions to verify the model which is suggested in Chapter IV. Thin multilayer plates consisting of PS, PC or PMMA were used in the quenching experiments. The effect of initial temperature on the residual thermal birefringence was studied. The birefringence data were compared with the results of a numerical simulation based on the linear viscoelastic and photoviscoelastic constitutive equations for the mechanical and optical properties, respectively. In Chapter VIII, the model which is formulated in Chapter V is employed to simulate sequential co-injection molding of different amorphous polymers to describe the viscosity ratio and process conditions on interface evolution, encapsulation and flow-induced and thermally-induced birefringences.

Finally, the summary of the present research is given in Chapter IX.
CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Co-injection Moldings

Co-injection molding was invented in the early 1970s by researchers at Imperial Chemical Industries (ICI) in the United Kingdom [3-5]. Co-injection molding, sometimes referred to as sandwich injection molding, is a hybrid injection molding process that uses two separate and distinct resin components. Generally, the mechanics of this process relies on sequential injection of two materials through the same gate or gates or simultaneous injection of both skin and core materials after some initial amount of skin material is first injected into the cavity. As a result, an encapsulated sandwich-structure product is obtained with the core material embedded within the skin material. The advantages of the sandwich structure are akin to those derived from co-extruded sheets and films and bicomponent fibers. Co-injection molding eliminates many of the manufacturing steps required by conventional lamination and coating processes, combining the desired properties of two or more polymers by melt fabrication. Different properties of these two polymers and their distribution in the moldings greatly affect the applications of this molding process. Co-injection molding can offer significant quality advantages due to the skin material. The combination of two different materials can provide properties, which cannot be obtained from a single resin. The skin layer can use
special polymers to provide hardness, impact strength, surface properties, chemical and flame resistance, compression strength, printability, EMI shielding and other functions. Co-injection molding can also offer significant cost advantages due to the core material. The core layer can contain recycled or inexpensive materials. It may also reduce part weight, part cost, injection pressure, residual stresses and warpage when compared to the traditional single material injection molding.

In co-injection molding, two (dissimilar but chemically and rheologically compatible) polymers are injected into a mold cavity simultaneously or sequentially. Getting the proper combination of two polymer resins into the same cavity makes co-injection molding more difficult than traditional injection. One of the crucial factors for the success of the co-injection molding process is the combination of suitable skin and core materials. Therefore, a number of key issues need to be considered when choosing these materials [6]. First of all, both materials should exhibit similar shrinkage and thermal expansion behavior. A mismatch in the behavior may lead to sinkmarks, component warpage, high residual stresses, delamination and lower interfacial bond strength. Secondly, the materials must show some degree of bonding at the skin-core interface. Good bond strength between skin and core is achieved through interfacial diffusion governed by compatibility or solubility between the polymer melts. A lack of adhesion between skin and core layers leads to internal stresses from molding causing delamination under external loads, reducing the overall strength of the molding. Finally, both polymers must have a similar range of processing temperatures since they are injected simultaneously through a single injection nozzle. A significant temperature differential between the skin and core material may cause degradation of the material.
with the lower melting point during injection. The skin should have the same or preferably lower viscosity than the core. A high viscosity skin results in a low flow rate and the core melt may break through the skin and form the surface layer. This can be avoided by controlling cylinder temperatures or by using a lower melt index material in the core.

Even after selecting a suitable combination of polymers, very often the success in co-injection molding is achieved after a long trial and error learning process. For example, two-channel co-injection molding can be used to produce hybrid window moldings for automotive glazing applications [6]. For a core material, polycarbonate without chemical or ultraviolet resistance instead of glass could be combined with a weatherable, chemically resistant skin. However, the combination of two transparent plastics may generate a large amount of hazing if the mold filling was not controlled properly. This behavior results from significant interfacial mixing between skin and core caused by turbulence during the injection cycle within the system and a mismatch between refractive indices as well as the viscosity of both skin and core material.

Development of co-injection molding can be improved and become less time consuming if a suitable process model was available. However, modeling of such processes is not well developed and is mostly based on many simplifying hypotheses. The material distribution and the interface shape in moldings are the most important quality characteristic. The interface shape is influenced by a large number of parameters including material properties, process parameters and geometry. Therefore, it is very difficult to reliably achieve required the interface shape. Additionally, in the case of molding optical components, it is difficult to predict their optical performance. Therefore,
accurate numerical predictions of the process behavior and optical properties can help to achieve the optimal design of the product.

2.1.1 Technology

Prehistory of co-injection molding dates back to 1960’s when a structural foam molding was first introduced by Dow Chemical in a patent issued in 1962 [7]. This process is now available in a modified form as the DOW-TAF process which is a high-pressure process. Subsequently, Union Carbide developed a low-pressure process [8], in which the mold is not filled completely during injection. If the polymer melt fills the mold cavity completely, this is called a high-pressure process. The advantages of structural foam parts are stiffness in flexure, low warpage and weight reduction. However, it has a drawback of non-uniform coloration caused by swirl marks and a nonsmooth surface. The major development in later years has aimed at eliminating this drawback without affecting the advantages of structural foam. While a large number of processes have been proposed, only two methods have proved technically and economically viable [9]. These are the gas counter-pressure process and the multi-component process. In the gas counter-pressure process (e. g. Allied process, and Asahi-Dow process), the good surface is achieved by preventing foaming during injection through the use of a highly pressurized counter-gas in the cavity. Foaming can take place only towards the core as a result of volume contraction that occurs upon cooling. Mold cost is, however, very high because it needs to be completely sealed. In the multi-component process (e. g., ICI process, Hanning process), two materials are used in order to make the sandwich structured part which consists of an unfoamed polymer as the skin and a foamed polymer
as the core. As a result, the molded part has a smooth, uniformly colored skin like that of a conventional molding, as well as the advantages of a structural foam core [10,11]. Multi-component injection processes include all possible processes in which two or more materials are used in sequential and simultaneous co-injection (sandwich injection) and over-molding (sequential process).

Co-injection molding processing was originally developed in early 1970s by ICI in the UK [3-5] to produce molded parts with a foamed core and a solid skin. In co-injection molding, two different polymers are injected into a mold cavity sequentially or simultaneously in such a way that one polymer melt forms the skin and the other melt becomes the core. The first-injected melt cools and possibly solidifies at the surface as it comes into contact with cold mold, while the second-injected melt forces the first one towards the flow front while flowing beneath the skin layer formed by the first polymer. Unlike other multi-material molding processes, the co-injection process is characterized by its ability to completely encapsulate an inner core resin with an outer skin material. This encapsulation of one polymer by another provides a product in which only one material is evident, unless you section the product. A cross-section of a molding shows a three-layer structure: skin, core, and skin. That is why co-injection is sometimes referred to as sandwich molding [12,13].

The first version of the co-injection molding process is classified as the single-channel technique [3-5]. An injection molding machine with two injection units is used. The polymer melts are injected sequentially into a cold mold through an adjustable valve. The melt injected first forms the skin and surrounds the core, which is injected afterwards. The major disadvantages of this technique are a drop in mold cavity pressure and
stagnation of the melt front when switching from injection of skin melt to injection of core melt. This technique commonly has skin defects associated with the changeover from one material to another. A distinct switching mark is revealed on a component surface in the form of a dull ring. So, the technique is limited in practical applications to manufacturing simply shaped sandwich constructions with three layers.

In order to obtain a good surface quality without flow or switching marks and differences in gloss, melt flow needs to be maintained constantly. This is achieved by two-channel technique [14-16] developed by Battenfeld and Schloemann-Siemag. In this process a phase of simultaneous injection was used in conjunction with a specially designed injection nozzle, which has two separate concentric channels that can be independently controlled. For the two-channel technique used in the Battenfeld co-injection molding process having the nozzle configuration of two separate, concentric channels that can be independently operated, opened, and closed hydraulically, both skin and core materials could be injected simultaneously in a single injection phase. Therefore, a phase of simultaneous injection of skin and core avoids switching marks by maintaining a constant flow front velocity. The duration of the simultaneous injection phase depends on the material and especially on the mold geometry. As a result, more complex and flexible moldings, such as thick-walled parts with foamed cores and thin, solid layers, can be achieved in a product with good surface quality. Applications are, for example, shielding against electromagnetic interface (EMI) by a conductive layer inside the product [17], and the anti-electrostatic sandwich parts [18] which combine a conductive filled skin material with a cheaper unfilled core material based on the same material for good skin-core-adhesion. But the two channel simultaneous injection is more difficult to
control and requires time consuming trials. Also, the skin thickness close to the gate area usually becomes very thin. Viscous dissipation heat from the flowing melts can make the skin remelt and be flushed away in this region [19]. Therefore, some other techniques for sandwich molding, such as mono-sandwich and three-channel techniques may be preferred for some applications [12,19].

The mono-sandwich technique, which was developed by Ferromatik Milakron [12], uses a sequential injection process. It is similar to the single-channel technique. However, here two polymer melts are layered in one injection cylinder by melting the skin material in a separate side extruder and delivering it through a special hot runner to the front of the screw in the main cylinder. When a sufficient amount of melted material has accumulated in front of the screw, it starts rotating and feeds the core material. The injection is then done the same way as for normal injection molding by pushing the screw forward. Thus, the switching marks are not seen in this case because only one injection unit is used. Very thin walled parts can be produced by the method [19].

A three-channel technique has a nozzle with an extra channel for the skin in the center of the gate, which can reach the opposite side of the molding. The injection of skin material to the two surfaces can be regulated separately, which gives an additional possibility to control thickness. However, this special design can only be used with a central gate. For other gate geometries or multi-cavity moldings, the two-channel or single-channel technique is preferred.

In summary, the co-injection molding process mechanics relies on the sequential injection of two different materials through the same gate, or gates, or simultaneous injection of both skin and core materials after some amount of skin material is first
injected into the cavity. Sometimes an additional very small amount of skin material injection will cap the end of the sequence described.

Overmolding is a sequential process technique in which a preform produced in the initial injection phase is automatically transferred to a second, differently shaped cavity in the same mold. Then, a second material is molded into or around the preform through different injection points. It includes integrated injection molding, which employs movable cores or slides and two-color injection molding, which is to rotate the core of the mold in conjunction with two different sets of cavities [20,21].

As stated above, the co-injection molding was originally developed to be an alternative to the structural foam process using a foamed core combined with a solid skin. Today the process has developed toward several different material combinations using the skin material for sufficient surface properties (e.g. appearance, hardness, thermal or chemical resistance, soft touch), and the core material with sufficient mechanical properties for cost reduction (for example using recycled materials). Selden [19] provided a good review on common technologies for the manufacturing of sandwich molded products, material selection and material combinations. Eckardt [22] also provided a good review on the co-injection process charting new territory and opening new markets. According to him, products with tailor-made properties by combining skin and core materials can be obtained through co-injection molding. Some examples for these properties are: high quality surface without sink marks using foamed core, high quality skin/low cost core, reinforced skin/nonreinforced core, nonreinforced skin/reinforced core, flexible skin/rigid core, rigid skin/flexible core and skin/core with barrier properties for food storage. Eckardt [10] also described the typical defects encountered in multiple-
component (co-injection) process. These include incomplete filling, core breakthrough, poor foam core distribution, surface waviness, skin marks, voids, changeover marks, concentric rings resembling grooves on a phonograph record, matt (dull) surface, high density, weight fluctuation from shot to shot and no adhesion between skin and core. He also presented the methods to eliminate the defects, as indicated in Table 2-1.

Table 2-1 Defects Encountered in Co-injection Moldings [10].

<table>
<thead>
<tr>
<th>Defects</th>
<th>Corrective Action</th>
<th>Machine</th>
<th>Mold</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part not filled</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Glossy spot near gate</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>Streaks (splay) on surface</td>
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<tr>
<td>Core breakthrough</td>
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<tr>
<td>Poor core distribution</td>
<td></td>
<td>X</td>
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<td>X</td>
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<tr>
<td>Glossy spots</td>
<td></td>
<td>X</td>
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<tr>
<td>Surface waviness</td>
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<td>Flow lines (weld lines) after opening</td>
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<td>X</td>
<td>X</td>
<td></td>
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<tr>
<td>Matt (dull) surface</td>
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<tr>
<td>Sink marks</td>
<td></td>
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<tr>
<td>Voids</td>
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<td>Changeover marks (halo)</td>
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<tr>
<td>Concentric rings</td>
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<td>High density</td>
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<tr>
<td>Weight fluctuations</td>
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<tr>
<td>After blow</td>
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<tr>
<td>Poor adhesion between skin and core</td>
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A number of cost and quality advantages offered by co-injection molding over conventional injection molding are described [12,13,22-26]. In the case of thick-wall products, co-injection is preferred to conventional structural foam due to their superior surface appearance. A combination of properties not available in a single resin can be achieved by combining different materials and reduction in part cost by using lower cost materials in the core. Co-injection may be the most effective manufacturing technique for ensuring both highly recycled material content and repeatable, high-quality products.

2.1.2 Experimental Studies

Co-injection molding requires advanced technical skills, because many molding factors are involved. To understand the internal sandwich structure formation and the melt flow behavior, it is important to properly design the co-injection molding process. Over the past three decades, many experimental studies dealing with co-injection molding have been published [27-54]. The experiments were mainly performed in order to elucidate the effect of processing conditions and material properties on the interface shape, material distribution and mechanical properties. Donovan et al. [27] were the first to carry out an experimental study on sequential sandwich injection molding process with special nozzle design using a two annular channel technique and various molds including plaque, disk, telephone housing and telephone handle molds. They applied this process to recycle thermoplastics. The experimental studies had been conducted to determine the effects of processing parameters on the amount of scrap material that can be encapsulated and its effect on impact strength. A wide variety of acrylonitrile-butadiene-styrene (ABS) molding compounds were used, including various colors of virgin ABS compounds and
various grades of scrap ABS compounds. They found that approximately 40 percent of
the total shot can be molded beneath virgin plastic in parts having stringent appearance
requirement.

Most of early experimental studies published on isothermal co-injection molding
under various processing conditions and material combinations have been done by White
et al. [28-31]. White and Dee [28] investigated the sequential injection of polyethylene
and polystyrene into the end-gated rectangular mold using modified Instron rheometer
combined with a nozzle mold instead of a capillary die. They indicated that two phase
melt flow in injection molding was sensitive to differences in rheological properties of
polymer melts. They found that very different phase distributions could be induced by
reversing the order of injection of skin and core melts of grossly different rheological
properties. Later, White and Lee [29] performed sequential co-injection using an Instron
capillary rheometer, where polymethyl methacrylate (PMMA) and low density
polyethylene (LDPE) as skin melts and LDPE and polystyrene (PS) as core melts were
injected into a mold in the form of an annular ring and a core, respectively. The melt with
the lower viscosity did encapsulate the melt with the higher viscosity during the flow in
the runner section, and a skin-core sandwich configuration resulted in the cavity.
However, if the annulus contains a higher viscosity melt, phase inversion may occur. In
an isothermal sequential cavity filling of two melts, Young et al. [30,31] reported
experimental observations for various material combinations using PS and HDPE with
different viscosities LDPE and polypropylene (PP) for sequential co-injection molding. A
center-gated disk and end-gated rectangular mold were prepared. They indicated that the
phase distribution is very sensitive to the viscosity ratio of core to skin material, which
primarily influences the interfacial shape in sandwich-molded parts. For material combinations with a very large viscosity ratio, the core melt does not penetrate sufficiently deep into the skin melt resulting in non-uniform skin thickness. On the other hand, a very small viscosity ratio causes the second melt to completely penetrate through the first giving rise to breakthrough phenomenon. They found that the most uniform skin-core structures were obtained when the skin melt exhibits a slightly lower viscosity than the core melt. They also found that temperature sensitivity of the viscosity for the skin is very important to the development of encapsulation.

Sequential co-injection molding of filled and unfilled polymers under non-isothermal conditions was carried out by Akay [32] using a center-gated disk mold. He investigated skin/core structure development, interface adhesion and interface instability. The materials investigated were chalk- and glass-fiber filled polypropylene (PP) and unfilled polyethylene (PE). He found that crucial processing conditions for obtaining a certain type of skin/core structure under non-isothermal flow are different from isothermal flow by White and co-workers [28,29]. To achieve uniform skin/core structure, injection speed and the temperature of the melts and the mold are more important than the viscosity ratio. The combination of materials is not significant in obtaining a skin/core structure for reinforced polymer, but it is important in obtaining extensive phase interlocking. The latter is reduced, if the flow rate and the mold temperature are low. Interface instability occurs when the skin melt has higher viscosity than the core melt and when a high injection speed is used. Optimum fiber orientation along the flow direction was obtained only when the fiber-filled material was injected first.
Mold filling studies in a center-gated disk for sequential injection molding were also done by Schlatter et al. [33] to test the influence of processing parameters on the interface location. They utilized the mono-sandwich technique on two polystyrene (PS) melts with different viscosity for skin and core materials. As mentioned before, the technique was developed by Ferromatik Milakron [12]. The effect of processing parameters including flow rate, temperature, and volume ratio of skin to core melt, which was colored in a masterbatch, were investigated. In particular, the influence of injection velocity on the skin thickness was found to be more significant than the influence of viscosity ratio and injection temperature because of the shear thinning effect. The increased core injection rate and skin temperature lowered the skin thickness. They concluded that generally, a high skin temperature and flow rate and a low core temperature are beneficial to get a desirable high core content.

Flow behavior in the center-gated rectangular mold during the sequential co-injection process was investigated by Derdouri et al. [34]. They used ABS as both skin and core materials and ABS containing a black pigment as a core material and polycarbonate (PC) as a skin material for visualization. The skin/core ratio was varied to gain further basic understanding of the flow behavior in terms of the mold and melt temperatures, the injection speed and the skin/core viscosity ratio. They concluded that, in addition to the viscosity ratio having an important effect on the onset of breakthrough of the core through the skin, there is a critical skin/core ratio below which breakthrough occurs. For a given geometry, injection speeds and materials with similar viscosities, breakthrough is more sensitive to the mold temperature than to the melt temperature. In subsequent study, Nguyen et al. [35] used sequential co-injection molding as a method
for visualization. Skin/core material combinations were PC/ABS, high melt flow index (MFI) PC/PC and PC/high MFI PC. A small amount of pigment was added to the core polymer as a tracer material. They found that the stable interface between the skin and core materials can be obtained when the skin material has a lower viscosity and that fingering instability occurred when the core material has much lower viscosity than the skin.

The kinematics of flow behavior of core material and breakthrough phenomenon using a spiral-flow mold in the sequential sandwich injection molding was also investigated by Watanabe et al. [36]. The mold diameter, viscosity ratio and the melt temperature of skin and core materials were varied. The materials used in their experiments were three different viscosity grades of PCs with a black masterbatch, for a tracer material, used as a core melt and ABS used as only a core melt. The flow behavior of materials was categorized into four regions ranked in the filling order: primary injection, core advance, core expansion, and breakthrough region. The breakthrough phenomenon hardly occurred, when the cavity thickness was large, skin melt temperature was high, skin melt viscosity was low, the melt strength was high and the draw ratio of skin melt is high. They concluded that the breakthrough phenomenon depends not only on the melt strength of the freezing layer of the skin material but also on the draw ratio of the skin material at the flow front. In subsequent study, Watanabe et al. [37] investigated the flow behavior of skin and core melts to elucidate the flow patterns leading to breakthrough in sequential and simultaneous co-injection molding using a spiral-flow mold of rectangular cross section. For visualization, core material was loaded with a black master batch. PC/ABS blend was used as the skin material and ABS was used as
the core material. They found that the flow length of core expansion region increased with increasing time of simultaneous injection of skin and core materials. A wider and thinner core layer was generated with an increase of time of simultaneous injection. Processing variables that control the occurrence of breakthrough phenomenon in sandwich injection molded rectangular bars was also investigated by Watanabe et al. [38,39]. The core volume, injection speed and the skin/core viscosity ratio were varied. The effect of mold cavity thickness and skin material temperature on skin material viscosity, melt strength, and draw ratio were also studied using a spiral-flow mold. The flow length of the core material effectively was increased by increasing injection speed of the core material. It was found that the flow length of the core material was longer when the core material viscosity was lower than that of the skin material. However, in this case, breakthrough occurred much earlier. To avoid it, the core volume needed to be decreased. In contrast, breakthrough did not occur when the viscosity of the core material was higher than that of the skin material. Similar observations were made by Nguyen et al. [35] Furthermore, it was found that the flow length in the core expansion region increased and breakthrough phenomenon was delayed as the thickness of the mold cavity increased. The draw ratio corresponding to occurrence of melt fracture in the melt tension test is related to draw ratio of skin material at the flow front. As the mold temperature increased a higher draw ratio in the skin occurs. This is caused by a decrease of viscosity at the higher mold temperature, leading to ease of extension of the flow front of the skin material when pushed by the core material. Thus, a greater core volume can be accommodated.
Table 2-2 Compatibility of Various Material Pairs [19].

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+ = Good Adhesion, ○ = Poor Adhesion, - = No Adhesion
Selden [19] reviewed literature dealing with sandwich injection molding of thermoplastics. Table 2-2 shows results on adhesion of various material combinations that can serve as a guide to molders. A major portion of his review discussed the effects of viscosity ratio and injection molding parameters on mold filling, layer thickness and resulting mechanical properties. Selden [40] also investigated sandwich injection molding of incompatible polymer pairs (PA and PP). He observed that strong interfacial bonds could be formed by adding a relatively low amount of suitable conventional compatibilizer prior to co-injection molding of incompatible materials. He also measured the interfacial bond strength and a corresponding improvement of mechanical properties. This improvement was explained by the presence of interface instability caused by viscous fingering during the mold filling, giving mechanical interlocking between the two phases. Selden [41] went to investigate the effects of processing conditions in the monosandwich injection molding on material distribution and layer thickness in three dimensions. Square plates were molded with polyamide 6 (PA 6) as a skin material, and a 20% glass fiber-reinforced polybutyleneterephthalate (PBT) as a core material. Among five molding parameters including injection velocity, mold temperature, skin and core temperature, and core content, three parameters, namely, the injection velocity, core temperature, and core content were found to be the most significant process variables affecting skin/core distribution along the flow direction. A high core temperature at low injection velocity and high core content are the most important variables controlling uniformity of skin and core thickness. The volume of injected core is the most significant factor leading to a breakthrough phenomenon. That is, the core content should be decreased and/or injection velocity increased to prevent breakthrough. A uniform core
thickness and increased flow length can be obtained by using low injection velocity, high core content, and high core temperature.

Kadota et al. [42] performed a sequential injection molding of PS/PP pair using an end-gated rectangular mold to investigate the structure gradients as a function of the process history and injection sequence. They found that injection speed had the greatest effect on the flow front shape and the thickness along the flow direction of the core PP. This was primarily caused by the effect of injection speed on the local kinematics through heat transfer. During injection at slower speeds, the local solid-liquid boundary propagated further into the core region. As a result, the core polymer spreads more uniformly in the flow direction. For the birefringence of PS as a skin melt and PP as a core melt, they found that the relative location of the maximum birefringence value for the skin region shifts towards the mold wall if the injection speed of the core melt is increased at the same mold temperature. It was also revealed that crystalline orientation in PP was high when it was used as a skin polymer. This was due to formation of the outer skin layer of the part, mainly caused by the additional deformation of the PP during secondary shearing by the PS injection. When PP was injected as a core layer, the orientation level in PP was found to be low and mainly concentrated near the PP/PS interface. The latter was a result of slower cooling of the PP core causing the relaxation of the chain orientation developed during the flow prior to the crystallization. When PS was used as a skin material, the maximum birefringence was observed at intermediate distances between the mold surface and PP/PS interface. The position of the maximum corresponding to solidified layer thickness moves towards the mold surface with an
increase of injection speed. The reduction of the thickness of the solidified layer is a result of increasing heat generated by the shearing of core PP at a high injection speed.

Parsons and Toyoda [43] investigated skin-core structure in the sequential mono-sandwich injection process using rigid polyvinyl chloride (PVC), as a skin material, and glass fiber-reinforced PVC (GFR-PVC), PP, ABS and PC as core materials. They found that near the gate only the core material was a present. In some cases, the core diverged into multiple or discontinuous layers and flow of the core ceased leaving a skin-only region further away from the gate. It was found that the skin and core layers were more uniformly distributed through the mold at a low injection speed.

Sequential co-injection of various skin-core combinations using unreinforced and glass fiber-reinforced PP into dumbell test specimens were studied by Messaoud et al. [44]. The effect of injection speed and ratio of a skin to core volume on material distribution were studied. They found that the most uniform skin-core distribution was achieved when the ratio of the volume was 2. Also, the injection speed of the skin melt was a dominating factor on the skin-core distribution more so than that of the core melt.

The study of simultaneous co-injection molding has received less attention. Somnuk and Smith [45] investigated the mold filling process of simultaneous injection of an end-gated rectangular plaque. Four grades of polypropylene (PP) with different viscosities were used. Viscosity ratios at a shear rate of $10^3$ s$^{-1}$ and a temperature of 235°C were used for comparison purposes. According to them, the main advantage of simultaneous co-injection was that it may be controlled virtually in an identical manner to conventional single component injection molding, if one would fix the length of the
simultaneous phase. In order to obtain optimum parts, it is necessary to select material pairs within the viscosity ratios of 0.82 and 1.83.

Lee et al. [46] performed simultaneous co-injection molding of an end-gated rectangular mold using LDPE, HDPE, and PS. They found that a further advantage of simultaneous co-injection is that materials with a broader range of viscosity ratios may be utilized. The major processing parameters which had the significant effect on the interface evolution of two polymer melts during the filling phase are the injection rate and the length of simultaneous injection.

Eigl and Langecker [47] used simultaneous co-injection molding to empirically determine the interrelation between important processing parameters and material properties and the essential effects of the melt flow during the mold filling process. PP homopolymer of different viscosities was used in most of the experiments to determine the influence of a material on the distribution of the core layer. Based on their experiments, a phenomenological approach is proposed to describe the layer thickness formation and the spatial distribution of the components in the molded parts with the purpose to construct a simulation model close to practical operation. Two forms of instability, namely, viscous fingering and delamination of skin and core components, arising from wave instabilities within the plane of flow and in the thickness direction of the mold were also investigated. The formation of viscous fingers was found to occur at low viscosity ratios of the core and skin melt. The unstable two-component flow can develop during the process, resulting in an uneven distribution of the core component and formation of a fingerlike structure. Another form of instability is delamination of skin and core components. It occurs when the simultaneous phase lasts too long. A value of
\[ \Pi = \left( D^1 N_{1,A} / Q \eta_A \right) \cdot LS \]  (\( D \) is the wall thickness, \( N_{1,A} \) is the first normal stress difference of the skin component, \( Q \) is the flow rate, \( \eta_A \) is the viscosity of the skin component, and \( LS \) is the length of the simultaneous phase) was found to determine flow instabilities corresponding to appearance of viscous fingering and breakthrough.

Chen et al. [48,49] used the skin-core-skin sequential co-injection molding process for the dynamic visualization of flow in a transparent mold. A mold consisting of three different cavities for visualization of the melt and fountain flow behavior in cavities with abrupt contraction and expansion, and the weld line formation in a cavity with a block insert was employed. Transparent PS was used as the skin material, whereas green-colored PS of the same brand was used for the core material. Flow of polymer melts and therefore, changes of the interface location during the packing stage was found to concentrate near the gate area. These effects decrease significantly at locations away from the gate. The fountain flow effect was clearly seen by observing that the core melt front movement catches up the skin melt front for the cavity with different thickness. During the packing stage, an additional skin melt flow was still significant and concentrated mainly around the gate area. In addition, for the cavity with a block insert, polymer melt might flow across the weld line when it was still hot at the center. The sidewall effect of the cavity was significant for thin parts.

Kuhmann and Ehrenstein [50] performed sequential mono-sandwich injection molding experiments using a low viscosity polyethersulfone (PES) filled with a conductive filler (45 wt %), as a skin material, and an unfilled high viscosity PES, as a core material. The influence of the processing parameters and the part geometry with or without ribs was studied. They showed that due to the development of a low conductive
filler percolation network in the skin layer sandwich products made from the PES with two different viscosities are suitable for use as antielectrostatic components. While the injection rate was found to hardly influence the filler distribution near the surface, it strongly affects skin/core distribution. Low viscosity ratios of core to skin material, due to different shear thinning behavior of the filled skin component and the unfilled core component do not cause flow instabilities affecting the core distribution.

The interface development and encapsulation in simultaneous co-injection molding of a center-gated disk type mold was studied by Li et al. [51,52] using a two-channel nozzle to obtain an encapsulated sandwich structure. The effect of rheological properties and processing conditions on the material distribution, penetration behavior, and breakthrough phenomena was investigated. They have shown that material pairs with a broad range of viscosities may be utilized in this process. For a specific material combination, the injection rate ratio was found to have the strongest effect on the interface position and thickness of core. The duration of simultaneous injection had a significant effect on the flow length of the core melt into the skin melt. However, the variation of the melt temperature showed only a slight affect on the interface evolution. Breakthrough phenomena were mainly determined by the volume of initially injected single phase melt and the rheological properties of material combination.

To obtain a two-layered sandwich structure, Li et al. [53,54] carried out simulation and experimental studies of pressure-controlled sequential sandwich transfer molding of two SBR rubber compounds under isothermal conditions. One SBR compound, which was intended for the skin material, is first laid up in the cavity. Then, another SBR compound, intended for the core material, is transferred to penetrate into the
skin material and to push the lay-up to fully fill the cavity, resulting in an encapsulated skin/core sandwich structure. Two cases involving different material combinations with different viscosity ratios have been studied. The rheological interaction of the skin/core components and the effect of processing conditions, such as the volume fraction transferred and pressure, were considered. The penetration and encapsulation behavior, and the interface development are found to be significantly affected by the rheological properties of the compounds and the volume fraction transferred. However, at a constant volume fraction transferred, the pressure imposed during transfer molding is found to have little effect on the interface development. Their experimental findings were in good agreement with the predictions based on a physical model and numerical simulation based on the Hele-Shaw approximation along with the kinematics and dynamics of interface evolution.

2.1.3 Simulation Approaches

Major modeling efforts of the co-injection molding process are a relatively recent undertaking. Only limited numerical simulations of the process have been attempted [27,33,46,55-75]. Most of these efforts were based on the use of the Hele-Shaw approximation to predict the interface evolution between skin and core materials during filling for the sequential co-injection [27,33,55-74], while a few of them considered the simultaneous co-injection process [46,75]. To obtain a full description of the flow process, the differential equations for conservation of mass, momentum and energy due to the dynamics interaction between skin and core materials are solved with corresponding simplifications. Therefore, the regular injection molding simulation designed for a single
material is no longer suitable for simulating co-injection molding process. Nevertheless, the basic theory can still be applied to the individual material regions, with the major challenge to track the interface shape, tracing individual components at any time and location in the cavity.

Earliest mold filling simulation of the sequential two-shot molding processes was performed by Donovan et al. [27] using a non-Newtonian viscosity model. They pointed out [75] that any reasonably well-behaved viscosity equation describing the dependence of the viscosity on temperature and shear rate can be used. In particular, they used two types of viscosity equations. In the first case the ratio of the viscosity at a given temperature and shear rate, $\eta$, to its value at the same temperature but at zero shear rate, $\eta_0$, is taken to be a function of a single parameter, $\eta_0 \gamma / T$.

Uhland [55] developed a numerical program to predict the radial position of the interface between the two molten polymers flowing in circular dies. For skin and core materials, a non-Newtonian viscosity was described by a power-law model with the temperature dependence by an exponential function. He included the viscous dissipation term and calculated the temperature, velocity fields, interface position, shear rates, shear stresses as well as the pressure drop. For the processing of thermo-sensitive polymer melts, it was found that most energy dissipation occurs in the outer less viscous phase. Based on these concepts, the shear stress at the wall, the pressure drop and the maximum residence time of a polymer can be reduced by introducing a less viscous fluid at the pipe wall such that the shear deformation in the outer layer becomes much greater than that in the core.
Lanvers et al. [56,57] implemented CADMOULD-3D with a phenomenological approach to describe the advancing flow front of the core material in three dimensional terms assuming that both materials have the same temperatures, velocities and shear stresses at the interface. They presented a refinement of the model describing the penetration behavior of the core component into the skin component by means of a phenomenological formulation, whose model exponents were determined by the correlation with the Melt Flow Index (MFI) of each individual component.

Michaeli and Galuschka [58] applied the similar phenomenological formula to their simulation program of co-injection molding. The basis of their approach was that the contour of the core material flow front is dependent on the MFI ratio of the participating components and that the contour of the core melt front had a direct effect on the two-dimensional distribution of the core material as well as on the wall thickness of the core and skin materials.

In order to trace the skin/core interface during the sequential injection of core polymer at a particular switch-over time after injection of skin polymer, Turng et al. [59-61] presented a methodology that employs the techniques of conventional injection molding analysis and the idea of residence time for simulating the sequential co-injection molding process with the fountain-flow behavior at the melt front based on a mass conservation to catch the actual phenomenon.

Similar to the approach Turng et al. [59-61], Wang [62,63] considered the simulation of injecting two polymers in sequential process without delay time at the switch-over position. One-dimensional mold filling with a flat melt front assumption is considered along with constant viscosity and no frozen layer. He defined residence time
as the time interval in which polymer particles reside in the cavity. This time was normalized with the filling time. He showed that the first portion of melts entering the cavity locates near the surface and the end of cavity. Also, high injection and packing pressure reduces the in-cavity residual stress and shrinkage with warpage being reduced at uniform pressure distribution in the cavity. However, no detailed explanations about this residence time approach have been given in their papers [59-63].

Chen et al. [64-66] also developed a simulation program based on the control-volume/finite-element method with a dual-filling-parameter particle-tracing scheme employed within each grid layer in the gapwise direction to trace the melt front advancements for both skin and core materials during sequential co-injection process. Although all these studies were more focused on simulations of the flow front of both skin and core components, an explanation of the interface treatment was not provided. It is our understanding that in their simulation the core component entering the cavity displaced the skin component in front of it by means of a steady-state plug-type flow. Therefore, a core thickness distribution had to be estimated beforehand.

Zoetelief et al. [67] studied multi-component injection molding by using a conservation of identity (which may be material, color, place, and time of injection) method. They applied a semi-analytical flow front model for particle tracking in order to locate the position of each component and to predict the interface distribution during the process. Similar to Tung et al. [59-61], they used the Cross model as a generalized Newtonian fluid model. According to them, neglect of viscoelasticity of the polymers proved to be not too serious mainly because the boundary and initial conditions are given by prescribed velocities. The mathematical formulation of the particle tracking problem
resulted in hyperbolic (scalar) convection equations which was solved by the Streamline Upwind Petrov Galerkin (SUPG) finite element method.

Schlatter et al. [33] proposed a thermo-mechanical model describing the sequential flow of the two polymers into the mold cavity based on Hele-Shaw approximation. The polymers are assumed to follow a shear-thinning power-law behavior with Arrhenius temperature dependence. A transport equation characterizing the displacement of the interface between the two melts was employed. The governing equations were solved using a modified finite volume scheme based on discontinuous Galerkin formulation. The model was also employed to an unsteady multi-fluids flow during sequential sandwich injection molding [68]. Their model did not take into account the breakthrough phenomena and the interfacial instabilities. Also, in their calculation the polymer melts were assumed to follow the power-law shear-thinning behavior. Actually, the simulation showed that shear rates were very low near the wall and at the center region, so the use of the power-law model might be one of the reasons that caused the difference between the experiments and their simulation. Nevertheless, the numerical simulation can qualitatively predict the trend of interface evolution observed in the experiments.

Palluch and Isayev [69] developed a new approach for the physical modeling and simulation in sequential co-injection molding and employed the control volume finite element method to calculate a one-dimensional two-layer flow of viscoelastic polymer melts with the transient multi-phase flow of amorphous and semicrystalline polymers. They predicted the transient interface movement during co-injection and stress-induced crystallization within the semicrystalline polymers. The effect of elasticity on the
interface development was also taken into account in their model. However, their theoretical model has not been verified by comparing the simulation results with experimental data.

Lee et al. [46] assumed a steady-state plug-type core melt flow during the cavity filling and calculated one-dimensional interface distribution between two phases in the simultaneous sandwich injection molding. They used the flow analysis network (FAN) and finite difference method to solve the governing equations for one dimensional non-isothermal, non-Newtonian flow in the simultaneous sandwich injection molding process. The FAN method is based on dividing the region of interest into cells and carrying out flux balance on these cells.

Xin and Jue [70] made dynamic simulation studies on sandwich injection molding process by employing the software of Moldflow Plastics Insight for the melt flow behavior and the mechanism of sandwich injection molding. They found that the relative fluidity of core to skin melts greatly influenced the penetration length of the core melt and the injection velocity of the melts greatly influenced the penetration length of the core melt among the process parameters. Although their studies were more focused on visual computer-based simulations of the penetration length of the core melt in sandwich injection, a detail explanation of the advancement of core melt was not provided. Furthermore, they did pay attention to the advancement of core melt and not to the interface for the skin and core materials.

Ilinca et al. [71-73] developed a three-dimensional finite element flow analysis code to solve sequential co-injection molding problems for non-Newtonian, non-isothermal flow in a center-gated rectangular plate and a C-shaped plate. Two additional
transport equations for tracking polymer/air and skin/core polymers interfaces are used to model the polymer/air and skin/core interfaces using a pseudo-concentration method. They concluded that the agreement with experimental data is excellent and represents a major improvement over the standard 2.5D approach.

Li and Isayev [75] formulated two-dimensional simulation of simultaneous co-injection molding, along with the interface treatment. Their theoretical approach, physical model, and numerical algorithm was based on the Hele-Shaw approximation. They presented systematically a detailed picture of the dynamics and kinematics of the interface evolution, providing a description of the multilayer flow and interface development during the multi-component injection-molding process. Their simulated and experimental results were found to be in good agreement [51].

Ilinca and Hetu [74] presented a three-dimensional finite element method for solving the sequential co-injection molding process for a spiral mold. Non-Newtonian, non-isothermal flow solutions are obtained by solving the momentum, continuity and energy equations. Two additional transport equations were solved for the evolution of the polymer/air and skin/core polymer interfaces and the final shape and depth of the core polymer. They predicted the core expansion phase, the core advance phase and the core breakthrough and compared with the experimental data of Watanabe et al. [37,39]. They found that the numerical model indicated very accurate predictions of the core expansion phase, the core advance phase and core breakthrough. They concluded that the beginning of the core expansion phase (the moment when the core material catches up on the melt front of skin material) and the occurrence of core breaking through the skin.
Although many studies have been done in the theoretical modeling of the co-injection molding, most of these studies did not consider the viscoelastic effects for the residual stresses and birefringence. Also there was no attempt to obtain the residual stresses and birefringence for each layer based on a viscoelastic model. It has been widely recognized that the prediction of the residual stresses and birefringence is most important properties in manufacturing the optimal co-injection-molded products.

2.2 Injection-Compression Molding

In recent years, the manufacturing of precision plastic optical parts with a strong request for high-quality parts such as lenses, disk substrates and other optical components by injection-compression molding processes are continuously gaining more importance.

2.2.1 Historical Background

Conventional injection molding (CIM) process [76] is one of the most widely employed polymer processing operations, being characterized by high degree of automation, high productivity and good dimensional stability of moldings. The process can make products with complex geometries in one production step. The process consists of three major stages including filling, packing and cooling stages. In the filling stage, a hot polymer melt rapidly fills a cold mold with a cavity of the desired shape. During the packing stage, extra material is forced into the cavity in order to compensate for shrinkage during solidification. Often the pressure during packing stage is much higher than the one during filling stage. After a certain time, the gate (cavity entrance) freezes and no more material can be allowed to enter the cavity. However, the product remains in
the mold until it is sufficiently solidified. This last part of the molding process is called the cooling stage. After mold opening and ejection, the product is allowed cooling to the room temperature. Many macro- and micro-devices such as watches and camera components, automotive crash, acceleration, distance sensors, read/write heads of hard disks, CD drives, medical sensors, pump, surgical instruments and telecommunications components, have been successfully injection molded. Despite many advantages, part defects such as uneven shrinkage, warpage, sink marks, residual stress, and part mechanical properties may be affected by the entire injection molding process. For example, one of the problems in traditionally molded plastic optical parts is an optical birefringence, which is caused by the molding in residual stresses. The optical birefringence is defined by a difference in an index of refraction for two optical waves polarized in perpendicular directions and propagating through the optical media. The optical birefringence can significantly reduce an optical performance (e.g. causing a double-vision) of an electronic device such as a liquid crystal display, a camera, etc.

On the other hand, in a compression molding (CM) process [76-79], polymer melt is compressed to flow by the moving platen of the mold to complete melt filling. The melt is then continued to be compressed by the pressure exerted from the mold wall of the core side. This process provides a more uniform pressure along the cavity wall and requires a low molding pressure for the postfilling process resulting in less part warpage and residual stress. However, this operation cannot achieve high productivity due to the labor-intensive charge installation. It also has a limitation for molding large parts of complex shape.
In recent years, the combination of CIM and CM is an example for the manufacturing of precision plastic optical parts with a strong request for high-quality parts such as lenses, disk substrates and other optical components. Though precision parts usually have simple geometrical shapes such as disks, plates, or cylinders, their dimensional accuracy and stability must be strictly satisfied [80]. The optical performance of moldings depends on internal part properties such as the frozen molecular orientation, residual stresses and birefringence. Several special injection molding techniques have been developed in order to fulfill the rising requirements on the part quality. Among them, the ICM to compact the polymer material for producing parts with dimensional stability and surface accuracy is a widely used process. By adding a compression stage after partial melt filling of the cavity, ICM process provides several advantages such as decreasing molding pressure [81] and clamp tonnage (typically 20 to 50% lower) [82], reducing cycle time and residual stress, minimizing molecular orientation and birefringence, packing evenly, reducing uneven shrinkage, overcoming sink mark and warpage, reducing density variation and increasing dimensional accuracy [83]. Thus, ICM process is good technique to manufacture high precision optical parts with improved optical performance. There are three types of injection-compression molding [84] depending on the initial thickness of the mold cavity compared with the nominal thickness of the molded part. The first type is often referred to as stamping or two-stage sequential ICM, in which the thickness of the mold cavity is set to be slightly larger than the nominal thickness of the part before injection. This thicker cavity allows the polymer melt to reach the extremities of the cavity under low pressure. At a certain time during or after the injection stage, the mold halves start to close, thereby reducing
the mold cavity thickness to the final thickness of the part. In stamping, the mold closing position is the set parameter on the machine. The two-stage sequential ICM (stamping) has a potential drawback, for example, the “hesitation” or “witness” mark resulting from flow stagnation during injection-compression transition at a switchover time. The second type is simultaneous ICM to eliminate this surface defect and to guarantee continuous flow of polymer melt. It is characterized by activation of mold compression while the polymer melt is being injected. The final type of injection-compression is coining or selective ICM. In this process, the thickness of the mold cavity is set to be slightly less than the nominal thickness of the part initially. As the screw moves forward, the cavity pressure and the mold cavity force exerted on the machine platen increase. When the force exerted by the melt on the mold is higher than the clamp force set on the machine, the mold is opened to decrease the cavity pressure. As the screw moves past a machine setpoint, the process switches from a volumetric flow rate condition to a packing pressure condition applied at the nozzle. During both the filling and packing stages, a balance is maintained between the mold cavity force and the clamp force. When the former is lower than the latter, the mold starts to close. This continuous mold opening and closing, often referred to as “mold breathing,” is distinctive from CIM and improves the mold filling and the replication of grooves or pits at the surface of the disks, and also reduces the packing pressure and residual stress in the part. For this type of ICM, the clamp tonnage rather than the displacement is the set parameter on the machine as a function of time. The major differences between the CIM and the ICM process are the cavity filling and the way of the compensation (further melt flow during packing phase or reduction of the cavity volume) of the thermal contraction during the cooling phase.
Klepek [85] used the injection/compression molding to mold thick optical lenses. Yang and Lien [86] studied the technological application of ICM on precision molding of parts with precision contours. They compared the quality of injection-compression-molded polystyrene (PS) convex lenses with that of injection molded PS and found that ICM produce lenses with better quality than those without compression with the same cooling time. They concluded that ICM was the better solution for molding of high-end plastic optical lenses. Yang et al. [83,87-89] experimentally investigated the quality of disks molded by injection/compression molding. They showed that the injection/compression molding enhanced dimensional accuracy, especially in the direction perpendicular to compression. Shin et al. [90] carried out experimental study to investigate the change in birefringence in optical disk under various processing conditions. They concluded that birefringence was affected most by the mold temperature and cooling time. Michaeli and Wielpuetz [91] investigated main processing parameters influencing the optical part quality of windscreen for window panes in the injection/compression molding process, using a design of experiments. In their experiments, the main influencing parameters on the optical part quality were the injection and compression velocity for the injection/compression molding as well as the injection velocity and the packing pressure for conventional injection molded parts. Chen and Young [92] studies the effects of adding compression to CIM process. In their study, a disk mold was designed to study the effects of the compression stage on the molding products. They found that compression improved conformity to cavity profile and reduced warpage significantly.
The surface contour of the molded lens may deviate from the original mold due to thermal shrinkage and residual stress in the postfilling stage. Since the thickness of an optical lens may vary a lot, non-uniform thickness shrinkage is usually observed in the molding process. This non-uniform shrinkage also affects the frozen-in stresses and distortion of the product after demolding. The developed in-mold residual stresses arise from two effects mainly, namely the flow induced stress due to the flow and the compression pressure and the thermally induced stress due to the cooling. The flow-induced stresses during the filling stage are an order of magnitude smaller than the thermally induced stresses, and thus are ignored in most of the analysis. In the postfilling stage, the material inside the mold cavity can be in glassy or rubbery phases depending on the local temperatures. Since the mold temperature is lower than that of the melt, a skin layer usually forms in injection stage, leaving a hot melt in the core region. As the material cools down, the skin layer begins to grow until the entire material through the thickness solidifies. In the mean time, residual stresses begin to develop in the solidified phase while melt still flows due to the imposed compression pressure. Therefore, the developed residual stresses largely depend on the local temperature histories of the solidified material and the surrounding melt pressure.

At the present time, the science-based design technique for the injection/compression molding of optical products has not been established. This is due to a lack of understanding of viscoelastic mechanical and optical behaviors of polymeric materials experienced during cavity filling of injection stage and squeezing flow occurring during compression stage. Numerical analysis of the process including the viscoelastic effect is quite difficult. Isayev and Hieber [93] were the first who proposed a
theoretical approach to relate the nonlinear viscoelasticity of polymers to the development of frozen-in molecular orientation (birefringence) in injection moldings. Also, Isayev and Azari [94] and Isayev et al. [95] carried out both theoretical and experimental investigations of squeezing flow of melt using nonlinear viscoelastic constitutive equations. They considered shear-free flow and channel flow with moving boundary squeezing melt similar to that occurring in the compression stage of ICM. Osswald and Tucker [96] presented a compression molding simulation for non-planar parts combining a finite element solution of the governing equations with a control volume scheme for tracking the moving flow front based on inelastic flow models. Kwon et al. [97,98] studied experimentally and numerically the birefringence distribution in injection/compression molded center-gated disk based on Leonov viscoelastic fluid model. Wang [99] used a Hele-Shaw fluid flow to predict the melt front advancement and the distribution of pressure, temperature history, and flow velocity dynamically during the injection melt filling, compression melt filling, and postfilling stages of the entire ICM process. Park et al. [100] presented a numerical simulation for a precision ICM of a center-gated disk using finite difference method (FDM) with the Leonov compressible viscoelastic fluid model and the Tait equation of state. Kim et al. [101] and Lee et al. [102] developed a numerical analysis based on a finite difference method for the governing equations of the symmetric radial flow and studied the distribution of birefringence in a center-gated disk after injection molding and injection/compression molding process using the Leonov model. Chen et al. developed a numerical algorithm to simulate the filling stage of the stamping type of ICM using an inelastic [103-105] and viscoelastic [106] numerical analysis. The effect of the processing conditions on
simulated and measured cavity pressure was studied [103]. The simulated and measured cavity pressures were in fair agreement. Although they studied the effects on average birefringence variation under various processing parameters, the gapwise birefringence distribution was not described. Based on the simulated results, it was found that ICM had a significant effect on reducing part shrinkage and provided much more uniform shrinkage within the molded parts. The results also showed that birefringence becomes smaller as the melt temperature increases, and as the mold closing velocity decreases. The flow rate and the mold temperature do not affect birefringence significantly.

Friedrichs et al. [107] used an incompressible viscous flow model to simulate the stamping type of ICM as part of a birefringence simulation. Kim et al. [101,108] presented a physical modeling and numerical analysis to investigate the effects of the compression stage in the stamping type of ICM using a viscoelastic flow model as part of birefringence simulation. They found that the ICM process reduced birefringence as compared with the CIM process and the mold temperature had significant effects on the density distribution in comparison with the other processing condition. Fan et al. [109] developed a code for the simulation of ICM of a CD-R using a compressible viscous flow model. Young [110] investigated the residual stresses and shrinkage of ICM pickup lens with large thickness variations. In simulating of the molding they used a Cross-WLF type equation for description of the viscosity. A modified Tait equation for the polymer density was utilized. The mold temperature and compression time were found to be the most important factors that affect the shrinkage of lens in the thickness direction, resulting in surface profile deviation.
2.3 Residual Stress and Birefringence

During the injection molding process the polymer undergoes simultaneous mechanical and thermal influences in the fluid, rubbery, and glassy states under non-isothermal flow. Such effects introduce residual stresses and strains into the final product, resulting in highly anisotropic mechanical behavior and warpage and shrinkage. Residual stresses and birefringence in injection molded products can be attributed to two main sources [76,111]. The first is due to the frozen-in flow-induced stresses and birefringence by the shear and normal stresses developed by the deformation of long-chain polymer molecules in the nonisothermal viscoelastic flow of the polymer during the filling and packing stage and by the incomplete relaxation of the deformed polymer molecules during the subsequent cooling stage of the injection molding process. The second type of residual molding stress is the thermally- and pressure-induced residual stresses, which are caused by differential shrinkage or nonequilibrium density change and the viscoelastic behavior of the polymer during its passage through the glass transition temperature to the room temperature after ejection from the mold, coupled with nonuniform shrinkage or non-equilibrium density changes due to the rapid, inhomogeneous cooling. The thermally-induced birefringence most often is referred to as the birefringence caused by the thermally-induced residual stress. Generally, the flow-induced residual stresses, caused by the orientation of polymer molecules in the direction of flow, are considerably smaller than the thermally-induced residual stresses. However, the former cannot be neglected because the frozen-in orientation of polymer molecules is responsible for the anisotropy of mechanical, thermal and optical properties and affects the long-term dimensional stability [112]. The residual stresses and birefringence largely affect the
mechanical properties, shrinkage and warpage, dimensional stability and end-use performance of molded products. In addition, birefringence affects the optical performance of an optical product. Reduction in the amount of frozen-in stresses and birefringence reduces the tendency of the moldings to craze and improves their dimensional stability on heating [113].

Over the years, the problem of modeling the residual stresses and birefringence turned out to be one of the most challenging tasks in the simulation of the injection molding process. Residual stress in injection molding was first considered in the classical work of Spencer and Gilmore [114], and it has been studied by many researchers ever since. Most of these studies are concerned with the understanding of the mechanism governing the formation of residual stresses in the injection moldings of amorphous polymers. Concerning general mechanisms for residual stresses and molecular orientation, attempts to incorporate these mechanisms in integrated quantitative models have been made. Tadmor [115] proposed a semiquantitative model based on macromolecular theory, bead-and-spring model, to explain the orientation distribution in injection molded products. Dietz, White, and Clark (DWC) [116] developed a simplified algorithm based on the linear viscoelastic Maxwell model to calculate residual stresses. The Leonov model [117,118] has been employed as a nonlinear viscoelastic constitutive equation by many researchers in analyzing the flow-induced residual stress and birefringence. Isayev and Hieber [93] studied the flow-induced residual stresses and birefringence in the one-dimensional filling and cooling stages in injection molding using the Leonov viscoelastic model. Baaijens [119] analyzed residual stress in injection molding of a rectangular plate, including the packing stage. In particular, Baaijens [119] applied the compressible
Leonov model to the flowing region to simulate the flow-induced residual stress and thermally-induced residual stress in the solidified layer by applying the linearized Leonov model. Flaman [120,121] presented a detailed analysis of injection molding based on a compressible version of the Leonov model to investigate flow-induced birefringence for thin strip cavity geometry. Shyu et al. [122] predicted the flow birefringence through the linear stress-optical rule based on the modified Leonov model for center-gated disk molds in all three stages of the injection molding process. Friedrichs et al. [107] predicted the flow-induced birefringence in a magneto-optical disk using the stress-optical rule based on an incompressible Leonov model. Kim et al. [101,108] numerically simulated the conventional injection and injection-compression molding processes including the compression process to predict the flow-induced birefringence and residual stresses in a center-gated disk by employing the Leonov constitutive model and Tait equation to take into account the compressibility of polymer materials in a center-gated disk. However, the above works did not take into account the thermally-induced birefringence and residual stress.

The theoretical works on the thermally-induced residual stresses in quenched amorphous polymers are generally originated from those developed for inorganic glasses. Roughly speaking, the theories can be divided into two categories: one is based on the instant freezing assumption, which states that above the glass transition temperature, the polymer can be treated as an idealized fluid and below the glass transition temperature, the polymer is solidified and treated as an idealized elastic material [123]. The other is based on the free volume relaxation assumption including viscoelastic constitutive equation relating the stresses to the strains of the polymer [93,124]. Santhanam [125]
predicted thermal residual stresses in injection molded parts by introducing the linear viscoelastic model. However, the predicted residual stresses were much higher than experimental results. Bushko and Stokes [126,127] briefly reviewed the development in modeling of thermal residual stresses, studied the residual stresses and dimensional changes caused by solidification using a thermoviscoelastic model and thought this model could be used to assess packing pressure effect in injection molding between two parallel plates. But these studies did not take into account the density relaxation phenomena of polymeric materials.

Schwarzl and Staverman [128] classified “thermorheologically simple” materials as materials in which all molecular changes are affected by temperature in the same way and specified the condition for the material relaxation function to satisfy the time-temperature equivalence principle. Consequently, only amorphous thermoplastics can be expected to exhibit such thermorheological simple behavior since both the change of crystalline structure and of interaction of polar groups will certainly depend on the temperature in a way different from that of the viscosities of flow in the amorphous, nonpolar parts of the material. The most appealing equation to many researchers among these kinds of theory was derived by Morland and Lee [129] who extended linear viscoelasticity to account for time-dependent temperature variations by introducing the concept of pseudotime or material time, in general a function of both time and space variables. The model was applied to a cylinder of incompressible linear thermorheologically simple material subjected to a steady-state temperature field. However, the thermal stresses due to nonhomogeneous thermal expansion were neglected in this model because of the assumption of incompressibility. Based on the free volume
theory, Shyu and Isayev [2,130,131] developed a physical model to predict the thermally-induced birefringence. They also performed experimental measurements of the birefringence in free quenching sample. Ghoneim and Hieber [132] attempted to predict thermal residual stresses including density relaxation phenomena, indicating that the density relaxation has a significant effect on the evolution of residual stresses. However, in their work, no attempt was made to compare numerical results with corresponding experimental results. Guo and Isayev [133] compared the thermoelastic model and thermoviscoelastic model to calculate the residual thermal stresses in freely quenched slabs of semicrystalline polymers, based on the modifications of the Indenbom theory [123] and Morland-Lee viscoelastic constitutive equation [129] with crystallization phenomena taken into account.

For amorphous polymers, it is well known that the flow and thermal stresses become residual due to the passage through its glass transition temperature. Although the residual flow stresses are an order of magnitude smaller than the residual thermal stresses, one cannot neglect the flow contribution to the overall residual stresses. The frozen-in molecular orientation due to flow contributes significantly to residual birefringence.

The residual flow stresses are difficult to measure. They cannot be measured directly. However, since flow stresses give rise to molecular orientation, the measurement of residual frozen-in birefringence is an indirect indication of the residual flow stresses. The overall residual stresses distribution in molded or quenched plastic parts can be measured by the layer removal method [134,135] and the hole drilling method [134].

The attempt to predict the birefringence, also called frozen-in orientation, for amorphous polymers was carried out by several researchers. The application of rheo-
optical rule provides a relationship between residual stress and birefringence for the samples formed in both shear and elongational flows. Janeschitz-Kreigl [136] was the first to derive a simple theoretical description of birefringence in molded parts. Using Newtonian fluid theory, he proposed a dynamic model for determining the thickness of the frozen polymer layer in injection molding. Dietz and White [137] extended the approach of Janeschitz-Kriegl [136]. Their approach is based on the formation of a frozen layer of polymer in the wall region and the use of an isothermal power-law model in the core. The thickness of the frozen layer is based on the transient one-dimensional conduction problem for a semi-infinite solid. Greener and Pearson [138], following the procedure developed by Janeschitz-Kriegl [136] and Dietz and White [137], analyzed a problem of frozen-in orientation in molded strips by treating the nonisothermal stress relaxation process in the post-filling stage on the basis of the viscoelastic constitutive equation of Marucci [139]. The attempt to incorporate the effects of three-dimensional viscoelasticity into the process was made by Isayev and Hieber [93]. They developed more rigorous model based on one-dimensional non-isothermal flow described by the Leonov viscoelastic constitutive equation for predicting the orientation during the filling and cooling stage. They calculated the frozen-in birefringence by the residual flow stresses via the stress-optical rule. In this research, they approximated that the shear and normal stresses start to relax after filling of the mold due to cessation of simple shear flow. However, the deformation will occur until the glass transition temperature is reached in the molding. Flaman [120,121] predicted the buildup of flow-induced molecular orientation in amorphous injection-molded products of simple geometry using the extended version of the viscoelastic material model developed by Leonov [117]. His
model was used to investigate the influence of the processing conditions and the pressure
dependence of the material functions on the pressure and birefringence profiles. Although
the residual flow birefringence of amorphous polymers was studied theoretically and
experimentally by many researchers for a long time, both the theoretical and
experimental studies of the residual thermal birefringence are limited. A numerical
simulation of thermally induced stress and warpage of injection-compression-molded
disks with a viscoelastic material model was developed by Fan et al. [140]. They found
that gravity has a significant effect on the magnitude and curvature behavior of PC disk
warpage. They concluded that a viscoelastic constitutive model is needed to predict the
transient development of warpage accurately. Shyu et al. [2,124,141] studied the residual
thermal birefringence in freely quenched plates of amorphous polymers. The measured
birefringence data were compared with the results of numerical simulation based on the
linear viscoelastic for mechanical properties and photoviscoelastic constitutive equations
for optical properties. In addition, Fan et al. [142] employed viscoelastic material model
integrated into a non-isothermal compressible flow simulation to calculate the flow- and
thermally-induced residual stresses and birefringence of injection-compression molded
disks by an integral stress-optical constitutive model with a time and temperature
dependent stress optical coefficient. They found that, for polycarbonate, the thermally
induced birefringence has a similar magnitude as the flow induced birefringence. The
mold and melt temperatures are shown to have a significant effect on the values of
birefringence. Simulation of flow and thermal birefringence and stresses developed
during the filling, packing, and cooling stages of the injection molding of a center-gated
disk by using hybrid finite element method (FEM) and finite difference method (FDM)
were carried out by Isayev et al. [130,131]. They employed the compressible nonlinear viscoelastic model for flow stresses, linear stress-optical rule for the flow birefringence, the linear viscoelasticity and photoviscoelasticity for the thermal stresses and thermal birefringence, respectively. They found that a second birefringence maximum appears between the center and the position of the first maximum due to flow in the packing stage. The predicted birefringence and extinction angle profiles are in good agreement with corresponding measurements in literatures for PS disk moldings.

2.4 Summary and Goals

The development trends currently emerging in co-injection molding process are essentially the combination of different processes, the combination of different materials and the integration of a wide range of functions within a single part for optical, physical or mechanical properties, the improvement of surfaces and properties, and also reduced material consumption and the recyclability of the materials employed. On the other hand, development of a new alternative polymer processing to fulfill the rising requirements on the part quality despite of the increasing economical demands, for example, decreasing molding pressure, reducing residual stress and birefringence by minimizing molecular orientation, evenly packing, reducing uneven shrinkage, overcoming sink mark and warpage, reducing density variation, increasing dimensional accuracy and so on is emerging. Much of the innovation potential lies in the injection molding process. Special injection molding processes, such as co-injection molding for the production of sandwich components and ICM for the production of particularly large optical parts with improved optical quality, are playing an increasingly large and important role in the processing of
plastics. From the literature review, it is seen that these processes offer numerous advantages over CIM. However, the main disadvantage in dealing with the multi-component injection molding and ICM processes mentioned above is that the processes are difficult to master. For co-injection molding, the requirement placed on product quality, production quality and also part precision is also rising and for ICM, the limitation of extra cost and application, for example, relatively expensive mold, high wearing of mold during the compression stage, requirement of control module for the compression stage and only application for high-volume products, such as CD, DVD and rear automotive windows or products with minimum molded-in residual stresses, such as optical lenses is emerging. Therefore, the challenge is to acquire engineering and manufacturing know-how on new materials and material combinations as well as on process variants to fully utilize the advantages and flexibilities of these processes.

The application of numerical modeling and simulation in the design of injection mold has gained increasing importance in conjunction with the introduction of CAE techniques. In the analysis of the increasingly complex special processes, i.e. multi-component molding and ICM, simulation is becoming an indispensable engineering tool to efficiently evaluate and verify the feasibility of the design and process, and further numerically optimize the design and process parameters without going through costly and time-consuming molding trials. Although existing literature describes the theoretical modeling and experimental study of the sequential co-injection molding, most of these studies did not consider the viscoelastic effects for flow-induced and thermally-induced contributions. In reality, it has not been easy to predict the residual stresses and birefringence from the combination of the flow-induced and thermally-induced
contributions because of lack of complete understanding of complicated behavior of polymeric materials in the co-injection molding process. For instance, in the case of co-injection molding process and ICM, nonlinear viscoelastic behavior during the filling, compressibility during the packing stage, nonequilibrium thermodynamics and volume relaxation phenomena for the rapid cooling process, photoviscoelastic effect during the solidification, and linear viscoelastic behavior after ejection, kinematics of the interface evolution only for co-injection molding and so on should be considered. Therefore, accurate predictions of the residual stress and birefringence for amorphous polymers require a complete set of appropriate and rigorous physical modeling for such complicate physical and optical behavior of polymeric materials and a corresponding numerical analysis system to solve the transport phenomena during the entire co-injection molding process and ICM.
CHAPTER III
THEORETICAL MODELING AND MATHEMATICAL FORMULATION OF INJECTION-COMPRESSION MOLDING

Injection-compression molding (ICM) has four operating stages in the following sequence: first is the injection stage at which polymer melt is injected to fill the mold cavity partially with a mold slightly open until the same material volume as volume of a final molded part to fill the cavity is completely injected into the cavity; second is the compression stage at which the mold is closed completely and the mold cavity is finally filled by polymer melt; third is the packing stage at which packing pressure is applied to compensate for the shrinkage of the polymer melt; and finally, the cooling stage at which the temperature and pressure are decreased so that the final plastic part is ready to be ejected. Figure 3-1 shows schematically the injection-compression molding process.

The objective of injection-compression molding simulation is to obtain information such as injection and compression time, pressure profiles, temperature profiles, and so on so as to set up the optimal molding operation conditions and optimal mold design. As mentioned in Chapter III, viscous models cannot describe the responses associated with the elastic nature of materials. Thus, although the use of the inelastic or viscous model suffices to ascertain the moldability, a viscoelastic model is in need for evaluating the residual stresses and birefringence. The residual stresses are usually separated into two parts. One part is the flow stresses resulting from flow during the
processing operation. The other is the thermal stresses resulting from the density change during the cooling process [76,111,143]. The coupling effects between the flow stresses and thermal stresses are usually neglected and they are evaluated independently of each other.

For simulation of the injection and compression stage, incompressibility is usually assumed. However, if one wants to include the packing stage in the simulation, the variation of density with temperature and pressure has to be considered.

In the present simulation all four stages of the ICM process – injection, compression, packing and cooling are considered and the cases studied are the injection-compression of PS and PC into center-gated disk molds. The modified Leonov model, which takes compressibility into account [117,118,144], is used to calculate the flow stresses and linear viscoelasticity is employed to calculate the thermal stresses [124,141]. The flow birefringence is related to the flow stresses through the linear stress-optical rule [145], while the thermal birefringence is calculated from the thermal stresses by using the photoviscoelastic constitutive [124,141]. The Tait equation [146] is used to describe the P-V-T relationship.

3.1 Theoretical Approach

The Hele-Shaw type of flow model is widely used to simulate the injection, injection-compression and co-injection molding processes. The result provides a reasonably accurate description of flow behavior of polymer melt in the three-dimensional thin cavities. Mold filling during the injection/compression molding process is comprised of two stages: partial injection mold filling of a polymeric melt into a
Figure 3-1 Schematic diagram of injection-compression molding process.
slightly open mold, and subsequent compression mold filling by complete closing of a mold. Inelastic [147] and viscoelastic [2,148] simulations of the injection stage have been already developed based on the control volume approach.

3.1.1 Governing Equations of Injection-Compression Molding Process

The governing equations and modeling for the injection molding simulation can be applied to the injection stage, packing stage and cooling stage of the injection-compression molding in exactly the same way. However, governing equations for the compression stage are slightly different from those for the filling stage of the injection molding.

Here the relevant governing equations for the viscoelastic polymeric flow under non-isothermal conditions are given.

With the coordinate system shown in Figure 3-2, the momentum equations in the absence of inertia and body forces are:

\[
\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xz}}{\partial z} = 0
\]  
(3.1)

\[
\frac{\partial \sigma_{yz}}{\partial y} + \frac{\partial \sigma_{zz}}{\partial z} = 0
\]  
(3.2)

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho v_x) + \frac{\partial}{\partial y} (\rho v_y) + \frac{\partial}{\partial z} (\rho v_z) = 0
\]  
(3.3)

where \( x \) and \( y \) are planar directions and \( z \) is the gapwise direction, \( \rho \) is the fluid density and \( \sigma_{ij} \) represents the total stress. \( v_x, v_y, \) and \( v_z \) are velocity components in the \( x, y \) and \( z \) directions, respectively.
Figure 3-2 Schematic diagram of compression molding.

The fountain flow at the melt front is neglected in the present analysis. Since the thickness of the cavity is much smaller than its planar dimensions, the velocity component in the gapwise direction, $z$, is assumed to be equal to zero. Therefore, the flow field is approximately planar, that is to say, $V = (v_x, v_y, 0)$. Moreover, for the thin cavity of an arbitrary planar geometry, the lubrication approximation [149] can be applied, so the velocity gradient in the flow direction is neglected, compared to the velocity gradient in the gapwise direction. In addition, the pressure is assumed to be constant in the gapwise direction, and only a function of $x$ and $y$. With these assumptions and by considering that $\frac{\partial \sigma_x}{\partial x} \ll \frac{\partial p}{\partial x}$ and $\frac{\partial \sigma_y}{\partial y} \ll \frac{\partial p}{\partial y}$ are valid, components of the momentum equation in the absence of inertia and body forces reduce to

$$\frac{\partial \sigma_z}{\partial z} - \frac{\partial p}{\partial x} = 0 \quad (3.4)$$
\[ \frac{\partial \sigma_{yx}}{\partial z} - \frac{\partial p}{\partial y} = 0 \]  

(3.5)

The mass balance equation for a compressible two-dimensional flow during injection stage is

\[ \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) = 0 \]  

(3.6)

In modeling of the nonisothermal ICM process, the momentum and the continuity equations are coupled with the energy equation. The energy equation can be written as:

\[ \rho C_p \left( \frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} \right) = \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + \Phi \]  

(3.7)

where \( C_p \) and \( k \) are specific heat and thermal conductivity, respectively.

It should be noted that the mechanical dissipation term, \( \Phi \), in the energy equation, Eq. (3.7), must contain the dissipation term arising from the elastic deformation, in addition to the viscous heating. Thus, based upon the viscoelastic constitutive equation, the mechanical dissipation function takes the form \([148,150]\).

\[ \Phi = 2\eta_{\text{strain}} v^2 + \sum_{k=1}^{N} \frac{\eta_k}{4\theta_k^2} \left[ \text{tr}C_k \left( \text{tr} \left( C_k^{-1} \right) - \text{tr}C_k \right) \right] + \frac{\text{tr}C_k^2}{\theta_k^2} - 3 \]  

(3.8)

There exist two particular types of ideal material, the nondissipative elastic solid and dissipative viscous liquid. The elastic solid has a definite shape and is deformed by external forces into a new equilibrium shape. It stores all the energy obtained from the work done by external forces during the deformation. This energy is then available to restore the body to its original shape on the removal of these forces. The viscous fluid, on
the other hand, has no definite shape and flows irreversibly under the external forces. When the action of external forces is released, the fluid can not revert from its deformed shape to its original one. Generally speaking, polymeric material displays the so-called viscoelastic properties which are intermediate between those of an elastic solid and a viscous liquid. Based upon nonequilibrium thermodynamics with local equilibrium hypothesis, Leonov [117,118,144] considered that the contribution to the deviatoric stress tensor, $\tau$, due to the viscous and elastic deformations of viscoelastic polymer media are superposed. Meanwhile, the elastic contribution can be decomposed into a number of relaxation modes, for each of which, for example, the $k^{th}$ mode, an elastic strain tensor, $C_k$, is introduced. Based upon the Eulerian high elasticity theory, the constitutive equation for a polymeric media was derived.

By employing the Leonov constitutive model [117,118,144], the stress field can be related to the velocity gradient field as follows:

$$\tau = -p\delta + \eta_0 \varepsilon \left( \nabla V + \nabla V^T \right) + \sum_{k=1}^{N} \eta_k C_k$$  \hspace{1cm} (3.9)

$$\frac{DC_k}{Dt} = -\nabla V^T C_k + C_k \left( \nabla V \right) + \frac{1}{2\theta_k} \left( C_k \cdot C_k - \delta \right) = 0$$  \hspace{1cm} (3.10)

$$\eta_0 = \sum_{k=1}^{N} \eta_k \frac{1}{1 - s_0}$$  \hspace{1cm} (3.11)

where $\tau$ is the deviatoric stress tensor, $\varepsilon$ is the rate of deformation tensor, $\delta$ is the unit tensor, $C_k$ is the elastic strain tensor (Finger measure) of the $k$-th relaxation mode, $V$ is the velocity vector, $T$ is the sample temperature, $\eta_0$ is the initial viscosity, $s$ is
the rheological parameter lying between 0 and 1, $\theta_k$ and $\eta_k$ is, respectively, the relaxation time and viscosity of the $k$-th mode, $N$ is total number of modes and $D/ Dt$ is the differential operator of the substantial derivative.

In the ICM simulation, the cooling rate effect on density $\rho(T,P)$ is assumed to follow the Tait equation [151]

$$v(\rho,T) = v_0(T) \left[1 - C \ln \left(1 + \frac{\rho}{B(T)}\right)\right]$$  \hfill (3.12)

$$v_0(T) = b_y + b_z \bar{T} \quad \text{if} \quad T > T_i$$  \hfill (3.13)

$$v_0(T) = b_y + b_z \bar{T} \quad \text{if} \quad T > T_i$$  \hfill (3.14)

$$= b_y + b_z \bar{T} \quad \text{if} \quad T \leq T_i$$  \hfill (3.15)

$$B(T) = b_{z,\exp}(-b_{z,\bar{T}}) \quad \text{if} \quad T > T_i$$  \hfill (3.16)

$$= b_{x,\exp}(-b_{x,\bar{T}}) \quad \text{if} \quad T \leq T_i$$  \hfill (3.17)

$$\bar{T} = T - b_3$$  \hfill (3.18)

$$T_i(p) = b_3^* + b_4^* p$$  \hfill (3.19)

where $C$ and $b_l$ are the material constants and $T_i$ is the transition temperature (either the melting temperature or glass transition temperature).

The parameters $\eta_k$ and $\theta_k$ of $k^{th}$ mode are temperature-dependent quantities based on the a WLF-type temperature dependence [148]:

$$\eta_k(T) = \eta_k(T_0) \cdot a_r / a_r^0$$  \hfill (3.20)

$$\theta_k(T) = \theta_k(T_0) \cdot a_r / a_r^0$$  \hfill (3.21)
\[
\begin{align*}
&t = \#
eq _{\text{ns}} \\
&\exp \left[ \frac{C_1 (T - T_1)}{C_2 + T - T_1} \right] \\
&\leq T > T_2
\end{align*}
\]

where \( a_T \) is the shift factor, \( T \) is the reference temperature depending on the polymeric material and, \( C_1 \) and \( C_2 \) are constants depending on the reference temperature.

By combining the equations of motion, Eqs. (3.4) and (3.5), the mass balance equations, Eq. (3.6), and the constitutive equation, Eq. (3.7), the governing equation for the flow during injection stage in ICM becomes:

\[
G \frac{\partial P}{\partial t} + H - \frac{\partial}{\partial x} (S_x \frac{\partial P}{\partial x}) - \frac{\partial}{\partial y} (S_y \frac{\partial P}{\partial y}) = 0
\]

The governing equation for the flow during compression stage in ICM becomes:

\[
G \frac{\partial P}{\partial t} + H - \frac{\partial}{\partial x} (S_x \frac{\partial P}{\partial x}) - \frac{\partial}{\partial y} (S_y \frac{\partial P}{\partial y}) - \rho_{z=h} v_c = 0
\]

\[
G = \int_0^h \left( \frac{\partial \rho}{\partial P} \right) dz
\]

\[
H = \int_0^h \left( \frac{\partial \rho}{\partial T} \right) \left( \frac{\partial T}{\partial t} \right) dz
\]

\[
S_x = \int_0^h (z \int_0^z \rho \ dz') \frac{dz}{\eta_s}
\]

\[
S_y = \int_0^h (z \int_0^z \rho \ dz') \frac{dz}{\eta_s}
\]

\[
\eta_s = \eta_0 + \sum \frac{\eta_k}{\theta_k} C_{i,xz} \frac{\partial v_i}{\partial z}
\]

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\[
\eta_y = \eta_0 s + \sum_{k=1}^{N} \frac{\eta_k C_{k,yz}}{\partial y / \partial z} \tag{3.30}
\]

The constitutive equation, Eq. (3.9), gives the following expressions for the components of the stress tensor

\[
\sigma_{xx} = -p + \sum_{k=1}^{N} \frac{\eta_k C_{k,xx}}{\theta_k} \tag{3.31}
\]

\[
\sigma_{yy} = -p + \sum_{k=1}^{N} \frac{\eta_k C_{k,yy}}{\theta_k} \tag{3.32}
\]

\[
\sigma_{zz} = -p + \sum_{k=1}^{N} \frac{\eta_k C_{k,zz}}{\theta_k} \tag{3.33}
\]

\[
\sigma_{xz} = \sigma_{zx} = \eta_0 s \frac{\partial v_x}{\partial z} + \sum_{k=1}^{N} \frac{\eta_k C_{k,xz}}{\theta_k} \tag{3.34}
\]

\[
\sigma_{yz} = \sigma_{zy} = \eta_0 s \frac{\partial v_y}{\partial z} + \sum_{k=1}^{N} \frac{\eta_k C_{k,yz}}{\theta_k} \tag{3.35}
\]

\[
\sigma_{xy} = \sigma_{yx} = 0 \tag{3.36}
\]

By substituting Eq. (3.9) into Eqs. (3.4) and (3.5) and taking into account the symmetry of boundary conditions with no slip at the mold wall, after integration one obtains:

\[
v_x = -\frac{\partial p}{\partial z} \int_{-z}^{z} \frac{\eta_x}{\eta_s} \, dz \tag{3.37}
\]

\[
v_y = -\frac{\partial p}{\partial z} \int_{-z}^{z} \frac{\eta_y}{\eta_s} \, dz \tag{3.38}
\]
3.1.2 Elastic Strain Tensor $C_{ik}$

To avoid the cumbersome numerical calculations, for a two-dimensional planar flow, the elastic strain tensor $C_{ik}$ is determined in the local streamwise coordinate system $(s, \theta, z)$ [150,152] with $s$ being the flow direction, $\theta$ being perpendicular to $s$ in the counterclockwise direction, $z$ being the thickness or gapwise direction as shown in Figure 3-3.

![Figure 3-3 Geometry of a center-gated disk with coordinate system](image)

The shear components $C_{i,\theta z}$ and $C_{i,\theta \theta}$ of the elastic strain tensor are assumed to be negligible. Then, all of normal components and the shear components of $C_{ik}$ are obtained by integrating Eq. (3.10) along the particle path.
In the case of a center-gated disk, the flow field is a diverging one, and $C_{k,\theta\theta}$ is not unity, the governing equations for the elastic strain tensor in the streamwise Cartesian coordinate system are:

$$\begin{align*}
\frac{\partial C_{ss,k}}{\partial t} + v_s \frac{\partial C_{ss,k}}{\partial s} &= 2 \left( -\frac{v_s}{s} \right) C_{ss,k} + 2 C_{sc,k} \frac{\partial v_s}{\partial z} - \frac{1}{2\theta_i} \left( C_{ss,k}^2 + C_{sc,k}^2 - 1 + \frac{A}{3} C_{ss,k} \right) \\
\frac{\partial C_{ss,k}}{\partial t} + v_s \frac{\partial C_{ss,k}}{\partial s} &= -\frac{v_s}{s} C_{sc,k} + C_{ss,k} \frac{\partial v_s}{\partial z} - \frac{1}{2\theta_i} \left( C_{ss,k}^2 + C_{zz,k}^2 \right) C_{ss,k} - \frac{A}{3} C_{sc,k} \\
\frac{\partial C_{ss,k}}{\partial t} + v_s \frac{\partial C_{ss,k}}{\partial s} &= 2 \frac{v_s}{s} C_{ss,k} \frac{\partial v_s}{\partial z} - \frac{1}{2\theta_i} \left( C_{ss,k}^2 - 1 + \frac{A}{3} C_{ss,k} \right) \\
\frac{\partial C_{zz,k}}{\partial t} + v_s \frac{\partial C_{zz,k}}{\partial s} &= \frac{1}{C_{ss,k}^2 + C_{zz,k}^2} \\
C_{zz,k} &= \frac{1}{C_{ss,k} + C_{zz,k}} \\
\frac{\partial C_{\theta\theta,k}}{\partial t} + v_s \frac{\partial C_{\theta\theta,k}}{\partial s} &= \left( C_{\theta\theta,k} - 1 \right) \left( C_{ss,k} + C_{zz,k} - 1 - \frac{1}{C_{\theta\theta,k}} \right) \\
\frac{\partial v_s}{\partial z} &= \gamma \frac{\partial v_s}{\partial z} \\
v_s &= \sqrt{v_x^2 + v_y^2}
\end{align*}$$

where $A = \left( C_{\theta\theta,k} - 1 \right) \left( C_{ss,k} + C_{zz,k} - 1 - \frac{1}{C_{\theta\theta,k}} \right)$.

The value of $C_{ik}$ at the entrance nodes are determined from the fully developed steady-state solution, $\frac{D}{Dt} C_{ik} = 0$, of the simple shear flow under isothermal condition [93,118] given by...
\[ C_{s,k}^{(0)} = \frac{\sqrt{2} X_s}{\sqrt{1 + X_s}} \]
\[ C_{s,k}^{(0)} = \frac{2 \gamma \theta_k}{1 + X_s} \]
\[ C_{z,k}^{(0)} = \frac{\sqrt{2}}{\sqrt{1 + X_s}} \]  

(3.46)

where \( X_s = \sqrt{1 + 4 \gamma' \theta_k^2} \)  

(3.47)

3.1.3 Melt Front Advancement in Compression Stage

The volumetric flow rate of melt during compression stage is equal to the rate at which the closing mold displaces a volume occupied by the filling process through the surface defined by melt front boundaries. The filling parameter associated with each control volume is taken into consideration for the mass flux from the moving surface. For control volumes located on the flow front, the filling parameter can be calculated from the occupied volume fraction and the additional volume fraction due to compression during a specified instant [153].

The total mass flow rate of melt through surface during compression stage is:

\[ Q_c = \sum_i \frac{\rho_i f_i V_i}{h_i} v_c \]  

(3.48)

where \( h_i \) is a half thickness at time \( t = k \), and \( f_i \) and \( V_i \) is the filling parameter and the volume of control volume \( i \), respectively.

Using the pressure gradient, the mass flow rate \( q_{Ni} \) from element \( N \) into the control volume \( i \) can be calculated by assuming constant velocity over the element. By equating the new mass of material in the control volume \( i \) at time \( t = k + 1 \) to the sum of the old mass at time \( t = k \) and the mass flow into the control volume during \( \Delta t \), the filling parameter \( f_i \) for each node can be calculated.
\[ \rho_i^{k+1} f_i^{k+1} V_i^{k+1} = \rho_i^{k} f_i^{k} V_i^{k} + \sum_N q_{Ni} \Delta t \]  

(3.49)

For each control volume \( i \), the mass at time \( t = k \) is:

\[ \rho_i^k V_i^k = \rho_{\text{avg}} \sum_N \frac{A_{Ni}}{3} 2h^k \]  

(3.50)

where \( \rho_{\text{avg}} \) is averaged density along the thickness, and \( A_{Ni} \) is the area of a triangular element \( N \) connected with node \( i \).

The mass at time \( t = k + 1 \) is:

\[ \rho_i^{k+1} V_i^{k+1} = \rho_{\text{avg}} \sum_N \frac{A_{Ni}}{3} 2(h^k - v_c \Delta t) \]  

(3.51)

By substituting Eqs. (3.50) and (3.51) into Eq. (3.49)) and setting \( f_i^{k+1} = 1 \), the time increment \( \Delta t_i \) required to fully fill the control volume at node \( i \) is:

\[ \Delta t_i = \frac{\rho_{\text{avg}} (1 - f_i^k) \sum_N \frac{A_{Ni}}{3} 2h^k}{\sum_N \left( q_{Ni} + 2v_c \frac{A_{Ni}}{3} \rho_{\text{avg}} \right)} \]  

(3.52)

For every melt front node the time increment is calculated, and the smallest value is selected as the next time increment.

From Eqs. (3.49) to (3.51), filling parameter at every melt front node can be updated as follows:

\[ f_i^{k+1} = \frac{f_i^k h^k}{h^k - v_c \Delta t} + \frac{\sum_N q_{Ni} \Delta t}{\rho_{\text{avg}} \sum_N \frac{A_{Ni}}{3} 2(h^k - v_c \Delta t)} \]  

(3.53)

For a partially opened mold with the compression stroke, numerical simulation of the injection mold filling is performed as described by Lee and Isayev [153]. When the
injected amount of melt inside cavity is exactly the same with the required final part volume, the process is switched to the compression stage. The computational domain during the transient compression stage is updated by changing the location of melt front and the half-gap thickness of the cavity with a time step for melt front advancement using Eqs. (3.52) and (3.53). The simulation is carried out until mold cavity is completely filled, checking the filling parameters.

3.1.4 Numerical Implementation

On the basis of the formulations described earlier, a numerical scheme using control-volume FEM/FDM for a two-dimensional flow in a center-gated disk (Fig. 3-3) has been developed. To solve the geometry equations, a set of appropriate boundary conditions should be given first. The control-volume FEM [150,154] with triangular elements and linear shape functions was used to solve Eqs. (3.23) and (3.24) with $G$ and $H$ to be constant in each control volume, and $S_x$ and $S_y$ to be constant in each element. The boundary conditions for Eqs. (3.23) and (3.24) in the injection, compression and packing stages are different. In the injection stage, the volume flow rates at the entrance nodes were specified, and the pressures at the melt front nodes were assumed to be zero with the pressure at the entrance nodes and flow rates at the melt front nodes to be solved. That is, in the injection stage

$$P = 0 \quad \text{at the melt front} \quad (3.54)$$

$$Q = Q_o \quad \text{at the gate or entrance} \quad (3.55)$$
In the packing stage, the entrance pressure was specified as an imposed packing pressure, with flow rates at the entrance nodes to be determined.

That is, in the packing stage:

\[ P = P_g \text{ at the gate or entrance} \]  \hspace{1cm} (3.56)

Besides, in the impermeable boundary region, the melt is in contact with the boundary of the mold, and the normal velocity components vanish. In addition, symmetric boundary conditions at the centerline and no slip at the solid wall of the cavity were assumed. Thus,

\[ v_x = v_y = 0 \quad \text{at } z = \pm h \]  \hspace{1cm} (3.57)

\[ \frac{\partial v_x}{\partial z} = \frac{\partial v_z}{\partial z} = 0 \quad \text{at } z = 0 \]  \hspace{1cm} (3.58)

\[ \sigma_{xz} = \sigma_{yz} = 0 \quad \text{at } z = 0 \]  \hspace{1cm} (3.59)

The additional boundary condition for the compression stage in ICM was used:

\[ v_z = -v_x \quad \text{at } z = \pm h \]  \hspace{1cm} (3.60)

In ICM, the temperature at the entrance nodes is generally assumed to be uniform and equal to the inlet melt temperature \( T_0 \).

\[ T = T_w \quad \text{at } z = \pm h \]  \hspace{1cm} (3.61)

\[ \frac{\partial T}{\partial z} = 0 \quad \text{at } z = 0 \]  \hspace{1cm} (3.62)

\[ T = T_0 \quad \text{at the gate or entrance} \]  \hspace{1cm} (3.63)

where \( T_w \) is the mold wall temperature.
To solve the pressure equations the whole domain of a disk-typed mold cavity is discretized into a series of three-node triangular elements in the x-y plane. Only one control volume is associated with each node. For each node of a triangular element, by connecting the centroid of each element to the midpoints of the three corresponding sides, the region enclosed by a contour in the counter-clockwise direction around each vertex node of a triangular element is specified as the subcontrol volume for this node as shown in Figure 3-4. The polygonal control volume that surrounds each vertex node is defined as the summation of sub-control volumes, which contains node N, and is enclosed by a contour C in the counter-clockwise direction.

Each finite element has a constant thickness. The thickness of an element is specified at the three nodal points. In order to accommodate a possible sudden change of cavity thickness, the nodal thickness is assigned separately for each element, so the thickness may be discontinuous across inter-element boundaries.

(a)                                 (b)
(a) Three-node triangular elements with sub-control volumes associated with the element. (b) The control volume associated with node N

Figure 3-4 Control volume-finite element method
3.1.4.1 Pressure Development

After applying the Galerkin weighted-residual procedure [155,156] or mass conservation to Eqs. (3.23) and (3.24) using a control-volume approach [157], and introducing linear interpolation functions as well as a finite-difference representation for the time derivative, the following governing equation for pressure [2] in the whole cavity domain is obtained:

\[ \sum_{i=1}^{ku} \left[ A^i G^i \sum_{j=1}^{3} E_{ij}^i p_{j+1}^i - p_j^i + \sum_{j=1}^{3} B_{ij}^i N^i p_j^i \right] = \frac{ku}{3} \Delta t A^i t + \frac{Q_N}{2} \]  

(3.64)

where \( E_{ij}^i = \begin{cases} \frac{22}{108} & \text{if } i = N \\ \frac{7}{108} & \text{if } i = N \end{cases} \)  

(3.65)

\[ \frac{1}{4A^i} \left[ S_x^i \begin{pmatrix} b_1^i & b_2^i \\
 b_2^i & b_3^i \\
 b_3^i & b_1^i 
\end{pmatrix} + S_y^i \begin{pmatrix} c_1^i & c_2^i \\
 c_2^i & c_3^i \\
 c_3^i & c_1^i 
\end{pmatrix} \right] \]  

(3.66)

\[ \begin{pmatrix} a_1^i \\
 a_2^i \\
 a_3^i 
\end{pmatrix} = 2A^i \begin{pmatrix} 1 & 1 & 1 \\
 x_1^i & x_2^i & x_3^i \\
 y_1^i & y_2^i & y_3^i 
\end{pmatrix}^{-1} \]  

(3.67)

\[ 2A^i = (x_2^i y_3^i - x_3^i y_2^i) + (x_3^i y_1^i - x_1^i y_3^i) + (x_1^i y_2^i - x_2^i y_1^i) \]  

(3.68)

\( Q_N = Q_{ent} \) for the entrance nodes where \( p \) is specified at the gate; \( Q_N \) is the total volumetric flow rate for each node at any instant for the whole cavity domain, \( ku \) is the total number of elements containing node \( N \), \( i \) is such that \( N = NELNOD(i,i) \), \( (x_1, y_1) \), \( (x_2, y_2) \), \( (x_3, y_3) \) are the \( x \)-\( y \) coordinate for each node.
triangular element, and \( a_i, b_i, c_i \) \((i=1, 2, 3)\) are the coefficients for the linear area-coordinate interpolation function for node \( i \) on element \( l \).

3.1.4.2 Elastic Strain Tensor

To calculate the flow-induced stresses during the filling and packing stages, the elastic strain tensor \( C_k \) for all relaxation modes of the Leonov model has to be calculated at each time step. Therefore, the governing equations of the elastic strain tensor for the streamwise coordinate, Eqs. (3.39) through (3.42), were discretized using a finite difference approach. Time derivatives were discretized using forward difference and space derivatives were discretized using backward difference at time \( t = t + \Delta t \) [158].

The final discretized equations are:

\[
F_1 = C_{ss,k}^{t+1} (n, j) - C_{ss,k}^t (n, j) + u_{ss}^{t+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{ss,k}^{t+1} (n, j) - C_{ss,k}^t (n-1, j) \right) - 2 \Delta t f_{ss}^{t+1} (n, j) C_{ss,k}^{t+1} (n, j) + 2 \Delta t \left( \frac{u_{ss}^{t+1} (n, j) - u_{ss}^t (n, j)}{s^{t+1} (n)} \right) C_{ss,k}^{t+1} (n, j) + \frac{1}{2 \theta_s} \left[ \left( C_{ss,k}^{t+1} (n, j) \right)^2 + \left( C_{ss,k}^t (n, j) \right)^2 \right] - 1 + \frac{A}{3} C_{ss,k}^{t+1} (n, j) = 0 \quad (3.69)
\]

\[
F_2 = C_{sc,k}^{t+1} (n, j) - C_{sc,k}^t (n, j) + u_{sc}^{t+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{sc,k}^{t+1} (n, j) - C_{sc,k}^t (n-1, j) \right) - 2 \Delta t f_{sc}^{t+1} (n, j) C_{sc,k}^{t+1} (n, j) + \frac{1}{2 \theta_c} \left[ \left( C_{sc,k}^{t+1} (n, j) + C_{sc,k}^t (n, j) \right) C_{sc,k}^{t+1} (n, j) + \frac{A}{3} C_{sc,k}^{t+1} (n, j) \right] = 0 \quad (3.70)
\]

\[
F_3 = C_{cz,k}^{t+1} (n, j) - C_{cz,k}^t (n, j) + u_{cz}^{t+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{cz,k}^{t+1} (n, j) - C_{cz,k}^t (n-1, j) \right)

+ \frac{1}{2 \theta_c} \left[ \left( C_{cz,k}^{t+1} (n, j) \right)^2 + \left( C_{cz,k}^t (n, j) \right)^2 \right] - 1 + \frac{A}{3} C_{cz,k}^{t+1} (n, j) = 0 \quad (3.71)
\]

\[
F_4 = C_{wz,k}^{t+1} (n, j) - C_{wz,k}^t (n, j) + u_{wz}^{t+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{wz,k}^{t+1} (n, j) - C_{wz,k}^t (n-1, j) \right)
\]

\[
\]
\[ +2 \Delta \tau t^{+1} C_{ij,k}^{+1}(n,j) + \frac{1}{2\theta_k} \left[ \{C_{ij,k}^{+1}(n,j)\}^2 - 1 + \frac{A}{3} C_{ij,k}^{+1}(n,j) \right] = 0 \]  

(3.72)

\[ C_{ij,k}^{+1}(n,j) = \left[ \frac{\left( \frac{1}{C_{ij,k}^{+1}} + \left\{ C_{ij,k}^{+1}(n,j) \right\}^2 \right)^2}{C_{ij,k}^{+1}(n,j)} \right] \]  

(3.73)

where \( A = \left( C_{ij,k}^{+1}(n,j) - 1 \right) \left( C_{ij,k}^{+1}(n,j) + C_{ij,k}^{+1}(n,j) - 1 - \frac{1}{C_{ij,k}^{+1}(n,j)} \right) \)  

(3.74)

and the superscript \( t \) represents the time step and the \( k \) represents the number of modes of Leonov model, \( \theta_k \) is the relaxation time of \( k \) mode, \( \Delta t \) is time step, \( n \) represents the nodes along the flow direction, \( j \) represents the nodes along the gapwise direction, \( C_{ij,k} \) represents the components of the elastic strain tensor in the Leonov model, \( u \) is the velocity in the streamwise direction and \( \gamma_s \) is the shear rate along the streamwise direction.

To determine the components of \( C_{ij,k} \) tensor, the Globally Convergent Method for Nonlinear Systems of Equations [159] that is closely related to the quasi-Newton method of minimization was implemented for the discretized system of equations of Eqs. (3.69) through (3.72). This method is powerful but the numerical computation of the Jacobian matrix represents a disadvantage [159]. However, for this case the Jacobian matrix is available analytically. In this work, the subroutine “fdjac” which calculate the Jacobian matrix numerically, was replaced by the function that provides the Jacobian matrix calculated analytically. Therefore, taking the derivatives of these equations with
respect the variables \( C^{t+1}_{ss,k}(n,j) \), \( C^{t+1}_{sc,k}(n,j) \), \( C^{t+1}_{zz,k}(n,j) \) and \( C^{t+1}_{\theta\theta,k}(n,j) \) we obtain the following Jacobian functions to obtain the Jacobian matrix:

\[
\begin{bmatrix}
\frac{\partial F_1}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_1}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_1}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_1}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\frac{\partial F_2}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_2}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_2}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_2}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\frac{\partial F_3}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_3}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_3}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_3}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\frac{\partial F_4}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_4}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_4}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_4}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\end{bmatrix}
= 0
\] (3.75)

where \( F_1 \), \( F_2 \), \( F_3 \) and \( F_4 \) are the Left Hand Side (LHS) of the Eqs. (3.69) through (3.72).

### 3.1.4.3 Temperature Distribution

For the solution of the energy equation, Eq. (3.7), the implicit FDM was used for the conduction and time derivative terms. To calculate the convection term \( \nu \frac{\partial T}{\partial x} \) in Eq. (3.7) during the filling and compression stages, the temperature distribution in the flow direction, is linearly interpolated within each element. The heat convective terms, \((\nabla \cdot \nabla) T\), at a node were evaluated by taking the area average of the values calculated at the center of the upstream elements of the node under consideration [150,152,160].

Based upon above discussion, the energy equation at each vertex node can be discretized as [2,161]:

\[
\begin{bmatrix}
\frac{\partial F_1}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_1}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_1}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_1}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\frac{\partial F_2}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_2}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_2}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_2}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\frac{\partial F_3}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_3}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_3}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_3}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\frac{\partial F_4}{\partial C^{t+1}_{ss,k}(n,j)} & \frac{\partial F_4}{\partial C^{t+1}_{sc,k}(n,j)} & \frac{\partial F_4}{\partial C^{t+1}_{zz,k}(n,j)} & \frac{\partial F_4}{\partial C^{t+1}_{\theta\theta,k}(n,j)} \\
\end{bmatrix}
= 0
\]
\[
\begin{aligned}
p_i c_p \left[ T_{i,j,k+1} - T_{i,j,k} \right] + \frac{1}{\sigma_{i,j}} \sum_{l=1}^{ku} \theta_{i,\ell} \sum_{m=1}^{3} E_{m,j,\ell,k} T_{i,j,k} \\
= \frac{k_h}{\Delta z^2} \left( T_{i,j,k+1} - 2T_{i,j,k+1} + T_{i,j,k+1} \right) + \Phi_{i,j,k}
\end{aligned}
\] (3.76)

with

\[
E_{m,j,\ell,k} = \frac{1}{2A \Lambda^l} \int_{z}^{b} dz \left( \Lambda_j B_m^l + \Lambda_j C_m^l \right)
\] (3.77)

\[
\sigma_i = \sum_{l=1}^{ku} \theta_{i,\ell}
\] (3.78)

where term \( \sigma_i \) is the total control volume associated with node \( i \) and \( \theta_{i,\ell} \) is the fraction of control volume containing element \( l \).

The dissipation function is:

\[
\Phi_{i,j,k} = \frac{1}{\sigma_{i,j}} \sum_{\ell=1}^{ku} \theta_{i,\ell} \left[ \eta_{i,j,k} s_{j,k}^l \gamma_{j,k}^2 + \sum_{q} \frac{\eta_{q,j,k}}{4\theta_{q,j,k}} \left( C_{i,q,j,k}^2 + 2C_{i,q,j,k}^2 + C_{i,j,k}^2 - 2 \right) \right]
\] (3.79)

where \( i, j \) are the node number in the x-y plane and the gapwise direction, respectively, \( k, k+1 \) represent time step \( t_k \) and \( t_{k+1} \); and \( \Delta t = t_{k+1} - t_k \), which is selected in order that only one partially-filled node gets filled for every time step; \( \Delta z = z_{j+1} - z_j \), and \( i = NELNOD(l,m) \), \( ku \) is total number of elements containing node \( i \), and \( l = NEL(i,m) \) is the \( m \)-th element which contains node \( i \).

### 3.1.4.4 Numerical Algorithm and Convergence

At each new time step, \( w+1 \), the velocity field and pressure field are first solved from Eq. (3.23) and Eq. (3.24) with elastic strain tensors solved from Eqs. (3.39) through
(3.41). During the solution process, the temperature obtained in the \( w \) time step is used to calculate the various physical quantities, such as \( \rho, \eta \) and so on. After obtaining the velocity field and pressure field, the energy equation, Eq. (3.7), with the pressure field and velocity field fixed, is solved to obtain the temperature field, and then the next time step is ensured.

The under-relaxation iteration method [150] was used to solve the pressure and temperature at each time step. In each iteration, new values of \( P^{w+1,\text{new}} \) and \( T^{w+1,\text{new}} \) are obtained from Eq. (3.64) and Eq. (3.76). The updated values \( P^{w+1,\text{updat}} \) and \( T^{w+1,\text{updat}} \) are put back in Eq. (3.64) and Eq. (3.76) for iterations, where \( \Omega_p \) and \( \Omega_T \) are weighting factors which are between 0 and 1. When the solutions converge, the old and updated values are almost same. Iterations terminate when the absolute change in the each property is less than some specified value. In particular, successive under-relaxation method is also used for calculation of pressure and temperature profile due to numerical stability. To converge the values of \( P_m \) and \( T_{m,j} \) at each time step, the following convergence criterion, \( \varepsilon_p \) and \( \varepsilon_T \) is used, respectively.

\[
\varepsilon_p = \frac{1}{\text{NODES}} \sum_{m=1}^{\text{NODES}} \left\{ \left\| \frac{P_{m}^{r+1} - P_{m}^{r}}{P_{m}^{r}} \right\| \right\} \leq 10^{-4} \tag{3.82}
\]

\[
\varepsilon_T = \frac{1}{\text{NODEZ} \cdot \text{NODES}} \sum_{m=1}^{\text{NODES}} \sum_{j=1}^{\text{NODEZ}} \left\{ \left\| \frac{T_{m,j}^{r+1} - T_{m,j}^{r}}{T_{m,j}^{r}} \right\| \right\} \leq 10^{-3} \tag{3.83}
\]
where $\text{NODES}$ and $\text{NODEZ}$ are the total number of node along the planar and the thickness directions, $m$ and $j$ are the number of each node along the planar and the thickness directions and $r$ is the number of iteration.

3.1.5 Residual Stresses and Birefringence in ICM Molding Parts

It is desirable to predict and investigate the residual stresses and birefringence in the products obtained at different processing conditions.

3.1.5.1 Flow Stresses and Birefringence

In the cooling stage, shear rate $\dot{\gamma}$, velocity $v$, and pressure $p$ can be taken to be zero, and Eqs. (3.39) to (3.41) become

$$\frac{\partial C_{ss,k}}{\partial t} = - \frac{1}{2\theta} \left( C_{ss,k}^2 + C_{sc,k}^2 - 1 + \frac{A}{3} C_{ss,k} \right)$$

(3.84)

$$\frac{\partial C_{sc,k}}{\partial t} = - \frac{1}{2\theta} \left( (C_{ss,k} + C_{sc,k}) C_{sc,k} + \frac{A}{3} C_{sc,k} \right)$$

(3.85)

$$\frac{\partial C_{sc,k}}{\partial t} = - \frac{1}{2\theta} \left( C_{ss,k}^2 - 1 + \frac{A}{3} C_{ss,k} \right)$$

(3.86)

Similarly, the convection, dissipation, and pressure terms in the energy equation can be omitted, and Eq. (3.7) reduces to one-dimensional heat conduction equation:

$$\rho C_p \left( \frac{\partial T}{\partial t} \right) = k \frac{\partial^2 T}{\partial z^2}$$

(3.87)

The shear stresses and normal stress differences are calculated according to the Leonov constitutive equation:
\[ N_1(s, \theta, z) \equiv \sigma_{sx} - \sigma_{zz} = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} \left[ C_{sx,k}(s, \theta, z) - C_{zz,k}(s, \theta, z) \right] \] (3.88)

\[ N_2(s, \theta, z) \equiv \sigma_{zz} - \sigma_{\theta \theta} = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} \left[ C_{zz,k}(s, \theta, z) - C_{\theta \theta,k}(s, \theta, z) \right] \] (3.89)

\[ N_3(s, \theta, z) \equiv \sigma_{sx} - \sigma_{\theta \theta} = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} \left[ C_{sx,k}(s, \theta, z) - C_{\theta \theta,k}(s, \theta, z) \right] \] (3.90)

\[ \tau_{sz}(s, \theta, z) = \eta_0 s \dot{\gamma} + \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} C_{sz,k} \] (3.91)

During the cooling stage, we set the shear rate to zero, \( \dot{\gamma} = 0 \). Therefore, Eq. (3.91) becomes

\[ \tau_{sz}(s, \theta, z) = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} C_{sz,k} \] (3.92)

The numerical scheme of computation for filling, packing and cooling stage in the injection-compression molding is summarized in the flow charter shown in Figure 3-5 for filling stage and Figure 3-6 for packing and cooling stages, respectively.
Figure 3-5 Flow chart for the simulation of filling stage in injection-compression molding process.
Figure 3-6 Flow chart for the simulation of packing and cooling stages in injection-compression molding.
The residual flow birefringence for amorphous polymers can be calculated by the stress-optical rule during the nonisothermal flow and the subsequent relaxation. The flow birefringence in $s-z$ plane, $\Delta n^f$, is given by

$$\Delta n^f = C_\sigma (T) \cdot \Delta \sigma(s,z,t)$$

(3.93)

where, $\Delta \sigma(s,z,t) = \sqrt{N_i^2(s,z,t) + 4\tau_{sz}^2(s,z,t)}$

(3.94)

and $C_\sigma$ is the temperature dependent stress-optical coefficient of polymer in the melt state [145].

Similarly, the birefringence in the $s-\theta$ plane is given by

$$n_{ss}^f - n_{\theta\theta}^f = C_\sigma (T) \cdot (\sigma_{ss} - \sigma_{\theta\theta})$$

(3.95)

where the subscript $fl$ indicates flow-induced birefringence components, $\Delta n$ and $n_{ss} - n_{\theta\theta}$ are the birefringence component in the planes $s-z$ and $s-\theta$, respectively. $\sigma_i (i = s, \theta)$ are the normal stresses in the $s$ and $\theta$ directions, respectively, and $\tau_{sz}$ is the shear stress in the $s-z$ plane.

3.1.5.2 Thermal Stresses and Birefringence

The residual thermal stresses and birefringence in injection-compression molded part are treated as those for freely quenched polymer plates and are calculated based on the linear viscoelasticity and photo-viscoelasticity with the volume relaxation effects included [1,141]. As a first approximation, we treated the residual thermal stresses and birefringence in ICM parts as those developed in freely quenched plates [141]. Based on the varying temperature fields, the changes in viscoelastic properties are determined and
utilized to calculate the thermal stresses until the polymer reaches thermal equilibrium with the molding system. For this case, the tensor of thermal stresses is

$$\sigma^\theta = \begin{bmatrix} \sigma_{ss}^\theta & 0 & 0 \\ 0 & \sigma_{\theta\theta}^\theta & 0 \\ 0 & 0 & 0 \end{bmatrix}$$  \hspace{1cm} (3.96)

where $\sigma_{ss}^\theta = \sigma_{\theta\theta}^\theta$.

The refraction index tensor due cooling alone is:

$$n^{th} = \begin{bmatrix} n_{ss}^{th} & 0 & 0 \\ 0 & n_{\theta\theta}^{th} & 0 \\ 0 & 0 & n_{zz}^{th} \end{bmatrix}$$  \hspace{1cm} (3.97)

3.1.5.3 Total Stresses and Birefringence

To the best of our knowledge, no single nonlinear constitutive equation is available to describe the rheological behavior of a polymer in both the glassy and melt states and in the transition region between them. Moreover, in the injection, compression and cooling stages, the dominant terms in the dynamic equations are different. Therefore, a further simplifying assumption was made that the coupling effects between the flow and thermal stresses are negligible, such that they can be evaluated independently. The constitutive equation used to calculate the flow and thermal stresses are different, as mentioned in the previous section. Thus, the total residual stresses are:

$$\sigma_{res} = \sigma_{res}^{fl} + \sigma_{res}^{th}$$  \hspace{1cm} (3.98)

Similarly, the total refraction index tensor is,
\[ \frac{n}{n} = n_0 \delta + n_{ih}^b + n_{ih}^f \]

\[
\begin{bmatrix}
  n_0 + n_{ih}^b + n_{ih}^f & 0 & n_{i}^b \\
  0 & n_0 + n_{ih}^b + n_{ih}^f & 0 \\
  n_{i}^f & 0 & n_0 + n_{ih}^b + n_{ih}^f
\end{bmatrix}
\]

\[ (3.99) \]

where subscripts \( res \) and superscripts \( fl \) and \( th \) stand for residual, flow, and thermal, respectively.

The birefringence measured in the \( rz \) plane is then

\[ \Delta n = \Delta n_{rc} = \left[ \left( \Delta n_{i}^b \right)^2 + \left( \Delta n_{i}^h \right)^2 + 2 \left( n_{i}^b - n_{i}^h \right) \left( \Delta n_{i}^h \right) \right]^{1/2} \]

\[ (3.100) \]

with the flow birefringence, \( \Delta n_{i}^b \), and the thermal birefringence, \( \Delta n_{i}^h \), being

\[ \Delta n_{i}^b = \Delta n_{i}^h = C_\sigma \left[ \left( \sigma_{i}^b - \sigma_{i}^h \right)^2 + 4 \left( \sigma_{i}^h \right)^2 \right]^{1/2} \]

\[ (3.101) \]

\[ \Delta n_{i}^h = n_{i}^b - n_{i}^h \]

\[ (3.102) \]

Since in free quenching \( n_{i}^b = n_{i}^h \), the birefringence in the \( r\theta \) plane becomes

\[ \Delta n_{r\theta} = \left( n_{i}^b - n_{i}^h \right) + \left( n_{i}^b - n_{i}^h \right) = n_{i}^b - n_{i}^h \]

\[ (3.103) \]
CHAPTER IV

THEORETICAL MODELING AND MATHEMATICAL FORMULATION FOR RESIDUAL BIREFRINGENCE IN FREELY QUENCHED MULTILAYER PLATES

During processing, polymer undergo simultaneous mechanical and thermal influences in the glassy, rubbery, and fluid states as a result of rapid nonisothermal cooling and transformation from the molten state to the solid state. This results in inhomogeneous densification of polymer articles and changes in viscoelastic properties [76,93,143,145]. These effects introduce frozen-in molecular orientation, residual stresses, and shrinkage in the products that in turn affect the physical, optical, and mechanical properties, dimensional stability, and appearance of the finished products. The frozen orientation manifests itself in the frozen-in birefringence phenomenon. Such induced residual stresses and birefringence can be attributed to two main sources. One is the flow stresses, including shear and normal stresses, induced during nonisothermal flow. The other is the thermal stress induced during the nonisothermal cooling process and inhomogeneous densification. As the cooling progresses, thermal stresses and birefringence develop and become residual when the polymer vitrifies [76,134]. Thus, it is desirable to predict and investigate the residual stresses and birefringence in the products obtained at different processing conditions because the residual stresses and birefringence strongly affect the end-use properties and warping of polymer products. Their accurate prediction will allow one to determine optimum processing conditions.
Although much progress has been made in the simulation of polymer processing, the problem of modeling the residual stress and molecular orientation is still in the developing stage being one of the most challenging tasks in polymer processing, in general, and CIM, ICM and co-injection molding, in particular. In fact, the factors governing the development of thermal residual stresses and birefringence during polymer processing have received much attention.

Bartenev [162,163] was evidently the first to propose the “instant freezing” theory for description of residual stresses in inorganic glasses. It treats the glass above a solidification (glass transition) temperature, \( T_s \), as an ideal fluid bearing no stresses due to low viscosity. On the other hand, below \( T_s \), glass is solidified and can be treated as an elastic material with no flow and stress relaxation as a result of high viscosity. Since the instant freezing assumption is too rough to describe the delicate time-temperature behavior of polymeric materials in the transition zone, significant deviation of the predictions from the experimental results was observed [164].

For a polymeric material at temperatures substantially below or above the glass transition temperature, the birefringence, \( \Delta n \) is proportional to the principal stress difference, \( \Delta \sigma \) by the following equation:

\[
\Delta n(t) = C_\sigma \Delta \sigma(t)
\]  

(4.1)

where \( C_\sigma \) is named the stress-optical coefficient, \( t \) is the time.

However, in the transition zone from the glassy to the rubbery state, \( C_\sigma \) is time, temperature and stress history dependent. Thus, Eq. (4.1) should incorporate the
viscoelastic behavior (mechanical memory) with the photoviscoelastic behavior (optical memory).

In this chapter, a methodology is developed to calculate the transient and frozen-in thermally-induced residual stresses and birefringence from mechanical and optical material functions. The residual birefringence and stresses in a freely quenching multi-layered plate are simulated and predicted based on stress relaxation experiments over a wide range of temperatures with simultaneous measurements of Young’s modulus ($E$) and the strain-optical coefficient ($C_{\varepsilon}$) and master curve of $C_{\varepsilon}$, the stress-optical coefficient ($C_{\sigma}$), and Young’s relaxation modulus. The numerical formulation is based on the quasi-static analysis with the hypothesis of infinitesimal deformations of linear viscoelastic multi-layered plates that experience one-dimensional heat conduction only along the thickness direction.

4.1 Theoretical

We consider an idealized problem of the free quenching of a multi-layered plate with the geometry and coordinate system shown in Figure 4-1.

4.1.1 Problem Setup

The plate is assumed to be infinite such that lateral dimensions of the plate are much larger than its thickness ($2b$). Initially, the plate is maintained at a uniform initial temperature ($T_i$). Then, it is subjected to symmetric cooling from both surfaces at a
coolant temperature ($T_w$) below $T_g$. Therefore, heat transfer occurs only in $z$. Thermal stresses are generated by the interactions between nonhomogeneous thermal contraction and changes in the polymer viscoelastic properties during cooling. Also, the thermal birefringence is generated through change in $C_\alpha$ or $C_\varepsilon$ during cooling.

Figure 4-1 Coordinate system for the free quenching of a multi-layered plate.
4.1.2 Temperature Distribution of the Multi-layered Plate in Free Quenching

The temperature distribution of the multi-layered plate was calculated by solving the one-dimensional heat transfer equation based on the assumption that the temperature varies only along the thickness direction.

\[ \rho C_p, \frac{\partial T}{\partial t} = k_j \left( \frac{\partial^2 T}{\partial z^2} \right) \]  

(4.2)

where \( \rho \) is the density, \( C_p \) is heat capacity and \( k \) is the heat conductivity and the indices \( j \) represents skin, core polymer melts or interface. Eq. (4.2) was numerically solved using the Crank-Nicolson method [165]. For the quenching experiments, the cooling media is water with which the surface of the multi-layer plate was in contact. Therefore, a convective boundary condition between the polymer and water should be imposed at the surface of the multi-layered plate given by

\[ -k_s \frac{\partial T}{\partial z} \bigg|_{z=b} = h \left( T \bigg|_{z=b} - T_f \right) \]  

(4.3)

where \( h \) is the heat transfer coefficient and \( T_f \) is the temperature of the cooling media, and indices \( s \) represents skin melt.

4.1.3 Constitutive Equations

To calculate the thermally-induced residual stress or birefringence in polymers the several approaches have been developed [119,120,123-125,127-129,132]. The approach employed in this work is the linear viscoelastic theory proposed by Morland and Lee [129]. This theory is based on linear viscoelasticity for thermorheologically simple materials and incorporates the shear relaxation modulus with the respect to time of
the mechanical response of the material. The constitutive equation for an isotropic linear viscoelastic material is given as follows

$$\sigma_{ij} = \int_0^t 2G(t-\tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{ij} - \frac{1}{3} I_{ij} \delta_{ij} \right] d\tau + \delta_{ij} \int_0^t K(t-\tau) \frac{\partial}{\partial \tau} [I_{\varepsilon}] d\tau \quad (4.4)$$

where, $\sigma_{ij}$ is the stress tensor, $\varepsilon_{ij}$ is the strain tensor, $\delta_{ij}$ is the unit tensor, $G$ is the time-dependent shear relaxation modulus, $K$ is the time-dependent bulk relaxation modulus and $I_{\varepsilon}$ is a bulk strain which is defined as:

$$I_{\varepsilon} = tr(\varepsilon) = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \quad (4.5)$$

where $\varepsilon_{xx}$, $\varepsilon_{yy}$ and $\varepsilon_{zz}$ are the strains in $x$, $y$ and $z$ directions, respectively.

The two terms on the right hand side of Eq. (4.4) represent the deviatoric and dilatational response of the viscoelastic material with respect to the elapsed time $(t-\tau)$. Accordingly, there is a possibility that two distinct shift functions govern the temperature-dependent shear and dilatation response. However, this possibility is excluded because the relaxation modulus in tension and bulk relaxation modulus for thermorheologically simple materials displays the identical shift property [166].

In comparison with the mechanical viscoelastic behavior, the photoviscoelastic behavior is less known. The photoviscoelasticity means that the stress-optical coefficient obtained from creep experiments and the strain-optical coefficient obtained from stress-relaxation experiments vary not only with temperature but also with time. The photoviscoelastic phenomenon can be clearly observed in the glass-to-rubber transition zone.
The first basic mathematical approach of photoviscoelasticity was given by Mindlin [167] who used a four-element mechanical model for the incompressible material and assumed that only the spring as elastic parts contribute to the birefringence. Later, Read [168-170] extended Mooney’s approach of molecular theory of viscoelasticity for bulk polymer under finite deformation to describe the optical behavior. Dill [171] expanded the refraction tensor function in power series for the case of small strain with the time-temperature superposition. Then he obtained the constitutive equation to calculate the refractive index tensor in polymers under small deformation [1,2,172]:

\[
\begin{align*}
n_{ij}(t) = & n^0 \delta_{ij} + \int_0^t C_{ij} \left( t - \tau \right) \frac{\partial}{\partial \tau} \left\{ \varepsilon_{ij} - \frac{1}{3} \delta_{ij} \varepsilon \right\} d\tau + \delta_{ij} \int_0^t \Delta_{ij} \left( t - \tau \right) \frac{\partial}{\partial \tau} \left\{ \varepsilon \right\} d\tau \\
\end{align*}
\]

where \( n_{ij} \) is the refraction tensor, \( n^0 \) is the isotropic refractive index, \( C_{ij} \) is the strain-optical coefficient, \( \Delta_{ij} \) is the bulk strain-optical coefficient, \( \varepsilon_{ij} \) is the strain tensor.

Free volume of polymers in an equilibrium state is dependent on temperature and pressure. When a polymer is quenched from above \( T_g \) to below \( T_g \), the equilibrium volume is reached gradually. Thus, a time-dependent volume relaxation is expected. The nonequilibrium state produced by the fast cooling introduces more free volume into the polymer than that available in the equilibrium state at same temperature. This additional free volume will accelerate all relaxation processes. Therefore, the linear viscoelastic models should be modified by including the effect of the nonequilibrium free volume. The volume contraction resulted from the nonequilibrium state can be divided by two distinct parts, an instantaneous contraction and a gradual contraction to get to the final equilibrium value. Therefore, the free volume in the volume contraction process becomes
time-dependent, and the nonequilibrium free volume should be included in the WLF equation.

The thermal strain due to the volume relaxation, $\varepsilon_T$, in a nonisothermal process can be described as follows [124,141]:

$$\frac{d\varepsilon_T}{dt} = \beta_g \frac{dT}{dt} - \frac{\varepsilon_T - \varepsilon_T^e}{\tau r}$$

(4.7)

where $\varepsilon_T$ and $\varepsilon_T^e$ are the actual and equilibrium thermal strain, respectively, at temperature $T$. The value of $\tau$ is the volume relaxation time at reference temperature $T_r$, and $\beta_g$ is the linear expansion coefficient in the glassy state. Physically, the first term on the right-hand side describes the instantaneous contraction and the second term gives the gradual contraction according to this first-order rate theory.

$$\varepsilon_T^e = \beta_i (T - T_i) \quad \text{if} \quad T \geq T_2$$

(4.8)

$$\varepsilon_T^e = \beta_i (T_2 - T_i) + \beta_g (T - T_2) \quad \text{if} \quad T < T_2$$

(4.9)

where $T_i$ is the initial temperature at $t = 0$, $T_2$ is the glass-transition temperature observed in experiments of infinite timescale where the free volume and conformational entropy become zero, and $\beta_i$ and $\beta_g$ is the thermal expansion coefficients in the rubbery and glassy states, respectively.

Leaderman [173] proposed that polymers exhibit time-dependent and temperature-dependent mechanical properties and most of polymers follow the time-temperature superposition principle. It states that a uniform shift in relaxation modulus, viscosity, and other characteristic functions of the material is observed with a constant change of temperature.
The shift factor \( a_r \) follows a modified form of the William-Landel-Ferry (WLF) equation as follows:

\[
\log a_r = -\frac{B(T - T_r)}{\alpha_f (T_r - T_2)(T_r - T_2 + T - T_r)}
\]

where \( B \) is constant [174], \( a_r \) is the shift factor, \( \alpha_f \) is the thermal expansion coefficient of the fractional free volume above \( T_2 \) and \( T_r \) is the reference temperature. This equation has a form identical to the WLF equation if \( C_1 \) and \( C_2 \) is defined as:

\[
C_1 = \frac{B}{\alpha_f (T_r - T_2)}
\]

\[
C_2 = (T_r - T_2)
\]

Eq. (4.10) is valid for polymer melts between \( T_g \) to \( T_g + 100^\circ\text{C} \) in which the constants \( C_1 \) and \( C_2 \) were evaluated by fitting the experimental data of the shift factors above the glass transition temperature. However, at temperatures below \( T_g \) the nonequilibrium free volume rather than the equilibrium volume should be considered because the WLF equation can not describe the relaxation behavior in the glassy state. To solve the problem, Rusch [175] suggested the concept of the “effective temperature” which is the temperature corresponding to the temperature of an equilibrium state that has the same amount of free volume as the nonequilibrium state.

This effective temperature is related to the actual temperature through

\[
T_{eff} = T + \frac{\varepsilon_f - \varepsilon_r}{\beta_i - \beta_f} \quad \text{if} \; T \geq T_2
\]
\[ T_{\text{eff}} = T_2 + \frac{\varepsilon_f - \varepsilon_r}{\beta_f - \beta_r} \quad \text{if } T < T_2 \]  

(4.14)

Therefore, the shift factor function becomes:

\[ \log a_r = \left[ -\frac{C_1(T_{\text{eff}} - T_r)}{C_2 + (T_{\text{eff}} - T_r)} \right] \]  

(4.15)

Eq. (4.15) is the same as Eq. (4.10) except that the effective temperature, instead of the actual temperature, is used due to the nonequilibrium free volume.

According to the time-temperature superposition principle, the shear relaxation modulus \( G \) after certain time \( t \) and at a temperature \( T \) corresponds to that at a pseudo-time defined by reduced time \( \xi \) at the reference temperature \( T_r \):

\[ \xi = \frac{t}{a_r(T)} \]  

(4.16)

For the nonisothermal process, the time-temperature superposition can be extended to a variable temperature field by new definition of the reduced time [176] which means that thermal history and the time dependence of \( G \) are accounted for a single variable.

\[ \xi = \int_0^t \frac{dt'}{a_r(T')} \]  

(4.17)

By introducing the reduced time into Eqs. (4.4) and (4.6) one obtains the following equations to calculate the thermally-induced residual stresses and the refractive index tensor in terms of the reduced time, respectively [176].

\[ \sigma_{ij}(\xi_m(t)) = \int_0^{\xi_m} 2G(\xi_m - \xi_m) \frac{\partial}{\partial \xi_m} \left[ \varepsilon_{ij}(\xi_m) - \frac{1}{3} I_\varepsilon(\xi_m) \delta_{ij} \right] d\xi_m \]
\[ + \delta_0 \int_0^{\xi_m} K (\xi_m - \xi_m) \frac{\partial}{\partial \xi_m} \left[ I_{\varepsilon} (\xi_m) - 3\varepsilon_T (\xi_m) \delta_0 \right] d\xi_m \] (4.18)

\[ n_0 (\xi, t) = n_0 \delta_0 + \int_0^{\xi} C_{\varepsilon} (\xi - \xi) \frac{\partial}{\partial \xi} \left\{ \varepsilon_0 (\xi) - \frac{1}{3} \delta_0 I_{\varepsilon} (\xi) \right\} d\xi + \delta_0 \int_0^{\xi} \Delta_{\varepsilon} (\xi - \xi) \frac{\partial}{\partial \xi} \left\{ I_{\varepsilon} (\xi) - 3\varepsilon_T (\xi) \right\} d\xi \] (4.19)

where \( \Delta_{\varepsilon} \) is the bulk strain-optical coefficient, \( \xi_m \) is the reduced time for the modulus and \( \xi_c \) is the reduced time for the strain-optical coefficient. It is noted that \( I_{\varepsilon} - 3\varepsilon_T \) means the strains resulting from a temperature change and it does not contribute to the pressure and birefringence. Eqs. (4.18) and (4.19) use the different reduced time for modulus and strain-optical coefficient because the shift factor for them may be different.

4.2 Numerical Simulation

A methodology is developed to calculate the frozen-in thermal birefringence from mechanical and optical material functions.

4.2.1 Heat Transfer Analysis

For one dimensional heat transfer problem, equation of conduction is

\[ \frac{\partial T}{\partial t} = \alpha_f \left( \frac{\partial^2 T}{\partial z^2} \right) \] (4.20)

where \( \alpha_f = \frac{k_j}{\rho_j C_{p,j}} \) (4.21)

with the initial and boundary conditions

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\[ T|_{z=0} = T_j \quad (4.22) \]
\[ \frac{\partial T}{\partial z}|_{z=0} = 0 \quad (4.23) \]
\[ -k_s \frac{\partial T}{\partial z}|_{z=\pm b} = h\left(T|_{z=\pm b} - T_f\right) \quad \text{at} \quad z = \pm b \quad \text{for} \quad t > 0 \quad (4.24) \]

where \( \alpha_j \) and \( h \) is the thermal diffusivity and the heat transfer coefficient, respectively.

### 4.2.2 Temperature History

For the solution of the energy equation, Crank-Nicolson finite difference scheme [165] is employed. Discretizing the spatial derivatives in Eq. (4.20) using forward difference of first order and central difference of second order, respectively yield:

\[ \frac{\partial T}{\partial t} = \frac{1}{\Delta t}\left(T^{n+1}_i - T^n_i\right) \quad (4.25) \]
\[ \alpha_j \frac{\partial^2 T}{\partial z^2} = \frac{1}{2\Delta z^2}\left(T^{n+1}_{i-1} + T^{n+1}_{i+1} + 2T^n_i - 2T^{n+1}_i + T^n_{i+1} + T^n_{i-1}\right) \quad (4.26) \]

where subscript \( i \) and \( n \) stands for each node along the thickness direction and time step, respectively.

Substituting Eqs. (4.25) and (4.26) into Eq. (4.20) yields the following equations for the interior nodes along the thickness direction:

\[ -\frac{\tilde{r}_j}{2} T^{n+1}_{i-1} + (1 + \tilde{r}_j) T^{n+1}_i - \frac{\tilde{r}_j}{2} T^{n+1}_{i+1} = \frac{\tilde{r}_j}{2} T^n_{i-1} + (1 - \tilde{r}_j) T^n_i + \frac{\tilde{r}_j}{2} T^n_{i+1} \quad (4.27) \]

where \( \tilde{r}_j = \frac{\alpha_j \Delta t}{\Delta z^2} \quad (4.28) \)
This equation is also valid for $i = 2$ to $i_{\text{max} - 1}$, with $i = 1$ and $i_{\text{max}}$ satisfying the boundary condition.

For the skin layer,

\[ \tilde{r}_j = \tilde{r}_i = \frac{\alpha_s \Delta t}{\Delta z^2} \quad (4.29) \]

where $\alpha_s = \frac{k_s}{\rho_s C_{p,s}}$. \quad (4.30)

For the interface between the skin and core layers,

\[ \tilde{r}_j = \tilde{r}_{\text{int}} = \frac{\alpha_{\text{int}} \Delta t}{\Delta z^2} \quad (4.31) \]

where $\alpha_{\text{int}} = \frac{\alpha_s + \alpha_c}{2}$. \quad (4.32)

For the core layer,

\[ \tilde{r}_j = \tilde{r}_i = \frac{\alpha_c \Delta t}{\Delta z^2} \quad (4.33) \]

where $\alpha_c = \frac{k_c}{\rho_c C_{p,c}}$. \quad (4.34)

To derive the first row of the band matrix, symmetry of the boundary condition at the center, Eq. (4.23) is used corresponding to no temperature gradient at the center of the plate. Discretization of the derivative in Eq. (4.23) using central differences of first order yields:

\[ \frac{\partial T}{\partial z} \bigg|_{z=0} = \frac{1}{2} \frac{1}{2\Delta z} \left[ \left( T_{i+1}^{n+1} - T_i^{n+1} \right) + \left( T_i^n - T_{i-1}^n \right) \right] = 0 \quad (4.35) \]

\[ T_{i-1}^n = T_i^n + \left( T_{i+1}^{n+1} - T_i^{n+1} \right) \quad (4.36) \]
Substituting Eq. (4.36) into Eq. (4.27), for the case of \( i = 0 \) in the centerline, \( z = 0 \), the following equation is obtained for the first row of the band matrix.
\[
(1 + \tilde{r}_i)T_0^{n+1} - \tilde{r}_iT_1^{n+1} = (1 - \tilde{r}_i)T_0^n + \tilde{r}_iT_1^n
\]
(4.37)

For the last row of the band matrix, the convective boundary condition at the surface of the plate is given by Eq. (4.24). For the discretization of the boundary, the equation is rewritten as:
\[
k_i \frac{\partial T}{\partial z} = hT_\infty - hT_i \quad \text{at} \quad z = \pm b \quad \text{for} \quad t > 0
\]
(4.38)

Discretization of the derivative and \( T_i \) in Eq. (4.38) yields
\[
k_i \frac{\partial T}{\partial z} = k_s \left[ \frac{1}{4\Delta z} \left\{ \left( T_i^{n+1} - T_{i+1}^{n+1} \right) + \left( T_i^n - T_{i-1}^n \right) \right\} \right]
\]
(4.39)
\[
-hT_i = -\frac{h}{2} \left( T_i^{n+1} + T_i^n \right)
\]
(4.40)

After substituting Eqs. (4.39) and (4.40) into Eq. (4.38) and rearranging it for \( T_i^{n+1} \), the following equation is obtained.
\[
T_i^{n+1} = T_i^{n+1} - \left( T_i^n - T_{i-1}^n \right) + CT_i^n - \frac{C}{2} \left( T_i^{n+1} - T_i^n \right)
\]
(4.41)
where
\[
C = \frac{4\Delta z h}{k_s}
\]
(4.42)

Substituting Eq. (4.41) into Eq. (4.27) yields the following equation for the last row of the band matrix based on the convective boundary condition:
\[
-\tilde{r}_{\max} T_{i_{\max}-1}^{n+1} + \left( 1 + \tilde{r}_i + \frac{\tilde{r} C}{4} \right) T_{i_{\max}}^{n+1} = \tilde{r}_i T_{i_{\max}-1}^n + \left( 1 - \tilde{r}_i - \frac{\tilde{r} C}{4} \right) T_{i_{\max}}^n + \frac{\tilde{r} C}{2} T_\infty
\]
(4.43)
Eqs. (4.27), (4.37) and (4.43) are a set of algebraic equations that can be arrayed in a band matrix of the form 
\[
\begin{bmatrix}
A & B & C
\end{bmatrix}
\begin{bmatrix}
T_i
\end{bmatrix}
= 
\begin{bmatrix}
RHS
\end{bmatrix},
\]
where \( T_i \) is the solution of the temperature at the present time. The discretized equation can be solved by means of a tridiagonal solver using the Equilibrium method [165]. After obtaining the thermal history for the multi-layered plate, the first order rate equation, Eq. (4.7), together with Eqs. (4.13) through (4.15) for each skin and core layer was solved by the fourth order Runge-Kutta method [165] to obtain the thermal strain \( \varepsilon \), the effective temperature \( T_{eff} \) and the shift factor \( a_r \) for the each skin and core layer. It should be noted that \( \varepsilon \), \( T_{eff} \) and \( a_r \) from each skin and core layer were averaged to obtain each value of the interface. Then \( \xi \) was determined from Eq. (4.17).

4.2.3 Stress and Strain Analysis

Due to the complication of utilizing linear viscoelastic constitutive equations, Eqs. (4.4) and (4.6), a further simplification can be done by making assumptions on stress and strain analysis. This results in more explicit forms in stresses, strains and birefringence [2,141].

For an infinite plate subjected to symmetrically uniform cooling, only contraction will be taken into account, resulting in only volume changing, in other words, no shear components on both stress and strain are imposed such that
\[
\sigma_{ij} = \varepsilon_{ij} = 0 \quad (i \neq j) \tag{4.44}
\]
Moreover, no surface traction is acting on the surfaces of plate, x-y plane.
\[
\sigma_{zz} = 0 \quad -b \leq z \leq b \tag{4.45}
\]
Therefore, the problem is reduced to a planar stress problem. Because the lateral dimensions are much larger than the plate thickness and the edge effect are neglected, the two non-zero normal stress components and two non-zero normal strain components are equal to each other, and the strain components are independent on \( z \). Consequently, it can be written that

\[
\sigma_{xx} = \sigma_{xx}(z,t) = \sigma_{yy} = \sigma_{yy}(z,t) \quad (4.46)
\]

\[
\varepsilon_{xx} = \varepsilon_{xx}(t) = \varepsilon_{yy} = \varepsilon_{yy}(t) \quad (4.47)
\]

Because the plate is free of constraints (no external forces), the resulting force is zero through the cross section.

\[
\int_{-b}^{b} \sigma_{xx}(z,t) dz = 0 \quad (4.48)
\]

It is seen that with this idealized problem of free quenching, the calculation of residual thermal stresses and birefringence is greatly simplified.

### 4.2.4 Thermal Stresses and Birefringence

Numerical simulation schemes were formulated to calculate the residual thermal stresses and birefringence in freely quenched multi-layered plates.

At first, expanding Eq. (4.18) yields the following equation:

\[
\left| \begin{array}{ccc}
\sigma_{xx} & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & \sigma_{yy} & \tau_{yz} \\
\tau_{zx} & \tau_{zy} & \sigma_{zz}
\end{array} \right| = \int_{\xi_m}^{\xi_f} 2G \left( \xi_m - \xi \right) \frac{\partial}{\partial \xi_m} \left[ \begin{array}{ccc}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\
\varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{array} \right] \left[ \begin{array}{ccc}
\frac{1}{3} & 0 & 0 \\
0 & I_{\varepsilon} & 0 \\
0 & 0 & I_{\varepsilon}
\end{array} \right] d\xi_m
\]

\[
\int_{0}^{\xi_f} K \left( \xi_m - \xi \right) \frac{\partial}{\partial \xi_m} \left[ \begin{array}{ccc}
I_{\varepsilon} & 0 & 0 \\
0 & 3\varepsilon_T & 0 \\
0 & 0 & 3\varepsilon_T
\end{array} \right] \left[ \begin{array}{ccc}
I_{\varepsilon} & 0 & 0 \\
0 & I_{\varepsilon} & 0 \\
0 & 0 & I_{\varepsilon}
\end{array} \right] d\xi_m = 0 \quad (4.49)
\]
Substituting the volume expansion bulk strain $I_\varepsilon$ given by Eq. (4.5) into Eq. (4.49), the strain components resulting from only temperature change become:

\[ \varepsilon_{xx} - \frac{1}{3} I_\varepsilon = \frac{1}{3}(2\varepsilon_{xx} - \varepsilon_{yy} - \varepsilon_{zz}) \quad (4.50) \]

\[ \varepsilon_{yy} - \frac{1}{3} I_\varepsilon = \frac{1}{3}(2\varepsilon_{yy} - \varepsilon_{xx} - \varepsilon_{zz}) \quad (4.51) \]

\[ \varepsilon_{zz} - \frac{1}{3} I_\varepsilon = \frac{1}{3}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}) \quad (4.52) \]

\[ I_\varepsilon - 3\varepsilon_T = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} - 3\varepsilon_T \quad (4.53) \]

where the thermal strain $\varepsilon_T$ is given by Eq. (4.7).

Substituting Eqs. (4.50) to (4.53) into (4.49) and rearranging them using the stress analysis of Eqs. (4.45) and (4.46), the stress components are obtained as:

\[ \sigma_{xx} = \sigma_{yy} = \int_0^{\xi_m} 2G(\xi_m - \xi_m) \frac{\partial}{\partial \xi_m} \left[ \varepsilon_{xx}(\xi_m) - \varepsilon_{zz}(\xi_m) \right] d\xi_m \quad (4.54) \]

\[ \sigma_{zz} = 0 = \int_0^{\xi_m} 2G(\xi_m - \xi_m) \frac{\partial}{\partial \xi_m} \left[ \frac{2}{3}\varepsilon_{xx}(\xi_m) - \frac{2}{3}\varepsilon_{zz}(\xi_m) \right] d\xi_m \]

\[ + \int_0^{\xi_m} K(\xi_m - \xi_m) \frac{\partial}{\partial \xi_m} \left[ 2\varepsilon_{xx}(\xi_m) + \varepsilon_{zz}(\xi_m) - 3\varepsilon_T \right] d\xi_m \quad (4.55) \]

Using the piecewise linear approximation [165], the integrals in Eqs. (4.54) and (4.55) were expanded as:

\[ \int_0^{\xi} A(\xi - \xi) \frac{\partial B(\xi)}{\partial \xi} d\xi = \sum_{k=1}^{j} \frac{B(\xi^k) - B(\xi^{k-1})}{\xi^k - \xi^{k-1}} \int_{\xi^{k-1}}^{\xi^k} A(\xi' - \xi) d\xi' \quad (4.56) \]

in which $B(\xi^k)$ where if $\xi = \xi^j$, $j$ denotes the current time step, is unknown and $B(\xi^k)$ where if $k < j$, $k$ denotes a previous time step, has been solved in the previous
time steps. Then the strain \( \varepsilon_{zz}(z,t) \) is obtained by Eq. (4.55) and the strain \( \varepsilon_{xx}(t) \) is derived by substituting Eq. (4.54) into Eq. (4.48). After calculation of \( \varepsilon_{xx}(t) \) and \( \varepsilon_{zz}(z,t) \) for skin and core regions, the \( \varepsilon_{xx}(t) \) and \( \varepsilon_{zz}(z,t) \) at the interface is obtained by taking an average from the value of \( \varepsilon_{xx}(t) \)'s and \( \varepsilon_{zz}(z,t) \)'s for a node of skin and a node of core near the interface of skin and core region, respectively. Then the stress history \( \sigma_{xx}(z,t) \) can be solved by Eq. (4.54) using \( \varepsilon_{xx}(t) \) and \( \varepsilon_{zz}(z,t) \) calculated earlier. The final discretized formulations are:

\[
G^{i,k} = \left[ \int_{\xi_{i,k-1}}^{\xi_{i,k}} G \left( \xi^{i,k} - \xi \right) d\xi \right] / \left( \xi^{i,k} - \xi^{i,k-1} \right) \quad (4.57)
\]

\[
A^{i,j} = -G^{i,j} \left( \varepsilon_{zz}^{i,j-1} - \varepsilon_{xx}^{i,j-1} \right) + \sum_{k=1}^{i-1} G^{i,k} \left[ \varepsilon_{zz}^{i,k} - \varepsilon_{zz}^{i,k-1} - \varepsilon_{xx}^{i,k} + \varepsilon_{xx}^{i,k-1} \right] \quad (4.58)
\]

\[
B^{i,j} = -\left( 2K_i - 4G^{i,j} / 3 \right) / \left( K_i + 4G^{i,j} / 3 \right) \quad (4.59)
\]

\[
\lambda^{i,j} = \begin{cases} 
-3\varepsilon_{zz}^{i,j} K_i & \text{if } T > T_g \\
-3\varepsilon_{zz}^{i,j} K_i - \left( K_s - K_i \right) \left[ \varepsilon_{xx}^{i,j} + 2\varepsilon_{zz}^{i,j} - 3\varepsilon_{zz}^{j} \right]_{T = T_g} & \text{if } T > T_s 
\end{cases} \quad (4.60)
\]

\[
\rho^{i,j} = \left( 4A^{i,j} / 3 - \lambda^{i,j} \right) / \left( K_i + 4G^{i,j} / 3 \right) \quad (4.61)
\]

\[
\varepsilon_{zz}^{i,j} = -\left( \int_{-b}^{b} 2 \left( A^{i,j} - G^{i,j} \rho^{i,j} \right) dz \right) / \left( \int_{-b}^{b} 2 \left[ G^{i,j} \left( 1 + B^{i,j} \right) \right] dz \right) \quad (4.62)
\]

\[
\varepsilon_{xx}^{i,j} = -B^{i,j} \varepsilon_{zz}^{i,j} + \rho^{i,j} \quad (4.63)
\]

\[
\sigma_{xx}^{i,j} = 2G^{i,j} \left( 1 + B^{i,j} \right) \varepsilon_{zz}^{i,j} + 2 \left( A^{i,j} - G^{i,j} \rho^{i,j} \right) \quad (4.64)
\]

where the first superscript \( i \) denotes discretization in \( z \) direction, the second superscript \( k \) or \( j \) denote discretization in time, and values of \( \left[ \varepsilon_{xx}^{i,j} + 2\varepsilon_{zz}^{i,j} - 3\varepsilon_{zz}^{j} \right]_{T = T_s} \)
are evaluated at the discretized position $i$ when the temperature there becomes equal to $T_s$.

After the strain history, $\varepsilon_{xx}(t)$ and $\varepsilon_{zz}(z,t)$, in the multi-layered plate was obtained, the birefringence was calculated as follows:

$$\Delta n_i = n_{xx} - n_{zz} = \int_0^{\xi} C_{c} \left( \xi_{c} - \xi \right) \frac{\partial}{\partial \xi} \left[ \varepsilon_{xx}(\xi) - \varepsilon_{zz}(\xi) \right] d\xi$$ \hspace{1cm} (4.65)

Similar to the stress calculation, using the piecewise linear approximation, Eq. (4.65) can be discretized to obtain the explicit formulation for birefringence calculation as follow:

$$\Delta n_i = n_{xx} - n_{zz} = \sum_{k=2}^{i} \frac{\varepsilon_{xx}^{k} - \varepsilon_{xx}^{k-1} - \varepsilon_{zz}^{i,k-1} + \varepsilon_{zz}^{i+1,k-1}}{\xi_c - \xi_i^k} \int_{\nu_{p,k}} C_{c} \left( \xi_{c}^{i,k} - \xi \right) d\xi$$ \hspace{1cm} (4.66)
CHAPTER V
THEORETICAL MODELING AND MATHEMATICAL FORMULATION FOR
CO-INJECTION MOLDING

5.1 Governing Equation of Co-injection Molding Process

To obtain a full description of the flow process, equations of the conservation of mass, momentum and energy for both skin and core materials along with equation considering the dynamics interaction of core and skin materials are solved with some corresponding simplifying assumptions. In addition, the flow behavior depends on corresponding rheological properties, thermal conductivity, specific heat and density of each material. Especially, the temperature dependence of polymer melt flow properties is also important. Therefore, the conventional injection molding simulation designed for a single material is no longer suitable for simulating co-injection molding process. Nevertheless, the basic theory can still be applied to the individual material regions, with the major challenge to track the interface shape, tracing individual components at any time and location in the cavity. Approach to the modeling of the co-injection molding processes is not being same because each modeling uses different viscosity function with the different temperature dependence of polymer melt.

The governing equations for the mold filling in co-injection molding are based on the application of the principles of conservation of mass and energy and a balance of forces. The conservation of mass balance for fluid motion has the following form:
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0
\]  
\hspace{1cm} (5.1) 

where \( \nabla \), \( \rho \) and \( \mathbf{v} \) are the “del” operator, the density of material, and the velocity vector, respectively. The force balance has the following form in vector-tensor notation:
\[
\frac{\partial}{\partial t} \rho \mathbf{v} + \nabla \cdot [\rho \mathbf{v} \mathbf{v}] = \nabla \cdot \mathbf{\sigma}
\]  
\hspace{1cm} (5.2) 

where \( \mathbf{\sigma} \) is the stress tensor.

The stress tensor can be divided into two parts
\[
\mathbf{\sigma} = -P \mathbf{\delta} + \mathbf{\tau}
\]  
\hspace{1cm} (5.3) 

where \( \mathbf{\tau} \) is the extra stress associated with flow, \( P \) is a scalar called isotropic pressure, and \( \mathbf{\delta} \) is the unit tensor. By substituting Eq. (5.3) into Eq. (5.2), the force balance has the following form:
\[
\frac{\partial}{\partial t} \rho \mathbf{v} + \nabla \cdot [\rho \mathbf{v} \mathbf{v}] = -\nabla P + \nabla \cdot \mathbf{\tau}
\]  
\hspace{1cm} (5.4) 

The energy equation in terms of temperature has the following form:
\[
\rho C_p \left( \frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) = k \nabla^2 T + \Phi
\]  
\hspace{1cm} (5.5) 

\[
\Phi = 2\eta_0 \varepsilon : \varepsilon + \sum_{k=1}^{N} \frac{\eta_k}{4 \theta_k} \left[ C_{e_k} : C_{e_k} - 3 \left( \frac{1}{3} I_{c_k} - \frac{1}{2} \left( \Pi_{c_k} - I_{c_k} \right) \right) \right]
\]  
\hspace{1cm} (5.6) 

where \( C_p \) is the heat capacity, \( k \) is the thermal conductivity, \( T \) is temperature, \( \Phi \) is viscous dissipation, \( \varepsilon \) is the rate of deformation tensor, \( C_{e_k} \) is the elastic strain tensor (Finger measure) of the \( k \)-th relaxation mode that represents the portion of total strain which will be recovered if all the stresses on the viscoelastic fluid are suddenly released, \( I_{c_k} \) and \( \Pi_{c_k} \) is the first and second invariant of \( C_{e_k} \). \( T \) is the temperature, \( \eta_0 \) is the
zero-shear-rate viscosity, \( s \) is the non-dimensional rheological parameter between 0 to 1; \( \theta_k \) and \( \eta_k \) are the modulus and viscosity of the \( k \)-th mode measured at a reference temperature \( T_r \).

In relating the stress field to the flow field, the Leonov model was chosen and used as the constitutive equation in this study [2].

\[
\tau = 2\eta_0 s \left[ e^{\frac{1}{3}(\text{tr}\tau)} \delta \right] + 2 \sum_{k=1}^{\infty} \mu_k \left( \frac{C_{ik} - \frac{I_{C_{ik}}}{3}}{\eta_k} \right) \tag{5.7}
\]

\[
\frac{DC_k}{Dt} = (\nabla \tau)^T C_i + C_i (\nabla \tau) - \left( \frac{\mu_k}{\eta_k} \right) \left[ C_i^2 + \left( \frac{I_{C_{ik}} - I_{C_{ik}}}{3} \right) C_i - \delta \right] \tag{5.8}
\]

\( \tau \) is the deviatoric stress tensor and \( \frac{DC}{Dt} \) is the differential operator of the substantial derivation.

The temperature-dependence of viscosity and relaxation time can be expressed by the following Arrhenius-type temperature dependence of viscosity and relaxation time will be used.

\[
\eta_k(T) = A_k \exp \left( \frac{T_k}{T} \right) \tag{5.9}
\]

\[
\theta_k(T) = B_k \exp \left( \frac{T_k}{T} \right) \tag{5.10}
\]

where \( T_k \) is the temperature sensitivity of viscosity and relaxation time related to the activation energy.
The governing equations for skin and core melt domains are coupled with the kinematic interface condition which relates the change in the moving boundary position to the local fluid velocity.

5.2 Interface Transport Equation in Co-injection Molding

The specific problem in co-injection molding is to track the evolution of the interface, such that a predictive computation can be useful to reach the optimum material configuration and encapsulated sandwich structure. Thus, the transport equations describing interface characteristics should be well established from the fluid dynamic and both interfacial kinematic and dynamic viewpoints. The location of the interface strongly depends on the rheological properties of the individual polymers and their interaction, as well as on the processing conditions.

Due to the time-dependent transient interface evolution between the skin and core, the interface is considered to be an internal moving boundary whose position is defined along the topological interface between two flow sub-domains. It is not known in advance and must be computed as a part of the solution. Therefore, the moving-boundary problems have additional degrees of freedom and additional equations, compared with fixed-boundary flow problems. The quantitative description of such problems depends on the understanding of the physical processes taking place on the interface and on the successful solution of the corresponding moving boundary problems. The knowledge in both these areas is far from complete [177]. Generally, two requirements that must be satisfied are the kinematic condition and the dynamic condition.
5.2.1 The Kinematic Condition

In general, the moving interface can be considered as a three-dimensional streaming surface along which particles move. Thus, from the kinematics point of view the interface evolution can be represented by the following equation:

\[ z = \delta(x, y, t) \]  \hspace{1cm} (5.11)

where \( z \) is the interface location between two flow sub-domains.

Since material points move with the interface, the conservation of mass at the moving interface should be satisfied at any time. Then, in the absence of surface tension the rate of displacement of the moving interface is related to the fluid velocity \( V \) at the interface through the following equation:

\[ \frac{\partial \delta}{\partial t} + \nabla \cdot \delta V = 0 \]  \hspace{1cm} (5.12)

where \( \delta \) is the velocity component in the thickness direction at the interface.

For a thin plain cavity of molding process where Hele-Shaw approximation is applied, a two-dimensional planar flow is generally of main concern. Flow in the thickness direction is insignificant, meaning that \( \delta = 0 \). Therefore, for time-dependent problems, the above kinematic condition of the moving interface becomes

\[ \frac{\partial \delta}{\partial t} + u_i^{\delta} \frac{\partial \delta}{\partial x} + v_i^{\delta} \frac{\partial \delta}{\partial y} = 0 \]  \hspace{1cm} (5.13)

where \( u_i^{\delta}, v_i^{\delta} \) is the skin/core velocity at the interface, \( i \) represents skin or core polymer, respectively. \( \delta \) is the interface position between the skin and core melt.

For steady-state moving interface, the above kinematic equation, Eq. (5.13), reduces to
\[ V^\delta \cdot n = 0 \]  \hspace{1cm} (5.14)

where \( n \) is the normal unit vector to the interface.

5.2.2 The Dynamic Conditions

In co-injection molding process, a sharp interface is assumed to exist between the skin and core materials, which means there is no macroscopic mixing at the interface. Therefore, the continuity of the velocity \( V \) and the total stress tensor \( \sigma \) across the skin-core interface should be satisfied, that is:

\[ V^c = V^s, \quad \sigma^c = \sigma^s \]  \hspace{1cm} (5.15)

\[ \sigma = -pI + \tau \]  \hspace{1cm} (5.16)

where the subscripts \( c \) and \( s \) denote the core and skin, respectively, \( p \) is the hydrostatic pressure, \( \tau \) is the extra stress tensor, \( I \) is the unit tensor, and \( \sigma \) is the total stress tensor.

The stress boundary conditions at the interface in thickness direction are given by the equivalence of the total normal stresses rather than by continuous shear stresses at the interface which were used in all previous simulations.

\[ \sigma_{zz,c} = \sigma_{zz,s}, \quad \sigma_{zz,c} = -p_c + \tau_{zz,c}, \quad \sigma_{zz,c} = -p_s + \tau_{zz,s} \]  \hspace{1cm} (5.17)

The presence of viscoelastic normal stresses at the interface created a discontinuity in the shear stress. The stronger the difference in the first normal stress difference between the two phases, the more severe will be the jump in the shear stresses.

\[ \Delta \tau_{xz} = \frac{\partial \delta}{\partial x} \cdot \Delta \sigma_{xx} = \frac{\partial \delta}{\partial x} \cdot \Delta N_{1x} \]  \hspace{1cm} (5.18)
\[ \Delta \tau_{xz} = \tau_{xz,s} - \tau_{xz,c} \]  
(5.19)

\[ \Delta \sigma_{xz} = \sigma_{xz,s} - \sigma_{xz,c} = N_{1x,s} - N_{1x,c} = \Delta N_{1x} \]  
(5.20)

where \( \delta \) is the core layer thickness.

In this study, though a nonlinear viscoelastic fluid is assumed along with the Hele-Shaw approximation, it can be assumed for simplicity that the pressure and the shear stress are continuous at the interface. Then Eq. (5.15) can be reduced to:

\[ \left( \eta \frac{\partial V}{\partial z} \right)_c = \left( \eta \frac{\partial V}{\partial z} \right)_s \]  
(5.21)

The thermal conditions at the interface should also be identified, in other words, the temperature and heat fluxes are continuous on the interface:

\[ T_c = T_s, \quad \left( k \frac{\partial T}{\partial z} \right)_c = \left( k \frac{\partial T}{\partial z} \right)_s \]  
(5.22)

5.2.3 Filling Stage

During the flow of hot skin and core melts into a mold cavity in the filling stage, the flow stresses start to build up.

5.2.3.1 Governing Equations and Interface Evolution

In this research, we consider the idealized simulation problem of co-injection molding process. During the filling stage, skin polymer melt for sequential co-injection molding initially at a uniform temperature \( T_0 \), flows into the cavity under a fully developed Poiseuille-type flow. Following assumptions are made:
a. Skin and core melts are assumed incompressible fluids.

b. The thin film approximation is employed.

c. No slip condition at the wall, and the interface.

d. The inertial force in the momentum equation is neglected due to a small Reynolds number.

e. The thickness of the cavity is much smaller than its planar dimensions, then the velocity component in the gapwise direction is taken to be zero and the velocity gradient in the flow direction is neglected.

f. The pressure is independent of the gapwise direction.

g. The pressure is assigned to be zero at the melt front.

h. The thermal conduction in the flow direction and the thermal convection in the gapwise direction are negligible.

i. No fountain flow at the melt front is taken into account.

j. Thermal conductivity and heat capacity for skin and core materials are assumed to be constant.

k. A sharp interface is assumed to exist between the skin and core fluids. The fluid is not miscible at the interface.

Therefore, the governing equation for an incompressible, non-isothermal fluid, mass, motion and energy balance equations in a center-gated disk cavity are given by:

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{5.23}
\]

\[
\frac{\partial P}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} = 0 \quad \frac{\partial P}{\partial y} + \frac{\partial \tau_{yz}}{\partial z} = 0 \tag{5.24}
\]
\[
\rho C_p \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = k_{ah,j} \left( \frac{\partial^2 T}{\partial z^2} \right) + \Phi, \quad (5.25)
\]

\[
\Phi = 2s\eta_c tr \left( \varepsilon^2 \right) + \sum_{k=1}^{N} \frac{\eta_i}{4\theta_k^2} \left[ \frac{1}{3} \cdot tr \left( \sum_{k=1}^{N} \left( C^{-1} - tr C^{-1} \right) \right) + tr \left( tr C^{-2} \right) - 3 \right] \quad (5.26)
\]

where \( u \) and \( v \), the velocity in the flow and width direction; \( z \), the thickness direction, \( p \), the pressure; \( \tau_{zx} \) and \( \tau_{zy} \), the shear stresses; \( \Phi \) is the energy dissipation function; indices \( i \), skin or core polymer melt.

The boundary and initial conditions for velocity fields, temperature and pressure or volume flow rate are

\[
T \big|_{z=0} = T_0 \quad \text{at} \quad t=0; \quad T \big|_{z=b} = T_w; \quad \frac{\partial T}{\partial z} \big|_{z=0} = 0 \quad (5.27)
\]

\[
\left. u \right|_{z=b} = \left. v \right|_{z=b} = 0; \quad \left. \frac{\partial u}{\partial z} \right|_{z=0} = \left. \frac{\partial v}{\partial z} \right|_{z=0} = 0 \quad (5.28)
\]

\[
\frac{\partial P}{\partial n} = 0 \quad \text{no penetration at all solid boundary} \quad (5.29)
\]

\[
Q = Q_{ent} \quad \text{at the gate} \quad (5.30)
\]

where \( b \) is the half of the gap thickness.

To determine the velocity, stresses and temperature fields by solving the governing equations, a constitutive equation is required. In the present research, the non-isothermal viscoelastic flow calculations during the cavity filling are based on the Leonov non-linear viscoelastic constitutive equation [117].

For shear flow, the Leonov viscoelastic constitutive equation reduced to

\[
\sigma_{ii} = -P_i \delta + 2s\eta_{0,i} \left( T \right) s_1 + \sum_{k=1}^{N} \frac{\eta_{0,i} \left( T \right)}{\theta_{k,i} \left( T \right)} C_{k,i} \quad (5.31)
\]
where \( \varepsilon \) is the deformation-rate tensor defined as:

\[
\varepsilon = \frac{1}{2} \left( \nabla V + \nabla V^T \right)
\]  

(5.32)

\( \eta_0 \) is the zero-shear-rate viscosity defined as:

\[
\eta_0(T) = \sum_{k=1}^{N} \frac{\eta_k(T)}{1 - s}
\]  

(5.33)

The temperature-dependence of viscosity and relaxation time can be expressed by the Arrhenius-type temperature dependence of Eqs. (5.9) and (5.10).

In addition, \( C_{k,i} \) is the elastic strain tensor of the \( k^{th} \) mode for skin or core melt governed by the following evolution equation [178].

\[
\frac{C_{k,i}^v}{\delta t} + \frac{1}{2\theta_{k,i}} \left( C_{k,i} \cdot C_{k,i} + C_{k,i} \left( \frac{I_{k,i} - I_{k,i}}{3} - \delta \right) \right) = 0
\]  

(5.34)

where indices \( i \) is skin or core polymer melt, \( I_{k,i} \) and \( I_{k,i} \) are the first and second invariants of the elastic strain tensor \( C_{k,i} \), \( C_{k,i}^v \) is the upper convected Jaumann derivative of the \( C_{k,i} \) defined as [179].

\[
C_{k,i}^v = \frac{D}{Dt} C_{k,i} - \nabla V^T \cdot C_{k,i} - C_{k,i} \cdot \nabla V
\]  

(5.35)

where \( \frac{D}{Dt} C_{k,i} \) is the differential operator of the substantial derivative of \( C_{k,i} \) with respect to time defined as:

\[
\frac{D}{Dt} C_{k,i} = \frac{\partial}{\partial t} C_{k,i} + \nabla_i \cdot C_{k,i}
\]  

(5.36)
Although the solution of kinematic equation, Eq. (5.13) leads to the exact location of the moving interface, its determination is not obvious. Thus, further efforts must be made towards incorporating the kinematic and dynamic equations with the conservation equations of fluid (mass and momentum equations). For the incompressible flow during the filling stage, integrating mass continuity equation over the core layer thickness leads to

\[
\int_0^\delta \frac{\partial u_c}{\partial x} dz + \int_0^\delta \frac{\partial v_c}{\partial y} dz = 0
\]  

(5.37)

The local flow rates per unit width in the x and y directions are

\[
q'_c = \int_0^\delta u_c dz = \delta \cdot u_c
\]

(5.38)

\[
q'_c = \int_0^\delta v_c dz = \delta \cdot v_c
\]

(5.39)

where \( u_c \) and \( v_c \) are the average velocities of core material in the x and y directions, respectively.

The derivatives of Eqs. (5.38) and (5.39) with respect to \( x \) and \( y \) are:

\[
\frac{\partial q'_x}{\partial x} = \int_0^\delta \frac{\partial u_c}{\partial x} (x, y, z) dz + u_c^\delta \cdot \frac{\partial \delta}{\partial x}
\]

(5.40)

\[
\frac{\partial q'_y}{\partial y} = \int_0^\delta \frac{\partial v_c}{\partial y} (x, y, z) dz + v_c^\delta \cdot \frac{\partial \delta}{\partial y}
\]

(5.41)

Combining Eqs. (5.37), (5.40) and (5.41) leads to

\[
\frac{\partial q'_x}{\partial x} + \frac{\partial q'_y}{\partial y} = V^\delta \cdot \nabla \delta = u_c^\delta \cdot \frac{\partial \delta}{\partial x} + v_c^\delta \cdot \frac{\partial \delta}{\partial y}
\]

(5.42)

where \( u_c^\delta \) and \( v_c^\delta \) are the core melt velocity components at the interface \( \delta \).
Following the same procedure for the skin material, one can obtain

\[
\frac{\partial q_s^x}{\partial x} + \frac{\partial q_s^y}{\partial y} = -\nabla^\delta \cdot \nabla \delta = -\left( u_s^x \frac{\partial \delta}{\partial x} + v_s^y \frac{\partial \delta}{\partial y} \right)
\]

(5.43)

where \( u_s^x \) and \( v_s^y \) are the skin melt velocity components at the interface \( \delta \).

By adding Eq. (5.42) to Eq. (5.43), one obtains the mass balance equation as a function of the whole gapwise-averaged velocity \( \nabla (\bar{\mu}, \bar{\nu}) \):

\[
\nabla \cdot (b\bar{V}) = 0
\]

(5.44)

where

\[
\bar{V} = \int_0^\delta V_c dz + \int_\delta^b V_s dz
\]

(5.45)

Using the concept of the average velocity over the layer thickness of each material (skin/core) as given by Eqs. (5.38) and (5.39), Eqs. (5.42) and (5.43) can be written in the form:

For the core polymer:

\[
\nabla \cdot (\delta \bar{V}_c) = \bar{V}_c^\delta \cdot \nabla \delta
\]

(5.46)

For the skin polymer:

\[
\nabla \cdot [(b - \delta) \bar{V}_s] = \bar{V}_s^\delta \cdot \nabla (b - \delta)
\]

(5.47)

Considering Eq. (5.13), Eqs. (5.46) and (5.47) can be also written, respectively, as:

\[
\nabla \cdot (\delta \bar{V}_c) = -\frac{\partial \delta}{\partial t}
\]

(5.48)
\[ \nabla \cdot [(b - \delta)\vec{V}_c] = \frac{\partial \delta}{\partial t} \]  

(5.49)

Thus, Eqs. (5.46) and (5.47) or Eqs. (5.48) and (5.49) let each material layer (skin/core) satisfy the mass continuity with Eq. (5.44) satisfying the total mass continuity.

After the integration of Eq. (5.2) with the lubrication approximation over the thickness of the skin and core polymer, respectively, with the use of the symmetry boundary condition at the center line, Eq. (5.28), the following relationship between the skin and core polymer is obtained

\[ \nabla p \cdot z = \eta_c \frac{\partial V_c}{\partial z} \]  

(5.50)

with \( 0 \leq z \leq \delta \) for the core polymer and \( \delta \leq z \leq b \) for the skin polymer.

The integration of Eq. (5.50) over each layer thickness gives the relationship between the velocities at the interface of skin/core polymer and at the central line. The use of the boundary condition of no slip at the wall leads to the following equations:

for the core fluid \( 0 \leq z \leq \delta \)

\[ \nabla p \int_0^\delta \frac{z}{\eta_c} dz = V_c \bigg|_{z=0} - V_c \bigg|_{z=b} \]  

(5.51)

and for the skin fluid \( \delta \leq z \leq b \)

\[ \nabla p \int_\delta^b \frac{z}{\eta_s} dz = -V_s \bigg|_{z=0} \]  

(5.52)

Considering continuity of the velocity at the interface \( z = \delta \), i.e. Eq. (5.15), one obtains
Finally, a further integration of Eq. (5.48) over the skin and core polymer thickness, respectively, with the use of the continuity of the shear stress and of the velocity at the interface between skin and core materials, Eqs. (5.15) and (5.22), leads to the following expressions for the average velocity \( \bar{V}_c \) and \( \bar{V}_s \).

For the core polymer:

\[
\delta \bar{V}_c = -\nabla p \int_0^b \left[ \int_{\delta}^{\eta_c} \frac{z}{\eta_c} \, dz + \int_{\delta}^{b} \frac{z}{\eta_s} \, dz \right] \, dz
\]

or

\[
\delta \bar{V}_c = -\nabla \cdot S_c
\]

with

\[
S_c = \int_{\delta}^{\eta_c} \frac{z^2}{\eta_c} \, dz + \delta \int_{\delta}^{b} \frac{z}{\eta_s} \, dz
\]

and

\[
\eta_c = \eta_{0,c} + \sum_{k=1}^{N} \left( \frac{\eta_{k,c}}{\theta_{k,c}} C^{k,k,c} \right) \left( \frac{\partial \bar{V}_c}{\partial z} \right)
\]

For the skin polymer

\[
(b - \delta) \bar{V}_s = -\nabla p \int_0^b \left[ \int_{\delta}^{b} \frac{z}{\eta_s} \, dz \right] \, dz = -\nabla p \int_{\delta}^{b} \frac{z(\delta - \delta)}{\eta_s} \, dz
\]

or

\[
(b - \delta) \bar{V}_s = -\nabla \cdot S_s
\]
with \[ S_s = \int_{z_s}^{b} z(z - \delta) \rd z \] (5.60)

and \[ \eta_s = \eta_{s,0} S_s + \frac{\sum_{k=1}^{N} \left( \eta_{k,s} \frac{C_{c,k,s}}{\theta_{c,k,s}} \right)}{\frac{\partial V_x}{\partial z}} \] (5.61)

Combining Eqs. (5.46) and (5.47) or Eqs. (5.48) and (5.49) with Eqs. (5.55) and (5.59) leads to for the core melt

\[
\frac{\partial \delta}{\partial t} + \frac{\partial}{\partial x} \left( -S_c \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( -S_c \frac{\partial p}{\partial y} \right) = 0
\] (5.62)

or

\[
V_c \cdot \nabla \delta + \frac{\partial}{\partial x} \left( S_c \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( S_c \frac{\partial p}{\partial y} \right) = 0
\] (5.63)

and for the skin melt

\[
\frac{\partial (b - \delta)}{\partial t} + \frac{\partial}{\partial x} \left( -S_s \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( -S_s \frac{\partial p}{\partial y} \right) = 0
\] (5.64)

or

\[
V_s \cdot \nabla (b - \delta) + \frac{\partial}{\partial x} \left( S_s \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( S_s \frac{\partial p}{\partial y} \right) = 0
\] (5.65)

These are the transient interface evolution equations for the interface tracking. It should be mentioned that similar interface transport equation as Eq. (5.63) is also used by Schlatter et al. [33,68], and Palluch and Isayev [69].

Adding Eq. (5.62) and Eq. (5.64), or adding Eq. (5.63) and Eq. (5.65) give the following well-known Hele-Shaw type governing equation for both materials in the
whole cavity domain which can be used to solve the pressure gradient distribution and velocity field:

$$\frac{\partial}{\partial x} \left( S_x \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( S_y \frac{\partial p}{\partial y} \right) = 0$$

(5.66)

$$S_x = \int_0^\delta \frac{z^2}{\eta_{s,c}} dz + \int_0^\delta \frac{z^2}{\eta_{s,s}} dz, \quad S_y = \int_0^\delta \frac{z^2}{\eta_{s,c}} dz + \int_0^\delta \frac{z^2}{\eta_{s,s}} dz$$

(5.67)

where $\eta_{s,c}$, $\eta_{s,s}$, $\eta_{s,c}$, and $\eta_{s,c}$ are $x$, $y$ components of Eqs. (5.57) and (5.61).

Here $\delta$ is half thickness of the core melt in the gapwise direction, $\eta_c$ and $\eta_s$ are viscosity for the core and skin melts, respectively. At $\delta = 0$, Eq. (5.66) reduces to governing equation for the single-phase injection molding.

The flow-induced stress tensor $\sigma$ developed during the filling stage of sequential co-injection molding process is calculated by the Leonov model for the incompressible fluids of Eq. (5.31). The evolution equation for the elastic strain tensor $C_{s,i}$ for the skin and core melts is rewritten by expanding Eq. (5.34) as:

$$\frac{\partial}{\partial t} C_{s,i} + V \cdot \nabla C_{s,i} - \nabla V \cdot C_{s,i} - C_{s,i} \cdot \nabla V + \frac{1}{2} \delta_{i,j} \left( C_{s,i} + C_{s,j} + \frac{\Pi_{s,c} - I_{s,c}}{3} \right) = 0$$

(5.68)

To avoid the cumbersome numerical calculations, for a two-dimensional planar flow, the elastic strain tensor is determined in the local streamwise coordinate system $(s, \theta, z)$, where $s$ is the flow direction, $\theta$ is perpendicular to $s$, the counterclockwise direction, and $z$ is in the gapwise direction. The velocity field for the local streamwise coordinates in disk-type cavity is given by $u_s(z), \quad v = w = 0$.  

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Therefore, the velocity gradients are:

\[
\nabla V = \nabla V^T = \begin{bmatrix}
-\frac{u_j}{s} & 0 & \partial u_i / \partial z \\
0 & 0 & 0 \\
\partial u_i / \partial z & 0 & 0 
\end{bmatrix} \tag{5.69}
\]

With the shear component \( C_{i\theta} \) and \( C_{\theta z} \) being zero, the elastic strain tensor for the streamwise coordinate is:

\[
C_{k,i} = \begin{bmatrix}
C_{ss,k,i} & 0 & C_{sz,k,i} \\
0 & C_{\theta\theta,k,i} & 0 \\
C_{sz,k,i} & 0 & C_{zz,k,i} 
\end{bmatrix} \tag{5.70}
\]

Due to incompressibility of the Leonov model, the determinant of the elastic strain tensor \( C_{k,i} \) is equal to unity. Therefore, the following equation should be satisfied.

\[
\text{det } C_{k,i} = C_{ss,k,i} C_{\theta\theta,k,i} C_{zz,k,i} - C_{sz,k,i}^2 C_{\theta\theta,k,i} = 1 \tag{5.71}
\]

Dot product terms in Eq. (5.68) are given as follow:

\[
\nabla V^T \cdot C_{k,i} = \begin{bmatrix}
-\frac{u_j}{s} & 0 & \partial u_i / \partial z \\
0 & 0 & 0 \\
\partial u_i / \partial z & 0 & 0 
\end{bmatrix} \begin{bmatrix}
C_{ss,k,i} & 0 & C_{sz,k,i} \\
0 & C_{\theta\theta,k,i} & 0 \\
C_{sz,k,i} & 0 & C_{zz,k,i} 
\end{bmatrix} = \begin{bmatrix}
-\frac{u_j}{s} C_{ss,k,i} + \partial u_i / \partial z C_{sz,k,i} & 0 & -\frac{u_j}{s} C_{sz,k,i} + \partial u_i / \partial z C_{zz,k,i} \\
0 & 0 & \partial u_i / \partial z C_{ss,k,i} \\
0 & \partial u_i / \partial z C_{sz,k,i} & 0 
\end{bmatrix} \tag{5.72}
\]
\[
C_{i,j} \cdot \nabla V = \begin{vmatrix}
C_{ss,k,i} & 0 & C_{sz,k,i} & -\frac{u_s}{s} & 0 & \frac{\partial u_s}{\partial z} \\
0 & C_{\theta \theta,k,i} & 0 & 0 & 0 & 0 \\
C_{sz,k,i} & 0 & C_{zz,k,i} & \frac{\partial u_s}{\partial z} & 0 & 0 \\
\end{vmatrix}
\]

\[
= \begin{vmatrix}
-\frac{u_s}{s} C_{ss,k,i} + \frac{\partial u_s}{\partial z} C_{sz,k,i} & 0 & C_{ss,k,i} & \frac{\partial u_s}{\partial z} \\
0 & 0 & 0 & 0 \\
-\frac{u_s}{s} C_{sz,k,i} + \frac{\partial u_s}{\partial z} C_{zz,k,i} & 0 & C_{sz,k,i} & \frac{\partial u_s}{\partial z} \\
\end{vmatrix}
\quad (5.73)
\]

\[
C_{k,i} \cdot C_{k,i} = \begin{vmatrix}
C_{ss,k,i} & 0 & C_{sz,k,i} & 0 & C_{sz,k,i} \\
0 & C_{\theta \theta,k,i} & 0 & 0 & C_{\theta \theta,k,i} \\
C_{sz,k,i} & 0 & C_{zz,k,i} & 0 & C_{zz,k,i} \\
\end{vmatrix}
\]

\[
= \begin{vmatrix}
C_{ss,k,i}^2 + C_{sz,k,i}^2 & 0 & C_{sz,k,i} \left( C_{ss,k,i} + C_{zz,k,i} \right) \\
0 & C_{\theta \theta,k,i}^2 & 0 \\
C_{sz,k,i} \left( C_{ss,k,i} + C_{zz,k,i} \right) & 0 & C_{zz,k,i}^2 + C_{sz,k,i}^2 \\
\end{vmatrix}
\quad (5.74)
\]

\[
\nabla V \cdot \nabla C_{k,i} = u_s \frac{\partial C_{k,i}}{\partial z}
\quad (5.75)
\]

The first and second invariants of elastic strain tensor \( C_{k,i} \) in Eq. (5.68) are written as:

\[
I_{\text{I}} = tr C_{k,i} = C_{ss,k,i} + C_{\theta \theta,k,i} + C_{zz,k,i}
\quad (5.76)
\]

\[
I_{\text{II}} = tr C_{k,i}^{-1} = C_{\theta \theta,k,i} C_{zz,k,i} + C_{ss,k,i} C_{zz,k,i} - C_{sz,k,i}^2 + C_{ss,k,i} C_{\theta \theta,k,i}
\quad (5.77)
\]

where

\[
C_{k,i}^{-1} = \begin{vmatrix}
C_{\theta \theta,k,i} & 0 & -C_{sz,k,i} \quad C_{ss,k,i} \\
0 & C_{ss,k,i} & 0 & -C_{sz,k,i} \quad C_{\theta \theta,k,i} \\
-C_{\theta \theta,k,i} & 0 & C_{ss,k,i} & C_{\theta \theta,k,i} \\
\end{vmatrix}
\quad (5.78)
\]

Substitution of Eqs. (5.71), (5.76) and (5.77) into Eq. (5.68), leads to
\[
\frac{\partial}{\partial t} \mathbf{C}_{i,j} + \mathbf{V}_i \cdot \nabla \mathbf{C}_{i,j} - \nabla V_i^T \cdot \mathbf{C}_{i,j} - \frac{1}{2\theta_i} \mathbf{C}_{i,j} \cdot \nabla \mathbf{V}_i + \frac{1}{2\theta_i} \left( \mathbf{C}_{i,j} \cdot \mathbf{C}_{i,j} - \mathbf{I} \right) = 0 \tag{5.79}
\]

Substituting Eqs. (5.72) through (5.75) into Eq. (5.79), the governing equations for the elastic strain tensor of the \( k \)th mode in the streamwise coordinate system are [2]:

\[
\frac{\partial C_{ss,k,i}}{\partial t} + u_{i,j} \frac{\partial C_{ss,k,i}}{\partial s} = 2 \left( -\frac{u_i}{s} C_{ss,k,i} + 2 C_{ss,k,i} \frac{\partial u_{i,j}}{\partial z} - \frac{1}{2\theta_i} \left( C_{ss,k,i}^2 + C_{ss,k,i}^2 -1 + \frac{A}{3} C_{ss,k,i} \right) \right) \tag{5.80}
\]

\[
\frac{\partial C_{s\alpha,k,i}}{\partial t} + u_{i,j} \frac{\partial C_{s\alpha,k,i}}{\partial s} = -\frac{u_i}{s} C_{s\alpha,k,i} + \frac{1}{2\theta_i} \left( C_{s\alpha,k,i}^2 + C_{s\alpha,k,i}^2 -1 + \frac{A}{3} C_{s\alpha,k,i} \right) \tag{5.81}
\]

\[
\frac{\partial C_{ss,\alpha,k,i}}{\partial t} + u_{i,j} \frac{\partial C_{ss,\alpha,k,i}}{\partial s} = 2 \frac{u_i}{s} C_{ss,\alpha,k,i} - \frac{1}{2\theta_i} \left( C_{ss,\alpha,k,i}^2 -1 + \frac{A}{3} C_{ss,\alpha,k,i} \right) \tag{5.82}
\]

\[
C_{ss,k,i} = \frac{1 + C_{ss,k,i}^2}{C_{ss,k,i}} \tag{5.83}
\]

where \( A = (C_{ss,\alpha,k,i}^2 -1) \left( C_{ss,k,i} + C_{ss,\alpha,k,i} -1 - \frac{1}{C_{ss,\alpha,k,i}} \right) \) \tag{5.84}

\[
\ddot{\gamma}_i = \frac{\partial u_{i,j}}{\partial z} = \sqrt{\left( \frac{\partial u_i}{\partial z} \right)^2 + \left( \frac{\partial u_j}{\partial z} \right)^2}, \quad u_{i,j} = \frac{\partial P}{\partial s} \frac{\partial}{\partial z} \left( \eta_i z \right) \tag{5.85}
\]

\[
\eta_i = \eta_0 z_i + \sum_{k=1}^{N_i} \eta_{i,k} \mathbf{C}_{k,i} \tag{5.86}
\]

The values of \( C_{k,i} \) at the entrance node are determined from the fully developed steady-state solution, \( \frac{DC_{k,i}}{Dt} = 0 \) of the simple shear flow under isothermal conditions [93,118] given by
\[ C_{ss,k,i}^{(0)} = \frac{\sqrt{2} X_k}{\sqrt{1 + X_k}} , \quad C_{sc,k,i}^{(0)} = \frac{2\Gamma}{1 + X_k} , \quad C_{cz,k,i}^{(0)} = \frac{\sqrt{2}}{\sqrt{1 + X_k}} \]  

(5.88)

where \( \Gamma = \theta_{k,i} \frac{\partial u_k}{\partial z} = \theta_{k,i} \dot{\gamma} \), \( X_k = \sqrt{1 + 4 \Gamma^2} \)  

(5.89)

5.2.3.2 Numerical Formulation and Simulation

The governing equations coupled with nonlinear viscoelastic constitutive equation need to be solved numerically in order to determine the pressure, flow rate, velocity, shear rate, viscosity, and shear and normal stresses profiles, and as well as the interface distribution and melt front advancement. However, these equations are highly nonlinear in nature. Thus, the approach based on a hybrid control volume finite element and finite difference method (CV/FEM/FDM) [147,148,180,181] is employed to solve the problems by using successive under-relaxation iteration.

To solve the pressure and interface evolution equations the whole domain of a disk-typed mold cavity is discretized into a series of three-node triangular elements in the x-y plane. Only one control volume is associated with each node. For each node of a triangular element, by connecting the centroid of each element to the midpoints of the three corresponding sides, the region enclosed by a contour in the counter-clockwise direction around each vertex node of a triangular element is specified as the subcontrol volume for this node as shown in Figure 3-4. The polygonal control volume that surrounds each vertex node is defined as the summation of sub-control volumes, which contains node \( N \), and is enclosed by a contour \( C \) in the counter-clockwise direction.
Each finite element has a constant thickness. The thickness of an element is specified at the three nodal points. In order to accommodate a possible sudden change of cavity thickness, the nodal thickness is assigned separately for each element, so the thickness may be discontinuous across inter-element boundaries.

The control-volume finite element method with triangular elements and linear shape functions is used to make the pressure and interface distribution on each element to be expressed by the nodal pressures and nodal interface position:

\[ p(x, y, t) = \sum_{j=1}^{3} L_j^l(x, y) p_j^l(t) \]  
\[ \delta(x, y, t) = \sum_{j=1}^{3} L_j^l(x, y) \delta_j^l(t) \]

where \( L_j^l(x, y) \) is the linear area-coordinate interpolation function for node \( j \) on element \( l \) \([148, 155, 181, 182]\), \( P_j^l(t) \) and \( \delta_j^l(t) \) denote the nodal pressures and the nodal interface positions, respectively. The linear shape functions for 2-D triangular elements can be written as:

\[ L_j^l(x, y) = \frac{1}{2A^l} \left( a_j^l + b_j^l(x + c_j^l y) \right) \quad (j = 1, 2, 3) \]

with \( a_j^l, b_j^l \) and \( c_j^l \) expressed as:

\[
\begin{bmatrix}
a_1^l & b_1^l & c_1^l \\
a_2^l & b_2^l & c_2^l \\
a_3^l & b_3^l & c_3^l
\end{bmatrix}
= 2A^l
\begin{bmatrix}
1 & 1 & 1 \\
x_1^l & x_2^l & x_3^l \\
y_1^l & y_2^l & y_3^l
\end{bmatrix}
= \begin{bmatrix}
x_2^l y_3^l - x_3^l y_2^l & x_1^l y_3^l - x_3^l y_1^l & x_1^l y_2^l - x_2^l y_1^l \\
y_2^l - y_3^l & y_3^l - y_1^l & y_1^l - y_2^l \\
x_3^l - x_2^l & x_1^l - x_3^l & x_2^l - x_1^l
\end{bmatrix}
\]

\[ A^l = \frac{1}{2} \begin{bmatrix}
1 & x_1^l & y_1^l \\
1 & x_2^l & y_2^l \\
1 & x_3^l & y_3^l
\end{bmatrix} \]
where $A_i$ is the area of the triangular element and $(x_i, y_i)$ is the coordinates of each node of the element $i$.

After applying the Galerkin weighted-residual procedure [155,156] or mass conservation to Eq. (5.66) using a control-volume approach [157], and introducing linear interpolation functions as well as a finite-difference representation for the time derivative, the following governing equation for pressure in the whole cavity domain is obtained [161]:

\[
\sum_{i=1}^{k_u} \sum_{j=1}^{2nu^3} S_i^j B_{i,j}^l p_{i,j}^N = Q_N
\]

with

\[
B_{i,j}^l = \frac{-1}{2A_l} \begin{bmatrix}
b_1^2 + c_1^2 & b_2 b_1 + c_1 c_2 & b_3 b_1 + c_1 c_3 \\
b_2 b_1 + c_1 c_2 & b_2^2 + c_2^2 & b_3 b_2 + c_2 c_3 \\
b_2 b_1 + c_1 c_3 & b_2 b_2 + c_2 c_3 & b_3^2 + c_3^2
\end{bmatrix}
\]

where $Q_N$ is the total volumetric flow rate for each node at any instant for the whole cavity domain, $k_u$ is the total number of elements containing node N, and $i$ is such that $N = NELNOD(l,i)$, $N' = NELNOD(l,j)$ with $j=1, 2$ for strip elements. Also,

$Q_N = Q_{ent}$ for the entrance nodes where $p = p_g$ or $Q_{ent} = Q_g$ is specified at the gate;

$Q_N = 0$ for the internal fully-filled nodes;

$Q_N = Q_{out}$ for the melt-front nodes where $p = 0$ is assumed.

Similarly, the interface evolution equation, Eq. (5.62) or (5.63) leads to the following numerical formulation [161]:
\[
\sum_{i=1}^{i_N} \sum_{j=1}^{3} A^l_i D_{i,j} \frac{\delta S_{i,j}^{n+1} - \delta S_{i,j}^n}{\Delta t} + \sum_{i=1}^{i_N} \sum_{j=1}^{3} S^l_i B_{i,j}^l p_N^l = Q^c_N
\]

(5.97)

\[
D_{i,j} = \begin{bmatrix}
1 & 1 & 1 \\
3 & 6 & 6 \\
1 & 1 & 1 \\
6 & 6 & 3
\end{bmatrix}
\]

(5.98)

Where \( N = NELNOD(l,i) \) and \( N' = NELNOD(l, j) \); \( Q^c_N \) is the volumetric flow rate of the core component which is different for the control volume associated with different node. Similarly, it can be found that

\[
Q^c_N = Q_{\text{ent}}^c \quad \text{for the entrance nodes where } p = p_g \text{ or } Q_{\text{ent}}^c = Q_g^c \text{ is specified at the gate;}
\]

\[
Q^c_N = 0 \quad \text{for the internal fully filled nodes;}
\]

\[
Q^c_N = Q_{\text{out}}^c \quad \text{for the melt-front nodes where } p \neq 0.
\]

In addition, \( A^l \) is the area of each element associated with the node \( N \). \( D_{i,j} \) and \( B_{i,j} \) are element matrices. \( B_{i,j} \) is the influence coefficient of the nodal pressure to the net flow rate in element \( l \), and \( D_{i,j} \) is the influence coefficient of the nodal interface location on the net flow rate in element \( l \).

Since both Eqs. (5.95) and (5.97) are highly nonlinear mainly due to the dependency of \( S \) and \( S_c \) on the pressure field and interface position, an iterative numerical procedure is required. The successive under-relaxation can be employed. In turn, this requires that \( S \) and \( S_c \) be updated after every few iterations of the nodal pressures and
then the nodal interface positions. As soon as the global convergence of both the pressure field and interface distribution is obtained, the associated flow quantities such as the velocity, shear rate and viscosity can then be updated as well.

To calculate the flow-induced stresses during the filling and packing stages, the elastic strain tensor $C_k$ for all relaxation modes of the Leonov model has to be calculated at each time step. Therefore, the governing equations of the elastic strain tensor for the streamwise coordinate, Eqs. (5.80) through (5.84), were discretized using a finite difference approach. Time derivatives were discretized using forward difference and space derivatives were discretized using backward difference at time $t = t + \Delta t$ [158]. The final discretized equations are:

$$F_1 = C_{st,k}^{i+1} (n, j) - C_{st,k}^{i} (n, j) + u^{i+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{st,k}^{i+1} (n, j) - C_{st,k}^{i+1} (n-1, j) \right) - 2\Delta t \dot{\gamma}_{\text{rel}}^{i+1} (n, j) C_{st,k}^{i+1} (n, j)$$

$$+ 2 \frac{\Delta t u^{i+1}}{s^{i+1} (n)} C_{st,k}^{i+1} (n, j) + \frac{1}{2\theta_i} \left[ \left\{ C_{st,k}^{i+1} (n, j) \right\}^2 + \left\{ C_{st,k}^{i+1} (n, j) \right\}^2 \right] - 1 + \frac{A}{3} C_{st,k}^{i+1} (n, j) \right] = 0 \quad (5.99)$$

$$F_2 = C_{zz,k}^{i+1} (n, j) - C_{zz,k}^{i+1} (n, j) + u^{i+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{zz,k}^{i+1} (n, j) - C_{zz,k}^{i+1} (n-1, j) \right) - 2\Delta t \dot{\gamma}_{\text{rel}}^{i+1} (n, j) C_{zz,k}^{i+1} (n, j)$$

$$+ \frac{\Delta t u^{i+1}}{s^{i+1} (n)} C_{zz,k}^{i+1} (n, j) + \frac{1}{2\theta_i} \left[ \left\{ C_{zz,k}^{i+1} (n, j) + C_{zz,k}^{i+1} (n, j) \right\} C_{zz,k}^{i+1} (n, j) + \frac{A}{3} C_{zz,k}^{i+1} (n, j) \right] = 0 \quad (5.100)$$

$$F_3 = C_{zz,k}^{i+1} (n, j) - C_{zz,k}^{i+1} (n, j) + u^{i+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{zz,k}^{i+1} (n, j) - C_{zz,k}^{i+1} (n-1, j) \right)$$

$$+ \frac{1}{2\theta_i} \left[ C_{zz,k}^{i+1} (n, j) \right] - 1 + \frac{A}{3} C_{zz,k}^{i+1} (n, j) \right] = 0 \quad (5.101)$$

$$F_4 = C_{zz,k}^{i+1} (n, j) - C_{zz,k}^{i+1} (n, j) + u^{i+1} (n, j) \frac{\Delta t}{\Delta s} \left( C_{zz,k}^{i+1} (n, j) - C_{zz,k}^{i+1} (n-1, j) \right)$$
\[
+2 \frac{\Delta t}{s_{j}^{(i+1)}} C_{t, j}^{(i)}(n, j) + \frac{1}{2\theta} \left[ C_{t, j}^{(i+1)}(n, j) \right] - 1 + \frac{A}{3} C_{t, j}^{(i+1)}(n, j) = 0 \quad (5.102)
\]

\[
C_{z,z}^{(i+1)}(n, j) = \left[ \frac{\frac{1}{C_{t, j}^{(i+1)}} + \left[ C_{t, j}^{(i)}(n, j) \right]^{2}}{C_{n,n}^{(i)}(n, j)} \right]^{2} \quad (5.103)
\]

where \( A = \left( C_{t, j}^{(i+1)}(n, j) - 1 \right) \left( C_{n,n}^{(i+1)}(n, j) + C_{z,z}^{(i+1)}(n, j) - 1 - \frac{1}{C_{t, j}^{(i+1)}(n, j)} \right) \quad (5.104) \)

and the superscript \( t \) represents the time step and the \( k \) represents the number of modes of Leonov model, \( \theta_{k} \) is the relaxation time of \( k \) mode, \( \Delta t \) is time step, \( n \) represents the nodes along the flow direction, \( j \) represents the nodes along the gapwise direction, \( C_{ij, k} \) represents the components of the elastic strain tensor in the Leonov model, \( u \) is the velocity in the streamwise direction and \( \gamma_{s} \) is the shear rate along the streamwise direction.

To determine the components of \( C_{ij, k} \) tensor, the Globally Convergent Method for Nonlinear Systems of Equations [159] that is closely related to the quasi-Newton method of minimization was implemented for the discretized system of equations of Eqs. (5.99) to (5.102). This method is powerful but the numerical computation of the Jacobian matrix represents a disadvantage. However, for this case the Jacobian matrix is available analytically. In this work, the subroutine “fdjac” to compute forward-difference approximation to Jacobian matrix numerically, was modified to be replaced by the function that produces the Jacobian matrix calculated analytically. Therefore, taking the derivatives of these equations with respect the variables \( C_{n,n}^{(i+1)}(n, j) \), \( C_{z,z}^{(i+1)}(n, j) \).
we obtain the following Jacobian functions to obtain the Jacobian matrix:

\[
\begin{bmatrix}
\frac{\partial F_1}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_1}{\partial C_{zz}^{zz} (n, j)} & \frac{\partial F_1}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_1}{\partial C_{zz}^{zz} (n, j)} \\
\frac{\partial F_2}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_2}{\partial C_{zz}^{zz} (n, j)} & \frac{\partial F_2}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_2}{\partial C_{zz}^{zz} (n, j)} \\
\frac{\partial F_3}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_3}{\partial C_{zz}^{zz} (n, j)} & \frac{\partial F_3}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_3}{\partial C_{zz}^{zz} (n, j)} \\
\frac{\partial F_4}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_4}{\partial C_{zz}^{zz} (n, j)} & \frac{\partial F_4}{\partial C_{xx}^{zz} (n, j)} & \frac{\partial F_4}{\partial C_{zz}^{zz} (n, j)} \\
\end{bmatrix}
\]

\[= 0 \quad (5.105)\]

where \(F_1, F_2, F_3\) and \(F_4\) are the Left Hand Side (LHS) of the Eqs. (5.99) through (5.102).

It is important to notice that in Eqs. (5.99) through (5.102) and Eq. (5.105), the velocity component and the shear rate are not known a priori. Therefore, the calculation of the elastic strain tensor was done by iteration together with the subroutine that calculates the velocity and shear rate profiles. The latter values are updated each iteration.

In the present formulation for the temperature profile, a finite-difference grid is employed in the gapwise direction to store the temperature profile. In the finite difference representation of energy equation, an implicit form is used for the gapwise conduction term with the convection and viscous heating term evaluated at the earlier time. Due to the discontinuity of the pressure gradient, velocity and shear rate are not continuous at a given node, and across inter-element boundaries, an averaging scheme is needed for calculation of the nodal quantities related to the pressure gradient. In the current numerical formulation, a weighted average of each term in energy equation for each vertex node is based on the volume fraction that each element contributes to the
associated control volume. Besides, the shear rates and the thermal convection terms are evaluated at the centroid of each element. Because of numerical stability, only contributions from the adjacent upstream elements are considered to calculate convective term. This can be done by evaluating the dot product of the velocity \( V \) and displacement \( d\bar{x} \) vectors connecting the centroid of each element to a given node \([150,180]\). That is:

\[
\theta_{i,k}^{l} = \theta_{i,k}^{l}
\]

if \( V \cdot d\bar{x} < 0 \)

\[
0
\]

if \( V \cdot d\bar{x} \geq 0 \)  

\[(5.106)\]

where the term \( \theta_{i,k}^{l} \) is a fraction of the control volume containing element \( l \).

Based upon above discussion, the energy equation at each vertex node can be discretized as \([161]\):

\[
p_{i,c_{p,j}} \left[ \frac{T_{i,j,k+1} - T_{i,j,k}}{\Delta t_{k}} + \frac{1}{\sigma_{i,k}} \sum_{l=1}^{k_{i}} \sum_{m=1}^{3} E_{m,j,k}^{l} T_{i,j,k} \right]
\]

\[
= \frac{k_{th}}{\Delta z^2} \left( T_{i,j+1,k+1} - 2T_{i,j,k+1} + T_{i,j-1,k+1} \right) + \Phi_{i,j,k}
\]

\[(5.107)\]

with

\[
E_{m,j,k} = \frac{1}{2A_{l}A'} \int_{z_{0}}^{b} \dot{\gamma} dz \left( \Lambda_{l} B_{m}^{l} + \Lambda_{l} C_{m}^{l} \right)
\]

\[(5.108)\]

\[
\sigma_{i} = \sum_{l=1}^{k_{i}} \theta_{i,k}^{l}
\]

\[(5.109)\]

where term \( \sigma_{i} \) is the total control volume associated with node \( i \) and \( \theta_{i,k}^{l} \) is the fraction of control volume containing element \( l \).
The dissipation function \[150\] is:

\[
\Phi_{i,j,k} = \frac{1}{\sigma_{i,k}} \sum_{l=1}^{\text{ku}} \sum_{j,k} \left[ \eta_{i,j,k}^l s_{i,j,k}^l y_{i,j,k}^2 + \sum_{q} \eta_{q,j,k} \left\{ C_{i,q,j,k}^2 + 2C_{i,q,j,k}^2 + C_{i,q,j,k}^2 - 2 \right\} \right] \tag{5.110}
\]

where \(i, j\) are the node number in the x-y plane and the gapwise direction, respectively, \(k, k+1\) represent time step \(t_k\) and \(t_{k+1}\); and \(\Delta t = t_{k+1} - t_k\), which is selected in order that only one partially-filled node gets filled for every time step; \(\Delta z = z_{j+1} - z_j\), and \(i' = \text{NELNOD}(l,m)\), \(\text{ku}\) is total number of elements containing node \(i\), and \(l = \text{NEL}(i,m)\) is the \(m\)-th element which contains node \(i\); \(k, \rho, c, p, \eta, \gamma\) are values corresponding to core and skin melt, respectively.

At the interface between core and skin materials \(z = \delta\), the thermal boundary conditions given by Eq. (5.22) are applied.

The solution of Eq. (5.95), Eq. (5.97) and Eq. (5.107) requires iteration method due to the high nonlinearity. At each new time step, \(k+1\), the velocity field, pressure field and finally interface distribution are first solved from Eq. (5.95) and Eq.(5.97) with elastic strain tensors solved from Eqs. (5.99) through (5.102). During the solution process, the temperature obtained in the \(k\) time step is used to calculate the various physical quantities, such as \(\rho\), \(\eta\) and so on. After obtaining the velocity field and pressure field, the energy equation, Eq. (5.107), with the pressure field and velocity field fixed, is solved to obtain the temperature field, and then the next time step is ensured.

The under-relaxation iteration method \[150\] was used to solve the pressure and temperature at each time step. In each iteration, new values of \(P_m^{k+1,\text{new}}, \delta_m^{k+1,\text{new}}\) and
$T_{m,j}^{k+1,new}$ are obtained from Eq. (5.95), Eq. (5.97) and Eq. (5.107). The updated values $p_{m}^{w+1,\text{update}}$, $\delta_{m}^{w+1,\text{update}}$ and $T_{m,j}^{w+1,\text{update}}$ obtained from

$$p_{m}^{w+1,\text{update}} = (1 - \Omega_{p})p_{m}^{w+1,\text{old}} + \Omega_{p}p_{m}^{w+1,\text{new}}$$

(5.111)

$$\delta_{m}^{w+1,\text{update}} = (1 - \Omega_{\delta})\delta_{m}^{w+1,\text{old}} + \Omega_{\delta}\delta_{m}^{w+1,\text{new}}$$

(5.112)

$$T_{m,j}^{w+1,\text{update}} = (1 - \Omega_{T})T_{m,j}^{w+1,\text{old}} + \Omega_{T}T_{m,j}^{w+1,\text{new}}$$

(5.113)

are put back in Eq. (5.95), Eq. (5.97) and Eq. (5.107) for iterations, where $\Omega_{p}$, $\Omega_{\delta}$ and $\Omega_{T}$ are weighting factors which are between 0 and 1 for the pressure, interface distribution and temperature, respectively. Iterations terminate when the absolute change in the each property is less than some specified value. In particular, successive under-relaxation method is also used for calculation of pressure, interface distribution and temperature profile due to numerical stability. To converge the values of $P_{m}$, $\delta_{m}$ and $T_{m,j}$ at each time step, the following convergence criterion, $\varepsilon_{p}$, $\varepsilon_{\delta}$ and $\varepsilon_{T}$ is used, respectively.

$$\varepsilon_{p} = \frac{1}{\text{NODES}} \sum_{m=1}^{\text{NODES}} \left\{ \left| \frac{P_{m}^{r+1} - P_{m}^{r}}{P_{m}^{r}} \right| \right\} \leq 10^{-4}$$

(5.114)

$$\varepsilon_{\delta} = \frac{1}{\text{NODES}} \sum_{m=1}^{\text{NODES}} \left\{ \left| \frac{\delta_{m}^{r+1} - \delta_{m}^{r}}{\delta_{m}^{r}} \right| \right\} \leq 10^{-2}$$

(5.115)

$$\varepsilon_{T} = \frac{1}{\text{NODEZ} \cdot \text{NODES}} \sum_{m=1}^{\text{NODES}} \sum_{j=1}^{\text{NODEZ}} \left\{ \left| \frac{T_{m,j}^{r+1} - T_{m,j}^{r}}{T_{m,j}^{r}} \right| \right\} \leq 10^{-3}$$

(5.116)
where \( NODES \) and \( NODEZ \) are the total number of node along the planar and the thickness directions, \( m \) and \( j \) are the number of each node along the planar and the thickness directions and \( r \) is the number of iteration.

The volume of fluid (VOF) model \([183]\), with filling factor which varies between 0 and 1 for each component, is used to track the core melt front (core/skin interface in planar direction) and the skin melt front advancement. In the VOF method, the fluid volume is represented by a characteristic filling parameter \( F \), by which the movement of the melt front is advected by the velocity field. This parameter \( F \) is governed by:

\[
\frac{\partial F_i}{\partial t} + V \cdot \nabla F_i = 0
\]

The advection of the fluid volume is based on the mass conservation around each control volume. This conservation requires that the change of the filling factor of each melt front node at each time step is proportional to the net flow rate of fluid into the control volume, thus

\[
F_i^{n+1} = F_i^n + \frac{\sum q_{i,j} \Delta t}{V_i}
\]

where \( V_i \) is the total volume of the control volume associated with node \( i \), and \( q_{i,j} \) is the flow rate of fluid entering each subcontrol volume of node \( i \).

Once the filling factors of both the skin and core melts are updated using this equation, a new filled domain and subdomain can be defined with the advancement of both melt fronts for the next time step. The numerical scheme of computation for filling stage is summarized in the flow chart shown in Figure 5-1.
Figure 5-1 Flow chart for the simulation of filling stage in sequential injection molding process.
5.2.4 Packing Stage

During the packing stage, extra core material is forced into the cavity in order to compensate for shrinkage during filling stage due to solidification, and the packing pressure is built up and the corresponding density is increased.

5.2.4.1 Governing Equations and Boundary Conditions

Nonuniform pressure developed during the filling stage quickly approaches a uniform packing pressure that is typically much higher than pressure in the filling stage. The temperature field developed due to heat transfer in the mold causes the material to cool down to below the glass transition, $T_g$ or crystallization temperature, $T_c$. Specific volume decreases due to the temperature and pressure variation and also because of crystallization. A rapid non-homogeneous cooling of the polymer melts through $T_g$ or $T_c$, introduces a specific volume change, i.e. volumetric shrinkage. After a certain time, the cavity entrance (gate) freezes and no more material can enter the cavity. At this gate freezing point, the flow stresses start to relax since the cavity filling is completed. However, the product remains in the mold until it is sufficiently solidified. This last part of the molding stages is called the cooling stage. The general picture is that the post-filling stage is characterized by a short packing stage and relatively long cooling stage. After mold opening and ejection, the product was allowed to cool to room temperature.

In the packing phase of the co-injection molding the mold cavity is essentially filled up by the skin and core melts. To minimize the shrinkage of the molded products, which results from the significant thermal contraction of the polymer melt, it is necessary
to supply additional core melt into the cavity under high pressure after filling is completed. The combined effect of high compressibility and low thermal conductivity of hot core melt enables additional injection of core melt into the mold cavity. Therefore, the formulation for compressible polymeric flow is required for the packing phase. Compared with the filling stage, the entrance pressure is given with the flow rates at the entrance nodes to be determined in the packing stage. Since the additional material is injected to the mold by the packing pressure, the shear rate builds up during the early stage of packing. This flow continues until the gate freezing time. At this time, no more material can enter the cavity. Therefore the shear rate that was built up during the early stage of packing is reduced until the ejection time. As there also are no melt front nodes in this stage, the interface evolution equation to control the interface position is not needed any more. Therefore, governing equations are basically similar to the filling stage except for the additional terms for compressible fluid as given by:

\[
\frac{\partial \rho_i}{\partial t} + \frac{\partial}{\partial x}(\rho_i u_i) + \frac{\partial}{\partial y}(\rho_i v_i) = 0 \tag{5.119}
\]

\[
\frac{\partial P}{\partial x} + \frac{\partial \tau_{xz}}{\partial z} = 0 \quad \frac{\partial P}{\partial y} + \frac{\partial \tau_{yz}}{\partial z} = 0 \tag{5.120}
\]

\[
\rho_i C_{p,i} \frac{\partial T_i}{\partial t} = k_{th,i} \left( \frac{\partial^2 T_i}{\partial z^2} \right) + \Phi_i \tag{5.121}
\]

In this case, Tait equation is used to model the PVT behavior of the plastic material during the packing stage.
The initial conditions for pressure is

\[ P = P_{ent} \text{ at the gate} \quad (5.122) \]

where \( b \) is the half of the gap thickness.

The density \( \rho(p, T) \) is assumed to follow the Tait equation [151].

\[
\rho(T, p) = \rho_0(T) \left[ 1 - C \ln \left( 1 + \frac{p}{B(T)} \right) \right]^{-1} \quad (5.123)
\]

with

\[
\rho_0(T) = \frac{\rho_0(T_g^0)}{1 + \alpha \rho_0(T_g^0)(T - T_g^0)} \quad (5.124)
\]

\[
\alpha = \alpha_l \text{ if } T > T_t \quad (5.125)
\]

\[
\alpha = \alpha_s \text{ if } T < T_t \quad (5.126)
\]

\[
B(T) = b_{l1} \exp(b_{l2} T) \text{ if } T > T_t \quad (5.127)
\]

\[
B(T) = b_{s1} \exp(b_{s2} T) \text{ if } T < T_t \quad (5.128)
\]

\[
T_t(p) = T_g^0 + b_{\delta} p \quad (5.129)
\]

where \( C, b_{l1}, b_{l2}, b_{s1}, b_{s2} \) and \( b_{\delta} \) are material constants and \( T_t \) is the transition temperature (either the melting temperature or glass transition temperature) and \( \alpha_l \) and \( \alpha_s \) is the thermal expansion coefficient for rubbery and glassy state, respectively.
The viscoelastic constitutive equation is the same as shown in the filling stage, Eq. (5.31).

During the packing time the elastic strain tensor \( C_{k,i} \) of the \( k \)th mode for skin or core melt without any convection terms is governed by

\[
\frac{\partial}{\partial t} C_{k,i} + \frac{1}{2\theta_{k,i}} \left( C_{k,i} \cdot C_{k,i} - \delta \right) = 0
\]  

(5.130)

By combining the equations of motions, the mass balance equation and the constitutive equation, the governing equation for the packing stage [2] during co-injection molding becomes:

\[
G \frac{\partial p}{\partial t} + H - \frac{\partial}{\partial x} \left( S_x \frac{\partial p}{\partial x} \right) - \frac{\partial}{\partial y} \left( S_y \frac{\partial p}{\partial y} \right) = 0
\]  

(5.131)

where

\[
G = G_s + G_c = \int_0^z \left( \frac{\partial \rho}{\partial p} \right) dz + \int_s^b \left( \frac{\partial \rho}{\partial p} \right) dz
\]  

(5.132)

\[
H = H_s + H_c = \int_0^z \left( \frac{\partial T}{\partial t} \right) \left( \frac{\partial T}{\partial t} \right) dz + \int_s^b \left( \frac{\partial T}{\partial t} \right) \left( \frac{\partial T}{\partial t} \right) dz
\]  

(5.133)

\[
S_x = \int_0^z \frac{z^2}{\eta_{x,s}} dz + \int_s^b \frac{z^2}{\eta_{x,c}} dz, \quad S_y = \int_0^z \frac{z^2}{\eta_{y,s}} dz + \int_s^b \frac{z^2}{\eta_{y,c}} dz
\]  

(5.134)

5.2.4.2 Numerical Formulation and Simulation

Similar to the filling stage, after applying the Galerkin weighted-residual procedure [155,156] or mass conservation using a control-volume approach [157], and introducing linear interpolation functions as well as a finite-difference representation for
the time derivative, the following governing equation for pressure [2] in the whole cavity domain is obtained:

$$
\sum_{i=1}^{ku} \left[ A_i G_i \sum_{i=1}^{3} E_{i,N} \frac{P_{i+1}^k - P_i^k}{\Delta t} + \sum_{i=1}^{3} B_{i,N}^j P_i^{k+1} \right] = \sum_{i=1}^{ku} \frac{A_i^l}{3} H_i^l + \frac{Q_N}{2}
$$

(5.135)

where 

$$
E_{i,N}^l = \begin{cases} 
22/108 & \text{if } i = N \\
7/108 & \text{if } i = N 
\end{cases}
$$

(5.136)

$$
B_{i,j}^l = \frac{1}{4A^l} \left[ \begin{array}{ccc} b_1^l b_2^l b_3^l \\
 b_1^l b_2^l b_3^l \\
 b_1^l b_2^l b_3^l \end{array} \right] \left[ \begin{array}{ccc} c_1^l c_2^l c_3^l \\
 c_1^l c_2^l c_3^l \\
 c_1^l c_2^l c_3^l \end{array} \right]
$$

(5.137)

$$
\begin{bmatrix}
a_1^l & b_1^l & c_1^l \\
a_2^l & b_2^l & c_2^l \\
a_3^l & b_3^l & c_3^l
\end{bmatrix} = 2A^l \begin{bmatrix} 1 & 1 & 1 \\
x_1^l & x_2^l & x_3^l \\
y_1^l & y_2^l & y_3^l \end{bmatrix}^{-1}
$$

(5.138)

$$
2A^l = \left( x_2^l y_3^l - x_3^l y_2^l \right) + \left( x_1^l y_3^l - x_3^l y_1^l \right) + \left( x_3^l y_2^l - x_2^l y_3^l \right)
$$

(5.139)

$$
Q_N = Q_{ent} \text{ for the entrance nodes where } p = p_g \text{ is specified at the gate;}
$$

$$
Q_N \text{ is the total volumetric flow rate for each node at any instant for the whole cavity domain, } ku \text{ is the total number of elements containing node } N, \ i \text{ is such that } N = NELNOD(l,i) \text{, and } (x_1, y_1), (x_2, y_2), (x_3, y_3) \text{ are the } x-y \text{ coordinate for each triangular element, and } a_i, b_i, c_i \text{ (} i=1, 2, 3) \text{ are the coefficients for the linear area-coordinate interpolation function for node } i \text{ on element } l.
$$

The energy equation at each vertex node can be discretized as [180]:

$$
p c_p \left[ \frac{T_{i,j,k+1} - T_{i,j,k}}{\Delta t} \right] = \frac{k_h}{\Delta z^2} \left( T_{i,j,k+1} - 2T_{i,j,k+1} + T_{i,j,k-1+1} \right) + \Phi_{i,j,k}
$$

(5.140)

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5.2.5 Cooling Stage

The cooling stage, characterized by a slow pressure decrease, is treated as a nonisothermal process with zero flow. In this stage, the velocity $u$ and $v$, and the shear rate $\dot{\gamma}$ are set equal to zero. Both temperature and pressure will be decreasing during this phase. Figure 5-2 illustrates the flow chart for the simulation of packing and cooling stages in sequential injection molding.

Figure 5-2 Flow chart for the simulation of packing and cooling stages in sequential injection molding process.
5.2.6 Residual Stresses and Birefringence in Co-injection-Molded Parts

It is well known that the residual stresses and birefringence in the molding becomes frozen-in caused by the incomplete stress relaxation due to passing through the glass transition temperature.

5.2.6.1 Flow Stresses and Birefringence

From constitutive equation of Eq. (5.31), the normal stress differences and the shear stress are calculated as

\[
N_1(s, \theta, z) \equiv \sigma_{ss} - \sigma_{zz} = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} \left[ C_{ss,k}(s, \theta, z) - C_{zz,k}(s, \theta, z) \right]
\]

(5.141)

\[
N_2(s, \theta, z) \equiv \sigma_{zz} - \sigma_{\theta \theta} = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} \left[ C_{zz,k}(s, \theta, z) - C_{\theta \theta,k}(s, \theta, z) \right]
\]

(5.142)

\[
N_3(s, \theta, z) \equiv \sigma_{ss} - \sigma_{\theta \theta} = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} \left[ C_{ss,k}(s, \theta, z) - C_{\theta \theta,k}(s, \theta, z) \right]
\]

(5.143)

\[
\tau_{sc}(s, \theta, z) = \eta_0 \dot{\gamma} + \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} C_{sc,k}
\]

(5.144)

During the cooling stage, we set the shear rate to zero, \( \dot{\gamma} = 0 \). Therefore, Eq. (5.138) becomes

\[
\tau_{sc}(s, \theta, z) = \sum_{k=1}^{N} \frac{\eta_k}{\theta_k} C_{sc,k}
\]

(5.145)

and normal stress differences are calculated from Eqs. (5.141) through (5.143).

The residual flow-induced birefringence for the polymers can be calculated by the stress-optical rule during the nonisothermal flow and the subsequent relaxation. The flow birefringence in the x-y plane, \( \Delta n^{\beta} \), is given by
\[ \Delta n_{zz}^H = C_\sigma(T) \cdot \Delta \sigma(s, \theta, z) = C_\sigma(T) \sqrt{N_1^2(s, \theta, z) + 4\tau_{zz}^2(s, \theta, z)} \]  
(5.146)

\[ n_{ss}^H - n_{\theta\theta}^H = C_\sigma \left( \sigma_{ss} - \sigma_{\theta\theta} \right) \]  
(5.147)

\[ n_{\theta\theta}^H - n_{zz}^H = C_\sigma \left( \sigma_{\theta\theta} - \sigma_{zz} \right) \]  
(5.148)

where \( C_\sigma(T) \) is the stress-optical coefficient being constant for unsteady shear flow.

5.2.6.2 Thermal Stresses and Birefringence

The residual thermal stresses and birefringence in co-injection molded part are treated as those for freely quenched polymer plates as discussed in Chapter IV. The linear viscoelasticity and photoviscoelasticity with the volume relaxation effects \([1,141]\) are used to calculate the residual thermal stresses and birefringence of the plates with multilayered structure. As a first approximation, we treated the residual thermal stresses and birefringence in co-injection molded disks as those developed in freely quenched plates \([141]\). Based on the varying temperature fields, the changes in viscoelastic properties are determined and utilized to calculate the thermal stresses until the polymer reaches thermal equilibrium with the molding system. For this case, the tensor of thermal stresses is

\[ \sigma^H = \begin{bmatrix} \sigma_{ss}^H & 0 & 0 \\ 0 & \sigma_{\theta\theta}^H & 0 \\ 0 & 0 & 0 \end{bmatrix} \]  
(5.149)

where \( \sigma_{ss}^H = \sigma_{\theta\theta}^H \).

It is noted that for amorphous polymers such as polystyrene, polycarbonate and
polymethyl methacrylate, the stress-optical rule is valid until the glass transition temperature.

Therefore, the part of the refraction index tensor contribution from cooling alone is:

\[
\begin{bmatrix}
  n_{ss}^\beta & 0 & 0 \\
  0 & n_{\theta\theta}^\beta & 0 \\
  0 & 0 & n_{zz}^\beta \\
\end{bmatrix}
\]  \hspace{1cm} (5.150)

5.2.6.3 Total Stresses and Birefringence

To the best of our knowledge, no single nonlinear constitutive equation is available to describe the rheological behavior of a polymer in both the glassy and melt states and in the transition region between them. Moreover, in the injection, compression and cooling stages, the dominant terms in the dynamic equations are different. Therefore, a further simplifying assumption was made that the coupling effects between the flow and thermal stresses are negligible, such that they can be evaluated independently. Thus, the total residual stresses are:

\[
\sigma_{\text{res}} = \sigma_{\text{res}}^\beta + \sigma_{\text{res}}^h \tag{5.151}
\]

Similarly, the total refraction index tensor is,

\[
\begin{bmatrix}
  n_{ss}^h & 0 & 0 \\
  0 & n_{\theta\theta}^h & 0 \\
  0 & 0 & n_{zz}^h \\
\end{bmatrix} + \begin{bmatrix}
  n_{ss}^\beta & 0 & 0 \\
  0 & n_{\theta\theta}^\beta & 0 \\
  0 & 0 & n_{zz}^\beta \\
\end{bmatrix}
\]  \hspace{1cm} (5.152)
where subscripts \( \text{res} \) and superscripts \( \text{fl} \) and \( \text{th} \) stand for residual, flow, and thermal, respectively.

The total birefringence measured in the \( sz \) plane is then

\[
\Delta n = \Delta n_{sz} = \left[ \left( \Delta n^\beta_{sz} \right)^2 + \left( \Delta n^\text{th}_{sz} \right)^2 + 2 \left( n^\beta_{ss} - n^\beta_{zz} \right) \left( \Delta n^\text{th}_{sz} \right) \right]^{1/2} \quad (5.153)
\]

with the flow birefringence, \( \Delta n^\beta_{sz} \), and the thermal birefringence, \( \Delta n^\text{th}_{sz} \), being

\[
\Delta n^\beta_{sz} = C^\beta_n \left[ \left( \sigma^\beta_{ss} - \sigma^\beta_{zz} \right)^2 + 4 \left( \tau^\beta_{sz} \right)^2 \right]^{1/2} \quad (5.154)
\]

\[
\Delta n^\text{th}_{sz} = n^\text{th}_{sz} - n^\text{th}_{zz} \quad (5.155)
\]

Since in free quenching \( n^\text{th}_{ss} = n^\text{th}_{00} \), the birefringence in the \( s\theta \) plane becomes

\[
\Delta n_{s\theta} = \left( n^\text{th}_{ss} - n^\text{th}_{00} \right) + \left( n^\beta_{ss} - n^\beta_{00} \right) = n^\beta_{ss} - n^\beta_{00} \quad (5.156)
\]
CHAPTER VI

SIMULATION AND EXPERIMENTAL STUDY OF INJECTION-COMPRESSION MOLDING FOR AMORPHOUS POLYMERS

In this chapter, a two-dimensional simulation and experimental studies of the flow-rate controlled ICM were carried out. The physical model of a viscoelastic polymer melt flow during ICM was developed in Chapter III. The simulation results were compared with experimental data obtained on ICM center-gated disks of PS and PC. To investigate the effects of processing conditions on the residual stress and birefringence, the ICM experiments were carried out at different mold temperatures, melt temperatures, and compression strokes. Comparison between ICM and CIM were also made.

6.1 Experiments and Simulation

The following sections present materials and its characterization the experimental procedure and birefringence measurement for PS and PC ICM moldings.

6.1.1 Materials and Its Characterization

The two materials used in the experiments are polystyrene (Styron 615-APR) supplied by Dow Chemical Company and polycarbonate (PC Lexan 123) supplied by General Electric (GE) Plastics.
The thermal properties of PS and PC are assumed to be constant and independent of temperature. The densities of melts in filling stage are also taken to be constant. The physical properties of polymers are listed in Table 6-1. The data for rheological characterization of PS was used from the reference [2,184] at temperatures of 161, 180.5 and 200.5 °C. However, the rheological characterization of PC was performed at temperatures of 260, 273.3, 286.7 and 300 °C over a wide range of shear rate using an Advanced Capillary Rheometer (RH7). The viscosity data was plotted as a function of shear rate at different temperatures as shown in Figure 6-1 for PS and Figure 6-2 for PC. These data were fitted using the two relaxation modes for PS and six relaxation modes for PC. The viscosity data at different temperature were fitted to Eq. (6.1) by means of nonlinear regression [185].

\[
\eta = \eta_0 s + \sum_{k=1}^{N} \frac{2\eta_k}{1 + \sqrt{1 + 4\left(\frac{s}{\theta_k}\right)^2}}
\]  

(6.1)

The lines in these figures represent the nonlinear regression fit of the experimental data. The constants in the WLF equation which describes the temperature dependence of \( \eta_k(T_0) \) are \( C_1 = 8.285, \; C_2 = 131.9 \; \text{K}, \; T_r = 474.15 \; \text{K} \) for PS and \( C_1 = 7.230, \; C_2 = 163.4 \; \text{K}, \; T_r = 533.15 \; \text{K} \) for PC, respectively. The parameters obtained from the best fit are listed in Table 6-2. For the calculation of melt density of each polymer melt, P-V-T equation of state of Tait equation [146] with the parameters are listed in Table 6-3 was used.
Figure 6-1 Measured (symbols) [2] and fitted (curves) [122] viscosity of PS as a function of shear rate.
Figure 6-2 Measured (symbols) and fitted (curves) viscosity of PC as a function of shear rate.
Table 6-1 Physical Properties of Polymers.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PS</th>
<th>PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho^0 \times 10^3$ (Kg/m$^3$)*</td>
<td>1.04 [186]</td>
<td>1.16 [187]</td>
</tr>
<tr>
<td>$\rho \times 10^3$ (Kg/m$^3$)*</td>
<td>0.984 [186]</td>
<td>1.06 [187]</td>
</tr>
<tr>
<td>$C_p$ (J/Kg$\cdot$K)</td>
<td>1420 [186]</td>
<td>2150 [187]</td>
</tr>
<tr>
<td>$k$ (W/m$\cdot$K)</td>
<td>0.17 [186]</td>
<td>0.234 [187]</td>
</tr>
<tr>
<td>$h$ (J/s$\cdot$m$^2$$\cdot$K)</td>
<td>490 [2]</td>
<td>490 [2]</td>
</tr>
</tbody>
</table>

* $\rho^0$ at T=25 °C and $\rho$ at T=180 °C.
Table 6-2 Material Constants of PS and PC Used in the CIM and ICM Molding Simulations.

<table>
<thead>
<tr>
<th>Material constants</th>
<th>PS</th>
<th>PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>WLF equation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_1$</td>
<td>8.285</td>
<td>7.23</td>
</tr>
<tr>
<td>$C_2$ (K)</td>
<td>131.9</td>
<td>163.4</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>474.15</td>
<td>533.15</td>
</tr>
<tr>
<td>Leonov model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s$</td>
<td>0.0048</td>
<td>0.0001</td>
</tr>
<tr>
<td>$\eta_1$ (Pa·s)</td>
<td>2228</td>
<td>30.1</td>
</tr>
<tr>
<td>$\eta_2$ (Pa·s)</td>
<td>446.8</td>
<td>9.11</td>
</tr>
<tr>
<td>$\eta_3$ (Pa·s)</td>
<td>-</td>
<td>392</td>
</tr>
<tr>
<td>$\eta_4$ (Pa·s)</td>
<td>-</td>
<td>766</td>
</tr>
<tr>
<td>$\eta_5$ (Pa·s)</td>
<td>-</td>
<td>50.8</td>
</tr>
<tr>
<td>$\eta_6$ (Pa·s)</td>
<td>-</td>
<td>18.4</td>
</tr>
<tr>
<td>$\theta_1$ (s)</td>
<td>0.1466</td>
<td>2.1</td>
</tr>
<tr>
<td>$\theta_2$ (s)</td>
<td>0.00489</td>
<td>0.104</td>
</tr>
<tr>
<td>$\theta_3$ (s)</td>
<td>-</td>
<td>0.011</td>
</tr>
<tr>
<td>$\theta_4$ (s)</td>
<td>-</td>
<td>0.00115</td>
</tr>
<tr>
<td>$\theta_5$ (s)</td>
<td>-</td>
<td>0.00012</td>
</tr>
<tr>
<td>$\theta_6$ (s)</td>
<td>-</td>
<td>0.000016</td>
</tr>
</tbody>
</table>

Stress-optical coefficient & volume relaxation time

| $C_o^\sigma$ (Pa$^{-1}$) | $-5.2 \times 10^{-9}$ [2] | $5.6 \times 10^{-9}$ [2] |
| $\tau_e$ (s)             | 0.04 [2]                  | 0.3 [2]                  |
Table 6-3 Material Constants in Tait Equation.

<table>
<thead>
<tr>
<th>Tait equation</th>
<th>PS [187]</th>
<th>PC [187]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_{1,i}$ (m³/Kg)</td>
<td>970.8</td>
<td>862.8</td>
</tr>
<tr>
<td>$b_{2,i}$ (m³/Kg·K)</td>
<td>0.5788</td>
<td>0.549</td>
</tr>
<tr>
<td>$b_{3,i}$ (Pa)</td>
<td>$1.555 \times 10^8$</td>
<td>$1.565 \times 10^8$</td>
</tr>
<tr>
<td>$b_{4,i}$ (K⁻¹)</td>
<td>$3.019 \times 10^{-3}$</td>
<td>$2.738 \times 10^{-3}$</td>
</tr>
<tr>
<td>$b_{5,i}$ (m³/Kg)</td>
<td>970.8</td>
<td>862.8</td>
</tr>
<tr>
<td>$b_{2,3}$ (m³/Kg·K)</td>
<td>0.2429</td>
<td>0.2229</td>
</tr>
<tr>
<td>$b_{3,3}$ (Pa)</td>
<td>$2.008 \times 10^8$</td>
<td>$2.65 \times 10^8$</td>
</tr>
<tr>
<td>$b_{4,3}$ (K⁻¹)</td>
<td>$1.38 \times 10^{-3}$</td>
<td>$2.78 \times 10^{-3}$</td>
</tr>
<tr>
<td>$b_5$ (K)</td>
<td>360.2</td>
<td>422.2</td>
</tr>
<tr>
<td>$b_6$ (K/Pa)</td>
<td>$3.20 \times 10^{-7}$</td>
<td>$5.00 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

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6.1.2 ICM Experiments

The ICM experiments were carried out on a center-gated disk using Hull Hydraulic Transfer Molding Press. The schematic diagram of the ICM apparatus used in this experiment is shown in Figure 6-3. The machine is a vertical type injection unit with mechanical clamping system actuated by hydraulic pressure. The diameter and thickness of the center-gated disk are 12.7 cm and 0.3175 cm, respectively. The gate diameter is 1.36 cm. The schematic mold geometry is shown in Figure 6-4. The data acquisition system is connected to the injection-compression molding machine and records the pressure and the plunger position to measure the flow rate by means of linear velocity displacements transducer (LVDT). The pressure was monitored by one Dynisco PT435A pressure transducer mounted at center position of the mold.

The injection-compression molding experiments were carried out the following manner. PS and PC were respectively dried at 80 °C and 105 °C for 4 hours under vacuum conditions. The exact amount of PS and PC to fill the delivery system and cavity are used. Chips were made by compression molding under the temperature of 200 °C and 230 °C, respectively. By placing the chips into the cylinder of injection-compression molding, the ICM experiments were conducted under different processing conditions with varying mold temperatures, melt temperatures and compression strokes as shown in Table 6-4 and Table 6-5 for PC and PS, respectively. The switchover time is the elapsed time between the initial filling stage and compression stage.
Figure 6-3 Schematic diagram of ICM apparatus used in experiments.
Figure 6-4 Geometry of a center-gated disk with coordinate system.
6.1.3 Birefringence Measurements

A streamwise coordinate system was used to identify position for birefringence measurement. The directions of $s$, $\theta$ and $z$ are the flow, perpendicular and gapwise directions, respectively. The measurement of the average transverse birefringence, $< n_{ss} - n_{\theta\theta} >$, in injection-compression molded and injection-molded PS and PC disks samples at different radial distances, blocks of 1.5 cm in width were obtained from the disk mold, as shown in Figure 6-5 using an electric saw. To measure the birefringence distribution, $\Delta n$, in injection-compression molded and injection-molded PS and PC disks at different radial distances, slices of 0.5 and 1 mm in thickness were obtained parallel to the $s - z$, as shown in Figure 6-5. A low-speed diamond saw (Isomet™ low-speed saw, Buechler) at 120 RPM was used to make slices. After cutting the samples, the thickness of the slices was measured using a digital micrometer with a resolution of 0.001mm. The detailed cutting procedures for obtaining the specimens for average transverse birefringence, $< n_{ss} - n_{\theta\theta} >$, and birefringence $\Delta n$ are illustrated in Figure 6-5 (a) and (b). The retardation of the slices was measured using a cross-polarized optical microscope (Leitz laborlux 12 POL, Leitz Wetzlar) with a four-order tilting compensator for PS and a thirty-order compensator for PC (1592k, Leitz Wetzlar). To pinpoint the gapwise position at which the retardation of the slices was measured, a scale on the microscope eyepiece and a 40x magnification objective lens were used. The birefringence measurements were started 0.125 mm away from the mold surface (bottom wall) of the molded part since compensation of the light retardation was difficult to measure at the position closer to the mold surface. The average transverse birefringence, $< n_{ss} - n_{\theta\theta} >$,
was measured using a Gaertner optical polariscope (model L305) equipped with a seventh order Babinet compensator (model L-133-A).

The retardation was calculated from the readings of the compensator using the tables and calibration constants provided by the manufactures. Birefringence was determined by the retardation (phase difference) between two perpendicular plane-polarized wave motions passing through a sample and calculated as follows

\[ \Delta n = \frac{\Gamma}{d} \]  

(6.2)

where \( \Gamma \) is the retardation and \( d \) is the sample thickness.

To determine the sign of birefringence of PS and PC samples, the direction of slow axis in each sample was compared to the direction of slow axis shown on four-order and thirty-order tilting compensators which have opposite direction of slow axis. For example, the slow axis of PS sample is perpendicular to the flow direction due to the existence of benzene group on its side chain. For PS sample, the direction of the slow axis of the tilting compensators coincides with the direction of its slow axis. Therefore, the sign of birefringence of PS is negative. The direction of the slow axis for the PC sample is perpendicular to the direction of the slow axis of the tilting compensators. Therefore, the sign of birefringence of PC is positive.

6.1.4 Numerical Analysis Techniques

In this study, a center-gated disk mold was used in the injection-compression molding experiments. To simulate the molding process, discretized finite-element triangle meshes for a quarter of the disk cavity in two-dimensional planar surface were used. Due
to the symmetrical flow occurring in the process, only a quarter of disk cavity and half thickness have been considered for the cavity filling to reduce the computation times. In finite element modeling, a finer mesh typically results in a more accurate solution. However, as a mesh is made finer, the computation time increases. For the current simulations the disk mold was divided into 315 elements and 184 nodes in the planar direction based on the previous work of Shyu [2] who balanced mesh size with computation time as well as initial trials that showed a significant increase in computation time with minimal increases in elements and nodes. With these meshes, the CPU time to carry out calculations for one processing condition was 4-6 hours on Pentium IV 3 GHz PC.

For numerical simulation in the filling, compression and packing, the nonlinear viscoelastic model was used, with the two relaxation modes ($N=2$) for PS and with the six relaxation modes ($N=6$) for PC obtained by fitting the rheological data. The smallest relaxation times ($\theta_2$ for PS or $\theta_6$ for PC) are about $10^{-3}$ s for PS and about $10^{-5}$ s for PC.

The resulting set of nonlinear algebraic equations was solved with a globally convergent Newton’s method [159]. During the cooling stage the relaxation takes place. Therefore, transient calculations in all modes were employed to find the relaxation of the elastic strain tensor.
Figure 6-5 Cutting procedure used for preparing a specimen from an injection-compression molded disk, to measure average transverse birefringence $<n_{ts} - n_{sp}>$ (a), and birefringence $\Delta n$ (b).
### Table 6-4 Processing Conditions of Polystyrene (PS) for ICM and CIM Experiments and Simulation.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Melt temp. (°C)</th>
<th>Mold temp. (°C)</th>
<th>Volume flow rate (cm³/s)</th>
<th>Compression stroke (cm)</th>
<th>Compression speed (cm/s)</th>
<th>Switch over time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>230</td>
<td>40</td>
<td>13</td>
<td>0.15</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>230</td>
<td>60</td>
<td>13</td>
<td>0.15</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>230</td>
<td>80</td>
<td>14</td>
<td>0.15</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>190</td>
<td>60</td>
<td>14</td>
<td>0.15</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>210</td>
<td>60</td>
<td>14</td>
<td>0.15</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>6</td>
<td>230</td>
<td>60</td>
<td>15</td>
<td>0.1</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>230</td>
<td>60</td>
<td>16</td>
<td>0.2</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>210</td>
<td>60</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 6-5 Processing Conditions of Polycarbonate (PC) for ICM and CIM Experiments and Simulation.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Melt temp. (°C)</th>
<th>Mold temp. (°C)</th>
<th>Volume flow rate (cm³/s)</th>
<th>Compression stroke (cm)</th>
<th>Compression speed (cm/s)</th>
<th>Switch over time (sec)</th>
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<tbody>
<tr>
<td>1</td>
<td>260</td>
<td>40</td>
<td>25</td>
<td>0.15</td>
<td>0.4</td>
<td>1.12</td>
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<tr>
<td>2</td>
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<td>60</td>
<td>23</td>
<td>0.15</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>260</td>
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<td>26</td>
<td>0.15</td>
<td>0.4</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
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<td>60</td>
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<td>0.15</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
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<td>0.86</td>
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<tr>
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<td>260</td>
<td>60</td>
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<td>1.2</td>
</tr>
<tr>
<td>7</td>
<td>260</td>
<td>60</td>
<td>22</td>
<td>0.2</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>260</td>
<td>60</td>
<td>23</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
6.2 Results and Discussion

The following sections present the comparison between simulated and experimental pressure profile. The effect of processing conditions on the total residual birefringence $\Delta n$ and average transverse birefringence, $<n_s-n_{so}>$ were studied for PS and PC ICM moldings experimentally and numerically.

6.2.1 Pressure Profile

The experimental and simulation results of pressure profiles for the following representative set of injection-compression molding conditions for run 1 for PS in Table 6-4 are discussed. Run 1 was carried out at a melt temperature of 210°C, a mold temperature of 60°C, a volume flow rate of 14 cm$^3$/s, a compression stroke of 0.15 cm, a compression speed of 0.4 cm/s and switchover time of 1.1s. The measured pressure trace obtained directly from a pressure transducer located under the sprue at the center of cavity is shown in Figure 6-6 by symbols. Simulated pressure is given by solid trace in this figure. The dot line represents the displacement of the plunger. Generally, from this figure the simulated pressure trace during the filling, compression and at the beginning of the packing stage are in a good agreement with the experimental data. It can be seen that the pressure trace from the experiment increases monotonically during the filling. However, it is noted that there is a pressure drop between the filling stage and compression stage. The pressure drop mainly comes from the stress relaxation during the switchover time of 1.1 s. During this time the plunger does not move and stress relaxation occurs. Accordingly this was the only mechanism that governed the behavior of the pressure history during switchover time. When the compression stage starts, the pressure
immediately builds up followed by the overshoot at the beginning of the packing stage and then packing pressure is maintained during the whole packing time. In the packing stage, the measured pressure trace recorded by the pressure transducer under the sprue is taken as the entrance pressure for the pressure simulation. The time at the end of injection stage was 2.874. The switchover time is 1.1 s. The compression stage was ended up at time of 4.254 s and then the packing stage was started. In the cooling stage which starts right after end of packing time, the pressure decreases due to the release of the packing pressure and cooling. The filling, compression, packing and cooling stages can easily be distinguished based on the pressure trace and the displacement data in this figure.

6.2.2 Velocity and Shear Rate Profiles

As a representative example the predicted gapwise velocity profiles at the end of the injection stage during injection-compression molding for run 2 for PS in Table 6-4 are shown in Figure 6-7 (a). As expected, the velocity decreased with increasing radial positions from the gate and the melt flow diminished around $z/h=0.8$ due to cooling from the mold wall. However, as shown in Figure 6-7 (b), the velocity at the end of compression stage during injection-compression molding increased with the radius at the end of compression stage. Similar velocity profiles were also obtained in the studies of Kim et al. [101] and Chen et al. [106]. The velocity behavior is explained by considering the mass balance. Since the volumetric flow rate of the melt through the surface increased with the radius, the velocity through the section at a position far from the gate was greater than that near the gate due to the mass balance. In addition, the percentage reduction of the centerline velocity between $r=2.948$ cm and $r=4.46$ cm was 150% at the end of
injection stage (see Figure 6-7 (a)), whereas the percentage increase was only 45 % at the end of compression stage (see Figure 6-7 (b)). This is an indication that the squeezing flow during the compression stage causes the pressure distribution in the mold cavity to become more uniform, resulting in a reduction of the flow velocity difference with position.

Figure 6-8 (a) and (b) show the predicted gapwise shear rate profiles at the end of injection stage and at the end of compression stage, respectively, during injection-compression stage of run 2. Similar to the velocity behavior, the shear rate at the end of filling stage decreased with increasing radial positions from the gate. However, the shear rate at the end of compression stage increased with the radius.
Figure 6-6 Measure (symbols) and simulated (solid line) pressure at the center of the disk and displacement of plunger (dashed line) as a function of time for run 1 of PS: melt temperature=230°C, mold temperature=40°C, volume flow rate=13 cm³/s, compression stroke=0.15 cm, compression speed=0.4 cm/s and switchover time=1.1 s.
Figure 6-7 Predicted gapwise distribution of velocity $v_s$ at various radial positions for run 2 of PS at the end of injection (a) ($t=2.64$ s) and compression stages (b) ($t=4.16$ s) during injection-compression molding.
Figure 6-8 Predicted gapwise distribution of shear rate at various radial positions for run 2 of PS at the end of injection (a) \((t=2.64 \text{ s})\) and compression stages (b) \((t=4.16 \text{ s})\) during injection-compression molding.
6.2.3 Birefringence in PS

The following sections present the influence of the processing conditions on the simulated total residual birefringence, $\Delta n$, and average transverse birefringence, $<n_{\theta} - n_{\theta 0}>$, for PS ICM moldings. The total birefringence is comprised of both flow- and thermally-induced birefringence. The simulated results are compared with measurements.

6.2.3.1 Numerical Simulation of Transient Birefringence

The flow-induced birefringence is determined by the thermo-mechanical history that the polymer experiences during the polymer processing [188]. The build-up and relaxation of the shear and normal stresses that takes place during the polymer flow lead to a transient birefringence history during the molding process. The combination of the stress build-up and relaxation with the cooling process that the polymer experiences during ICM determines the final frozen-in residual birefringence in the molded part. During the injection and compression stages the polymer melt flows from the gate to the edge of the cavity. The stages are characterized by three different types of polymer flow. The first is the well-known fountain flow at the melt front in which the melt coming from the core towards the wall is elongated [115]. But in this simulation, this type of flow is not considered. Secondly, as the polymer melt flows from the gate along the radial direction, the circumference of the melt front increases resulting in elongation in the tangential direction with a rate proportional to the radial velocity. The third, from the rheological viewpoint, the polymer flow is the shear flow caused by the velocity gradient in the thickness direction. As soon as the polymer melt gets in touch with the mold
surface, solidification starts to develop toward the core so that the normal and shear stress in the solidified layer and the corresponding chain orientation are frozen in. But the rate of growing solidified layer slows down quickly because the heat convection also plays a major role during the polymer flow.

The development of the birefringence in the gapwise direction is determined by the combined effects of shear rate variation and temperature decay. The former is caused by the shear flow during the filling stage and subsequent packing stage due to the compressibility of the material. The temperature decay greatly increases the relaxation time of the polymer. During filling and compression stages, the velocity and shear rate decrease near the mold wall because of the solidification effect, narrowing the available cross section area of the channel for polymer melt flow. As a result, the velocity and shear rate increase in the region far from the mold wall, with the peak shear rate occurring in proximity of the solidified region. This effect coupled with the relaxation time increase caused by cooling, determines the gapwise distribution of the total residual birefringence along the radial direction of the disk.

The predicted transient gapwise flow birefringence distributions for the injection-compression molding conditions for PS run 2 in Table 6-4 were corresponding to the injection stage until the melt front reaches $r=4.838$ cm at an initial cavity thickness of 4.675 mm, followed by the compression stage with a switchover time of 1.1s until the cavity is completely closed.

To identify the effects of the compression stage on the birefringence in molded parts numerical simulations were performed to get the transient birefringence distributions for the each stage.
The evolution of the predicted gapwise flow-induced birefringence distribution, \( \Delta n^\theta \), at various radial positions at the end of injection stage and various times during the compression stage for run 2 of PS are shown in Figure 6-9 and Figure 6-10, respectively.

The transient maximum birefringence at the end of injection stage as shown in Figure 6-9 occurred at \( z/b = \pm 0.7-0.8 \) due to the dominant effect of the first normal stress difference during the injection stage. The peaks continually decreased in magnitude with the increasing radial position from the gate. During the switchover time, the stresses relax due to absence of flow. But stress relaxation process is retarded due to cooling. After the switchover time, the predicted transient gapwise birefringence distribution during the compression stage as shown in Figure 6-10 increased with compression time. The birefringence peaks increased in the radial direction, differing from the results obtained during the injection stage. This figure shows that the simulated transient birefringence, \( \Delta n \), before and after \( r=4.838 \text{ cm} \) corresponding to position of the melt front at the end of injection stage and after the switchover time, changes significantly. In particular, the magnitude of \( \Delta n \) decreased tremendously when the radius is over \( r=4.46 \text{ cm} \). This is due to the fact that, after the switchover time, the temperature is decreased along the gapwise direction in the control volume before the melt front causing an increase of the shear and normal stresses developed during the compression stage due to the increase of viscosity and relaxation time of the polymer melt. At the same time, since the temperature along the gapwise direction in the node to be newly filled after the switchover time is still high, the shear and normal stresses developed during the compression stage decrease due to the low viscosity and relaxation time of the polymer melt supplied by the core of the previous melt front node. The local minimum and the
local maximum appear near the wall region. This is caused by the change of the shear rate due to the narrowing of the duct caused by the solidification effect and by the frozen–in chain orientation in the filling and compression stages and slow relaxation in the cooling stage.

The predicted gapwise flow-induced birefringence distribution at the end of the compression stage at the various radial positions for PS run 2 are shown in Figure 6-11. At the end of the compression stage, a global maximum and local minimum of the birefringence can be seen with their magnitudes determined by the shear and normal stresses present at the time when the polymer melt at that gapwise position solidified as the control volume was filled at each time step.

The predicted gapwise distribution of the flow birefringence at the various radial positions at the end of the packing stage for PS run 2 is presented in Figure 6-12. In this work, it was difficult to precisely control the high packing pressure required to compensate the shrinkage of the polymer melt due to the cooling effect. This is due to the mechanical limitation of this ICM machine. Therefore, the packing stage in this work does not play a major role in development of the flow-induced birefringence. It may be noted that the birefringence near the wall does not change during the packing stage since the temperature near the mold wall is lower than the glass transition temperature, $T_g$. Therefore, the birefringence was frozen in this region. However, outside this region the stress relaxation is significant since the temperature is still high in this region. This figure shows that the predicted flow birefringence in the core is very low due to the fast relaxation of chain orientation immediately after completion of the compression stage at high temperature in the core.
The predicted gapwise residual flow birefringence distributions at the end of the cooling stage, when temperature through the gap becomes lower than the glass transition temperature, \( T_g \) are given in Figure 6-13 for PS run 2. In extensive wall region the distribution of birefringence remains almost same as that of birefringence after the end of the packing stage shown in Figure 6-12. Since the shear and normal stresses do not change below the glass transition temperature, the residual flow stress remains almost frozen during the cooling stage. However, the residual flow birefringence in the core is zero. This is because the complete relaxation of chain orientation after completion of the packing stage take place since the temperature is still high in this region. As described above, the birefringence near the wall remains almost unchanged after the end of compression till the end of the cooling stage because the polymer melt is already cooled down below the glass transition temperature. But the birefringence in the vicinity of the cavity center is found to be completely relaxed from the value at the end of filling because the packing pressure is low and it continue to relax until the end of cooling stage.
Figure 6-9 Predicted transient flow-induced birefringence ($\Delta n^f$) distributions in the gapwise direction at various radial positions at the end of the injection stage ($t=2.64$) s for the ICM under the processing conditions of PS run 2.
Figure 6-10 Predicted transient flow-induced birefringence ($\Delta n^c$) distributions in the gapwise direction at various radial positions during the compression stage at $t=3.8$ s (a) and $t=4.11$ s (b) for the ICM under the processing conditions of PS run 2.
Figure 6-11 Predicted transient flow-induced birefringence ($\Delta n^f$) distributions in the gapwise direction at various positions in the radial direction at various radial positions at the end of the compression stage $t=4.16$ s for the ICM under the processing conditions of PS run 2.

Figure 6-12 Predicted transient flow-induced birefringence ($\Delta n^f$) distributions in the gapwise direction at various radial positions at the end of the packing stage for the ICM under the processing conditions of PS run 2.
Figure 6-13 Predicted transient flow-induced birefringence ($\Delta n^f$) distributions in the gapwise direction at various radial positions at the end of the cooling stage for the ICM under the processing conditions of PS run 2.

6.2.3.2 The Effect of Mold Temperature

The predicted and measured gapwise distributions of the flow birefringence $\Delta n^f$ at various radial positions for PS runs No. 1, 2, and 3 are shown in Figure 6-14 at mold temperatures of 40 (a), 60 (b) and 80 °C (c) with a melt temperature of 230 °C at the end of cooling stage. As the mold temperature increases from 40 °C to 60 °C, finally to 80 °C, the overall flow-induced birefringence decreases with significant decrease of the thickness of solidified region due to the more stress relaxation at higher melt temperature.

Figure 6-14 shows that the birefringence decreases with increasing radius leading to lower flow velocity in the disk cavity as shown in Figure 6-7 (b). The development of the gapwise distribution of the birefringence is determined by the combination of the
effects of shear rate variation and temperature history. The former is caused by the shear flow during the filling and compression stages followed by packing stage due to the compressibility of the polymer melt. The temperature history of the polymer melt is also affected by the existence of the switchover time in this experiment. During injection, the velocity and shear rate decrease near the mold wall because of the solidification effect. During the switchover time, the solidification effect takes place without the polymer melt flow resulted in the stress relaxation. During the compression stage, the velocity and shear rate distribution in the gapwise direction with the peak shear rate occurring just outside the solidified region are developed. During the compression stage, the change of the shear rate distribution, coupled with temperature change caused by cooling, determines the gapwise distribution of the birefringence along the radial direction of the disk. As a result, at the end of compression stage, a global maximum and local minimum of the birefringence profile is developed by the shear and normal stresses. The packing stage does not affect the flow-induced birefringence because the packing pressure is not high enough to compensate the polymer shrinkage.

A local minimum and a local maximum of the birefringence can be seen in Figure 6-14, with their magnitudes determined by the normal stress difference when the polymer melt solidifies at that gapwise position. The birefringence for mold temperatures of 40, 60 and 80 °C showed a maximum value at the outer wall. The overall distribution of flow-induced birefringence remains almost unchanged with respect to the change in the mold temperature. However, its magnitude tends to increase slightly as the mold temperature is lowered, particularly near the mold wall and at the local maximum birefringence, because relaxation of stresses generated during the injection and
compression is hindered more significantly at the lower mold temperature. In addition, thickness of the frozen-in layer near the wall region at the mold temperature of 40 and 80 °C is different being higher at lower mold temperature. The increase of thickness of the frozen-in layer corresponded to an increase of the frozen layer developed during the injection and compression stages.

The predicted residual flow birefringence in the core is zero due to the fast relaxation of chain orientation immediately after completion of the filling stage, since the temperature is still high in this region. Evidently, the thermally-induced birefringence dominates in the core region.

Figure 6-14 Measured (symbols) and predicted (lines) residual flow-induced birefringence $\Delta n^b$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks obtained in runs 1, 2, 3 in Table 6-4 corresponding to mold temperature of 40 °C (a), 60 °C (b) and 80 °C (c). The contribution of thermal birefringence was not included in the predicted birefringence.
Figure 6-14 Measured (symbols) and predicted (lines) residual flow-induced birefringence $\Delta n_f$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks obtained in runs 1, 2, 3 in Table 6-4 corresponding to mold temperature of 40°C (a), 60°C (b) and 80°C (c). The contribution of thermal birefringence was not included in the predicted birefringence (continued).
The linear viscoelasticity and photoviscoelasticity with the volume relaxation effects were used to calculate the residual thermal stresses and birefringence [141]. In calculating the thermal birefringence relaxation modulus and strain-optical coefficient functions, reported early [1,141], were used. As a first approximation, we treat the residual thermal stresses and birefringence in CIM and ICM disks as those in freely quenched slabs. Predicted residual thermal birefringence distributions along the gapwise direction of PS slabs quenched from an initial temperature of 230 °C to different cooling temperatures are shown in Figure 6-15. It is found that as the cooling temperature increased the thermally-induced birefringence decreased.

To the best of our knowledge, no single nonlinear constitutive equation is available to describe the rheological behavior of a polymer in the glassy, rubber and fluid states and in the transition region between them. Moreover, in the filling, compression and cooling stages, the dominant terms in the dynamic equations are different. Therefore a further assumption was made that the coupling effects between the flow and thermal stresses are negligible, such that they can be evaluated independently. In the case of PS moldings, simulations showed that the thermally-induced birefringence, \( \Delta n^h \), near the wall was one order of magnitude lower than the flow-induced birefringence, \( \Delta n^f \). In this region, the flow-induced birefringence was negative, while the thermally-induced birefringence was positive. However, near the center, the magnitude of the flow-induced birefringence was almost negligible. This is because, when the flow stopped, the flow-induced birefringence relaxed near the center of the ICM moldings, due to the high temperature of this region. Therefore, it is possible to get the better qualitative and quantitative prediction of total residual birefringence compared with measured
birefringence by summation of the residual thermally induced and flow-induced birefringence. Figure 6-16 shows the measured and simulated total birefringence, $\Delta n$ for PS runs 1, 2 and 3 at various radial positions. It is found that when the thermally-induced birefringence was added to the corresponding flow-induced birefringence, the simulated total birefringence provided a better qualitative and quantitative description of the measured birefringence in PS ICM moldings. Simulations showed that the total birefringence near the wall was caused mainly by flow, based on the fact that the magnitude of the thermally-induced birefringence at this location was significantly lower than the corresponding flow-induced birefringence. However, the birefringence near the center was mostly caused by thermal stresses developed during cooling, since the flow-induced birefringence relaxed almost completely in this region after the cessation of the flow. Both predicted and measured birefringences show slightly concave shape in the core region, a global maximum near the mold surface and local maximum about $z/b = \pm 0.6-0.8$ of the disk. With a mold temperature of 80°C, the distribution of the birefringence at the end of cooling is similar to that with a mold temperature of 60°C, but the global maximum is lower than that a 60°C. The location of the global and local maximums at a mold temperature of 80°C are significantly and slightly shifted toward the surface for both sides, respectively, because of the smaller thickness of the solidified layers developed at higher mold temperature. The same trend for the distribution of birefringence could be found where mold temperature changed from 60°C to 40°C. In summary, as shown in Figure 6-16, increasing the mold temperature leads to a slight decrease of the birefringence with the position for local maximum peaks moving toward the wall.
The simulation results generally tend to underestimate the gapwise distribution of total residual birefringence because of neglect of the fountain flow and the delivery system. In particular, some differences are evident in the region between the location of maximum of $\Delta n$ and the center. Possibly, this discrepancy between experimental and predicted birefringence is due to neglect of contribution of flow in a delivery system consisting of contraction and expansion regions [76]. The flow in these regions provides additional contribution to birefringence. Therefore, the predicted birefringence underestimates the experimental one. This discrepancy was found all over the experimental data of PS ICM moldings in this work. Regardless, there is a qualitative agreement between the predicted overall total values of $\Delta n$ and experimental results.

![Figure 6-15 Predicted residual thermal birefringence $\Delta n^{th}$ of PS plates quenched from 230 °C to different cooling temperatures $T_i$.](image)

Figure 6-15 Predicted residual thermal birefringence $\Delta n^{th}$ of PS plates quenched from 230 °C to different cooling temperatures $T_i$. 
Figure 6-16 Measured (symbols) and predicted (lines) total residual birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks obtained in run 1, 2 and 3 in Table 6-4 corresponding to a mold temperature 40°C (a), 60°C (b) and 80°C (c). The contribution of thermal birefringence was included in the predicted birefringence.
6.2.3.3 The Effect of Melt Temperature

The effect of melt temperature on the distribution of birefringence and average transverse birefringence under non-isothermal flow conditions of ICM can be expected on rheological point of view because increasing the melt temperature decreases the viscosity of the polymer melt. However, a magnitude of the effect depends on the temperature sensitivity \( T_s \) or activation energy of viscous flow of the polymer melt.

Figure 6-17 (a), Figure 6-17 (b), and Figure 6-14 (b) show the predicted and measured gapwise distributions of the flow birefringence \( \Delta n_f \) with a mold temperature.
60 °C at various radial positions at the end of cooling stage for PS runs 4, 5 and 2 corresponding to different melt temperatures of 190°C (Figure 6-17 (a)), 210°C (Figure 6-17 (b)) and 230°C (Figure 6-14 (b)), listed in Table 6-4. The distribution of birefringence is very sensitive to the melt temperature and indicates higher outer peak and inner peak values at lower melt temperature. As aforementioned, the outer peak is due to the deformation during the injection and compression stages and the subsequent relaxation of molecular orientation in the intermediate region and frozen-in orientation near the surface. This flow-induced birefringence peak near the wall becomes smaller at higher melt temperature. This is because the viscosity of polymer decreased when the temperature increased. This led to a lower shear and normal stressed at given volumetric flow rate during the filling stage. Furthermore, the relaxation time, which inversely proportional to the melt temperature is decreased inducing a faster relaxation of the birefringence. Therefore, simulation showed that the global maximum of the flow-induced birefringence $\Delta n^f$ on the wall and the local maximum of the flow-induced birefringence $\Delta n^f$ near the wall significantly decreased when the melt temperature increased.
Figure 6-17 Measured (symbols) and predicted (lines) residual flow-induced birefringence $\Delta n_{fl}$ distribution in the gapwise direction at various radial position at the end of the cooling stage for the ICM disks obtained in PS run 4 and 5 in Table 6-4 corresponding to a melt temperature of 190°C (a) and 210°C (b). The contribution of thermal birefringence was not included in the predicted birefringence.
The predicted flow-induced birefringence $\Delta n^\theta$ at the core is zero due to the fast relaxation of chain orientation right after filling, since the temperature is still high in this region. Evidently, the thermally-induced birefringence dominates in the core region.

The residual thermal stresses and birefringence in freely quenched slabs were calculated based on the linear viscoelasticity and photoviscoelasticity with volume relaxation effects included [1,141], were used with the assumption of no coupling effect between flow- and thermally-induced birefringence. Increasing the melt temperature the thermally-induced birefringence increased. However, at a temperature well above $T_g$ the stress and birefringence relax very fast [1]. Therefore, above 190 °C, the contribution of the thermally-induced birefringence was comparatively minor compared to that of the flow-induced birefringence.

For the better qualitative and quantitative prediction of the total residual birefringence for the measured birefringence at various radial positions the residual thermal birefringence was added to the residual flow birefringence, according to Eq. (3.100). These results are given in Figure 6-16 (b) and Figure 6-18 (a) and Figure 6-18 (b). Compared with the melt temperature of 210 °C, the birefringence decreases significantly as the melt temperature increase to 230 °C due to the lower viscosity and faster stress relaxation. The gapwise distributions of the flow induced birefringence at different radial locations at the end of cooling for a melt temperature of 230 °C follow similar trends of those for melt temperatures of 210 °C and 190 °C with proportionally reduced its magnitude because of lower viscosity and faster stress relaxation at higher melt temperature. Similar to the effect of mold temperatures, a global maximum appears near the surface as the frozen-in birefringence during the filling and switchover time. A
local maximum is observed about $z/b = \pm 0.6-0.8$, which is caused by the frozen-in chain orientation in the filling and compression stages and slow relaxation in the cooling stage. At the end of cooling, the birefringence at the core region completely relaxes, and the global maximum in the solidified layers has also decreased significantly with its position slightly shifted to the mold wall with increasing melt temperatures. The change of the melt temperature has a larger effect on the gapwise flow-induced birefringence, due to the high temperature sensitivity of PS melt viscosity compared with the effect of mold temperature. Even though there is some deviation between measurement and simulations, the predicted overall total values of $\Delta n$ are qualitatively in agreement with experimental results.

The average transverse birefringence $<n_{ss} - n_{\theta\theta}>$ is directly measured by measuring the retardation of the normal incident laser beam. The predicted average transverse birefringence was calculated by the integration of the in-plane birefringence over the thickness of the disk. The average transverse birefringence as a function of radius for melt temperatures of 190°C, 210°C and 230°C with a mold temperature of 60 °C corresponding to PS run 4, 2, 5 in Table 6-4 is shown in Figure 6-19. As the mold temperature increases from 190 °C to 230 °C, the average transverse birefringence decreases significantly due to more stress relaxation at higher temperature. This birefringence also decreases with the radial direction [90,142]. Theoretical and experimental data on $<n_{ss} - n_{\theta\theta}>$ of the present study are in contrast with experimental data reported by Chen et al. [10] indicating a minimum birefringence at some radial distances. The simulation and experimental results of the average transverse
birefringence at all radial positions with melt temperatures of 190 °C, 210 °C and 230 °C are in qualitative agreement.

Figure 6-18 Measured (symbols) and predicted (lines) total residual birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks obtained in PS run 4 and 5 in Table 6-4 corresponding of a melt temperature 190 °C (a) and 210 °C (b). The contribution of thermal birefringence was included in the predicted birefringence.
6.2.3.4 The Effect of Compression Stroke

The ICM combining CIM and compression molding has been developed to incorporate the advantage of both molding processes. However, it has introduced new processing parameters such as compression speed, compression stroke and switchover time. Therefore, it is of great importance to determine the effects of the compression stage on the total birefringence in the molded parts. In this experiment, only the effect of compression stroke on the gapwise distribution of birefringence is considered. During the injection stage, the melt is injected into a cavity with an initial thickness that is initially greater than the nominal thickness by 1.0 to 2.0 mm.
Figure 6-20 (a), Figure 6-16 (b) and Figure 6-20 (b) show the predicted and measured gapwise distributions of the total residual birefringence, $\Delta n$, at a mold temperature of 60°C at various radial positions at the end of cooling stage for PS runs 6, 2 and 7 in Table 6-4 corresponding to compression strokes of 1 mm, 1.5 mm and 2 mm. Compared with a compression stroke of 1 mm, the birefringence decreases as the compression stroke increases to 1.5 mm because the flow of polymer melt is easier under large compression stroke resulting in low pressure and lower birefringence value. The gapwise distributions of the total birefringence at different radial locations at the end of cooling for a compression stroke of 2 mm follow similar trends as those for compression strokes of 1 mm and 1.5 mm. As the compression stroke increase, birefringence distribution decrease. The compression stroke of 1 mm showed higher global maximum birefringence than that of 2 mm. However, it should be noted that there is no distinct difference for the compression strokes of 1 mm and 1.5 mm due to the difference in switchover time. Larger switchover times allow more stress relaxation to take place. Since the switchover time of 1.2 s was used for a compression stroke of 1 mm, more stress relaxation yields the lower global maximum birefringence compared with the compression stroke of 1.5 mm with a switchover time of 1 s. A local maximum is also observed about $z/b = \pm 0.6-0.8$, which is caused by the frozen–in chain orientation in the filling and compression stages and slow relaxation in the cooling stage. At the end of cooling, the birefringence at the core region completely relaxes, and the local maximum has decreased significantly and has been slightly shifted toward the mold wall with increasing compression strokes. Even though there is some deviation, there is
qualitatively good agreement between results of the numerical simulations and the measurements for total residual birefringence, $\Delta n$. 

Figure 6-20 Measured (symbols) and predicted (lines) total residual birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks obtained in PS run 6 and 7 in Table 6-4 corresponding to a compression stroke of 1 mm (a) and 2 mm (b). The contribution of thermal birefringence was included in the predicted birefringence.
6.2.3.5 The Effect of Switchover Time

The switchover from the injection to compression stages is not instantaneous. This imposes a time lag between the injection and compression stages. This time lag is defined as the switchover time. To identify the effect of the switchover time in injection-compression molding process, we have intentionally excluded the switchover time, i.e., zero switchover time is employed in calculations. Then, the switchover time is considered in ICM, so the followed compression stage is delayed in this switchover time.

Figure 6-13 and Figure 6-21 show the simulated gapwise residual flow-induced birefringence, \( \Delta n \), distribution at various radial positions at the end of cooling stage in ICM disks without switchover time and with switchover time of 1.1 s in PS run 2 in Table 6-4.

Generally speaking, during the switchover time, there are two competing mechanisms. One is stress relaxation due to the absence of flow and dissipation energy. The other is high shear stress from the high viscosity of the polymer melts by cooling effect during compression after switchover time due to the heat transfer from the cold wall during switchover time. The dominating mechanism is determined by the duration of the switchover time. A shorter switchover time induced the first mechanism dominating due to lower pressure and faster stress relaxation, while longer switchover time make the second mechanism more important to determine the final birefringence distribution.

The simulated result in this work suggests that the switchover time is a relatively important parameter for PS. During the switchover time, the polymer melt is in a static condition and the cooling process takes place faster than during the injection stage because no viscous heating is generated due to the polymer flow. Therefore, stress
relaxation only takes place during the switchover time. The simulated results of Figure 6-21 show a local minimum and a local maximum of the birefringence at the switchover time of 0 s. Their magnitudes are mainly determined by the normal stress difference when the polymer melt at that gapwise position solidifies. However, when the switchover time was employed, the results show that the global and local maximum birefringence increases, while the gapwise position of local maximum of $\Delta n$ is shifted further away from the outer wall in Figure 6-13. This is due to the fact that the switchover time increases the cooling time reducing temperature of the polymer melt along the gapwise direction at position away from the melt front at the end of injection. Therefore, the viscosity of the polymer melts near the mold wall increases, leading to a higher shear rate, higher shear and normal stresses for the given compression speed.

![Graph showing predicted residual flow-induced birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks without switchover time for PS run 2 in Table 6-4.](image)

Figure 6-21 Predicted residual flow-induced birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks without switchover time for PS run 2 in Table 6-4.
6.2.3.6 Comparison between CIM and ICM

It is of great importance to find the effect of the compression stage on the birefringence in the molded parts. For this purpose, numerical analysis have been carried out for CIM process (i.e. without the compression stage) without packing stage and ICM process (i.e. with compression stage) with no switchover time and without packing stage.

Figure 6-22 shows the simulated gapwise flow-induced birefringence distribution along the radial direction for both CIM (a) and ICM (b) parts at the end of cooling stage. As shown in Figure 6-22, birefringence of ICM including the compression is dramatically decreased, especially near the mold surface. From these results of the numerical simulation, it is found that the compression stage after the injection stage certainly reduces the flow-induced birefringence level most notably near the cavity wall region. It is expected that more drastic decrease of birefringence can be obtained if the injection stage is applied at a wider cavity opening such that the compression stage becomes more dominant over the injection stage.

In this respect, one can conclude that the ICM process is more suitable for manufacturing precision optical products of good optical quality than the CIM process.

It is also interesting to find the difference in the average transverse birefringence in ICM and CIM moldings. The predicted and measured average transverse birefringence, \(-<n_{ss} - n_{tg}>\), as a function of the radial direction is compared in Figure 6-23 for both CIM (a) and ICM (b) disks at the end of cooling. This birefringence decreases with the radial direction [90,142]. It can be seen that the averaged transverse birefringence along the radial direction decreases with distance from the gate. The average transverse birefringence in the molding made by CIM is approximately twice as large as that made
by ICM. Regardless, the overall predicted values of $-<n_{ss} - n_{sd}>$ are in qualitative agreement with the experimental results.

Figure 6-22 Predicted residual flow-induced birefringence $\Delta n^f$ distribution in the gapwise direction at various radial positions at the end of the cooling stage in CIM (a) and ICM (b) disks for PS run 2 (Table 6-4) except for without switchover time and packing stage.
6.2.4 Birefringence of and Average Transverse Birefringence of PC

The following sections present the influence of the processing conditions on the simulated total residual birefringence, $\Delta n$, and average transverse birefringence, $<n_{\parallel} - n_{\perp}>$, for PC ICM moldings. The total birefringence is comprised of both flow- and thermally-induced birefringence. The simulated results are compared with measurements.
6.2.4.1 Numerical Simulation of Transient Birefringence

During the ICM process, the polymer undergoes drastic mechanical and thermal influences in fluid, rubbery, and glassy states. Such effects introduce residual stresses and frozen-in molecular orientation into the final molded parts. Flow stresses of amorphous polymers appear mostly as a result of the cavity filling, including injection and compression stage, under high strain rates that generate high shear stresses and the first and second normal stress differences during nonisothermal flow. The build-up and relaxation of the shear and normal stresses that takes place during the polymeric flow introduces a transient birefringence history during the polymer processing. The combination of the stress build-up and the relaxation with the cooling determines the final frozen-in residual birefringence in the final ICM molded part.

The final solid ICM part is obtained as a result of fluid flow and heat transfer process. First, as a polymer melt is injected into the mold, complex transient flow processes are developed along with fountain flow, in which hot polymer melt at the center is continually moved to the cold mold wall at the melt front leading to elongational flow [115]. In this simulation, this type of flow is not considered. Second, the polymer melt begins to solidify on contact with the cold mold surface, so that the thickness of local flow channel continuously decreases during the injection and compression processes. This solidification effect gradually propagates toward the core so that the normal and shear stresses in the solidified layer and the corresponding chain orientation are frozen in. But the rate of growing solidified layer slows down quickly because the heat convection also plays a major role during the polymer flow. Third, temperature
changes induced by heat transfer and viscous dissipation, results in continually changing local shear rates that affect the local orientation in the polymer melt.

The transient gapwise birefringence distribution in the ICM process is determined by the combined effect of shear rate change and temperature decay. During filling and compression stages, the velocity and shear rate decrease near the mold wall because of the solidification effect, narrowing the available cross sectional area of the channel for polymer melt flow. As a result, the velocity and shear rate increase in the region far from the mold wall, with the peak shear rate occurring in the vicinity of the solidified region. This variation of the shear rate determines the transient gapwise distribution of the flow-induced residual birefringence along the radial direction of the disk.

The predicted transient gapwise flow birefringence distributions for the following set of injection-compression molding conditions for run 2 for PC in Table 6-5 were discussed for an injection stage until the melt front reaches \( r = 4.838 \) cm and an initial cavity thickness of 4.675 mm, a melt temperature of 260\(^\circ\)C, a mold temperature of 60\(^\circ\)C, a volume flow rate of 23 \( \text{cm}^3/\text{s} \) and for a compression stage with a switch over time of 1.0 s, a compression stroke of 0.15cm and a compression speed of 0.4cm/s until the cavity is completely closed. The predicted gapwise flow birefringence distributions at the end of the compression stage at the various radial positions for this run are shown in Figure 6-24. This figure shows the simulated transient birefringence \( \Delta n \) when the disk cavity is completely filled. At the end of the compression stage, a local maximum and local minimum of the birefringence appear near the wall region, which is caused by the change of the shear rate and the shifting of the maximum of the shear rate toward core
due to the narrowing of the channel caused by the solidification effect. It is noted that for the radius above $r = 4.46$ cm, the magnitude of $\Delta n$ decreased tremendously. It is due to the fact that, after the switchover time, the temperature is decreased along the gapwise direction in the control volume before the melt front causing an increase of the shear and normal stresses developed during the compression stage due to the increase of viscosity and relaxation time of the polymer melt. At the same time since the temperature along the gapwise direction in the node to be newly filled after the switchover time is still high, the shear and normal stresses developed during the compression stage were lower due to the decrease of the viscosity and relaxation time of the polymer melt supplied by the core of the previous melt front node.

The predicted gapwise distribution of the flow birefringence at the various radial positions at the end of the packing stage is presented in Figure 6-25. The packing stage in this work does not play a major role in development of the flow-induced birefringence because the packing pressure is too low to compensate the shrinkage of the polymer melt due to the cooling effect. It may be noted that as the temperature near the mold wall is lower than the glass transition temperature, $T_g$, the birefringence near the wall does not change during the packing stage. Therefore, the birefringence was frozen in this region. However, outside this region the stress relaxation is significant since the temperature is still high in this region. This figure shows that the predicted flow birefringence in the core is very low due to the fast relaxation of chain orientation immediately after completion of the compression stage at high temperature in the core.

The predicted gapwise residual flow birefringence distributions at the end of the cooling stage, when temperature through the gap becomes lower than the glass transition
temperature, $T_g$ over the whole domain thickness are given in Figure 6-26. The distribution of birefringence remains almost same as that of birefringence after the end of the packing stage because the stresses vary very little below the glass transition temperature so that the residual stress remains almost fixed during the cooling stage. The residual flow birefringence in the core is zero due to the complete relaxation of chain orientation after completion of the packing stage. As described above, the birefringence near the wall remain almost unchanged after the end of compression till the end of the cooling stage because the polymer melts is already cooled down below the glass transition temperature. But the birefringence in the vicinity of the cavity center is found to be completely relaxed from the value at the end of filling when the packing pressure is not sufficient to compensate the shrinkage of the polymer melts. Birefringence continues to decrease with the packing time.
Figure 6-25 Predicted flow-induced birefringence ($\Delta n$) distributions in the gapwise direction at various radial positions at the end of the packing stage for the ICM under the processing conditions of PC run 2.

Figure 6-26 Predicted flow-induced birefringence ($\Delta n$) distributions in the gapwise direction at various radial positions at the end of the cooling stage for the ICM under the processing conditions of PC run 2.
6.2.4.2 The Effect of Mold Temperature

The processing conditions of ICM affect the final quality of ICM parts. To study effects of various ICM processing conditions on the gapwise distribution of birefringence and average transverse birefringence, extensive experiments were carried out. Numerical analyses of the ICM process were performed by varying mold temperature, melt temperature and compression stroke.

Figure 6-27 shows the predicted gapwise distributions of the flow-induced birefringence, $\Delta n^f$, and measured gapwise distributions of the total residual birefringence, $\Delta n$, at the end of cooling stage as a function of radius at mold temperatures of 40 °C (a), 60 °C (b) and 80 °C (c) and a melt temperature of 260 °C for PC run 1, 2 and 3.

As can be seen from Figure 6-27, the gapwise distribution of the birefringence is determined by the combination of the effects of shear rate change and temperature history. The former is caused by the shear flow during the filling and compression stages followed by packing stage, and the latter is also greatly affected by the existence of the switchover time in this research. During injection, the velocity and shear rate decrease near the mold wall because of the solidification effect. During the switchover time, the solidification takes place because the polymer melt cools down without flow. As a result, at the end of the compression stage, the peak shear rate occurs in the vicinity of the solidified region. This shear rate effect coupled with temperature decrease caused by cooling, determines the gapwise distribution of the birefringence along the radial direction of the disk.
As the mold temperature increased from 40 °C to 60 °C and the switchover time and volume flow rate are decreased from 1.12 s to 1.0 s and from 25 cm³/s to 23 cm³/s, respectively, the magnitude of flow birefringence along the gapwise direction decreased with significant decrease of the thickness of solidified region due to the more stress relaxation at higher temperature.

The difference of the flow birefringence between the mold temperature of 40 °C and 60 °C was more significant near the wall than in the center of the cavity, where the magnitudes of the birefringence is almost zero. In the case of the low mold temperature, the temperature decreased near the mold surface because of the increase of the heat transfer through the heat conduction from the cold wall. This increases the viscosity of the polymer, resulting in an increase of the shear and normal stresses and birefringence. Also the relaxation of the stresses generated during the injection and compression stages is hindered more significantly at the colder mold surface.

However, the magnitude of the flow birefringence along the radial direction increased even though the mold temperature is slightly increased from 60 °C to 80 °C. It is due to the fact that the switchover time and the volume flow rate for the case of mold temperature of 60 °C is 1.0 s and 23 cm³/s, respectively, while for the mold temperature of 80 °C it is 1.12 s and 26 cm³/s. If the volume flow rate is higher, the higher shear stress and normal stresses are developed. Even though the mold temperature and the volume flow rate is increased, longer switchover time results in the lower temperature along the gapwise direction at the mold temperature of 80 °C because the more heat transfer from the mold wall takes place. Due to the increase of viscosity of polymer melt at the longer switchover time an increase of the shear and normal stresses and birefringence occur.
It is also found that significant decrease of the thickness of the solidified region due to the more stress relaxation at higher mold temperature take place. As the mold temperature increases, the measured and predicted flow-induced residual birefringence decreases and the location of maximum birefringence are shifted toward wall. At higher mold temperature, it is due to the faster stress relaxation and thinner solidified layer at reduced rate of heat conduction.

Figure 6-27 Measured (symbols) and predicted (lines) residual flow-induced birefringence $\Delta n^f$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the PC ICM disks obtained in runs 1, 2 and 3 in Table 6-5 corresponding to mold temperature of 40°C (a), 60°C (b) and 80°C (c). The contribution of thermal birefringence was not included in the predicted birefringence.
Figure 6-27 Measured (symbols) and predicted (lines) residual flow-induced birefringence $\Delta n^f$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the PC ICM disks obtained in runs 1, 2 and 3 in Table 6-5 corresponding to mold temperature of 40°C (a), 60°C (b) and 80°C (c). The contribution of thermal birefringence was not included in the predicted birefringence (continued).
From comparison of the flow-induced birefringence distribution with measured birefringence shown in Figure 6-27, it is noted that the measured birefringence consistently indicate the existence of birefringence around the centerline. This kind of difference between the numerical and experimental results is due to fundamental deficiency of the present modeling which neglects the development of thermally-induced residual stress and birefringence that built up in the molded parts. A tensile residual stress develops in the center and a compressive stress near the mold surface similar to the residual stresses seen in free quenching. Evidently, the thermally-induced birefringence dominates in the core region.

With assumption of no coupling effects between flow and thermal residual stresses the residual thermal stresses and birefringence were calculated based on the linear viscoelasticity and photoviscoelasticity with volume relaxation effects included [141] independently of flow-induced residual stress. In calculating the thermal birefringence relaxation modulus and strain-optical coefficient functions, reported in [1,141], were used. Predicted residual thermal birefringence distributions along the gapwise direction of PC slabs quenched from an initial temperature of 260 °C to different cooling temperatures are shown in Figure 6-28. It is found that as the cooling temperature increased the thermally-induced birefringence decreased.

In the case of PC moldings, simulations showed that the thermally-induced birefringence, \( \Delta n^b \), near the wall was lower than the flow-induced birefringence, \( \Delta n^f \). In this region, the flow-induced birefringence was positive, while the thermally-induced birefringence was negative. However, near the center, the magnitude of the flow-induced birefringence was almost negligible. This is because, when the flow stopped, the flow-
induced birefringence relaxed near the center of the ICM moldings, due to the high temperature of this region. Therefore, when the thermally-induced birefringence was added to the corresponding flow-induced birefringence, the simulated total birefringence showed a qualitatively and quantitatively good agreement compared with measured birefringence.

These results are given in Figure 6-29. Both the predicted and experimental data show slightly concave shape in the core region of birefringence distribution with a maximum about $\frac{z}{b} = \pm 0.7-0.9$ near the surface. With a mold temperature of 80°C, the distribution of the birefringence at the end of cooling is similar to that at a mold temperature of 60°C, but the global maximum is lower than that at 60°C. The location of the global and local maximums at a mold temperature of 80 °C are respectively, significantly and slightly shifted toward the surface because of the smaller thickness of the solidified layer developed at higher mold temperature. The exactly same trend for the distribution of birefringence is found when the mold temperature decreased from 60°C to 40°C. In summary, as shown in Figure 6-29, mold temperature affects on the gapwise birefringence distribution such that an increasing of it leads to a slight decrease of the birefringence magnitude with the change of the position for maximum peaks.

It is interesting to note that the overall shapes of the predicted birefringence distribution are in qualitative agreement with experimental data for all cases. However, the simulation result generally tends to underestimate the gapwise distribution of total residual birefringence. Difference between the measured and simulated results may be attributed to neglection of the fountain flow and the delivery system. It is also possible a source of this discrepancy that the stress-optical coefficient might not be a constant as
used in the numerical simulation of flow birefringence. In particular, some differences between measured and predicted birefringence are evident in the region between the location of maximum of $\Delta n$ and the center. It is because of neglect of contribution of flow in a delivery system consisting of contraction and expansion regions [76]. The flow in these regions that was neglected in the present calculation provides an additional contribution to birefringence. Therefore, the predicted birefringence underestimates the measured one. This discrepancy was found all over the experimental data of PC ICM moldings in this work. Nevertheless, the predicted overall total values of $\Delta n$ are in a qualitative agreement with experimental results.

The average transverse birefringence $\langle n_{ss} - n_{\theta\theta} \rangle$ is directly measured by measuring the retardation of the normal incident laser beam. The predicted average transverse birefringence was calculated by the integration of the in-plane birefringence over the thickness of the disk. The average transverse birefringence as a function of radius for mold temperatures of 40 $^\circ$C, 60 $^\circ$C and 80 $^\circ$C and a melt temperature of 260 $^\circ$C is shown in Figure 6-30. As the mold temperature increases from 40 $^\circ$C to 80 $^\circ$C, the average transverse birefringence decreases due to more stress relaxation at higher temperature. This birefringence also decreases with the radial direction [90,142]. Theoretical and experimental data on $\langle n_{ss} - n_{\theta\theta} \rangle$ of the present study are in contrast with experimental data reported by Chen et al. [10] indicating a minimum birefringence at some radial distances. Even though some variation between the experimental data and simulated results of the average transverse birefringence at all radial positions with mold temperatures of 40 $^\circ$C, 60 $^\circ$C and 80 $^\circ$C may be attributed to various causes as discussed
early, the overall magnitude of the simulation result is a qualitative agreement with the experimental data.

Figure 6-28 Predicted residual thermal birefringence $\Delta n_{th}$ of PC plates quenched from 260 °C to different cooling temperatures $T_i$. 
Figure 6-29 Measured (symbols) and predicted (lines) total residual birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the PC ICM disks obtained in PC runs 1, 2 and 3 in Table 6-5 corresponding to mold temperature of 40°C (a), 60°C (b) and 80°C (c). The contribution of thermal birefringence was included in the predicted birefringence.
Figure 6-29 Measured (symbols) and predicted (lines) total residual birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the PC ICM disks obtained in PC runs 1, 2 and 3 in Table 6-5 corresponding to mold temperature of 40°C (a), 60°C (b) and 80°C (c). The contribution of thermal birefringence was included in the predicted birefringence (continued).
Figure 6-30 Measured (filled symbols) and predicted (open symbols) average transverse birefringence $<n_{s}\theta-n_{w}\theta>$ as a function of the radial position for PC runs 1, 2 and 3 (Table 6-5) corresponding to mold temperature of 40°C (a), 60°C (b) and 80°C (c).

6.2.4.3 The Effect of Melt Temperature

The effect of melt temperature on the gapwise distribution of birefringence, $\Delta n$, and average transverse birefringence, $<n_{s}\theta-n_{w}\theta>$, of ICM can be related to rheological behavior of polymer melts. Increasing the melt temperature decreases the viscosity of the polymer melt. A magnitude of the effect depends on the temperature sensitivity ($T_s$) or activation energy of the polymer.

The predicted and measured gapwise distributions of the flow birefringence, $\Delta n^f$, in PC ICM at a mold temperature of 60°C at various radial positions at the end of cooling stage for run 4, 2 and 5 are shown in Figure 6-31 (a), Figure 6-27 (b) and Figure 6-31 (b) corresponding to melt temperature of 240°C, 260°C and 280°C, respectively. The
distribution of birefringence is very sensitive to the melt temperature and indicates higher outer peak values at lower melt temperature with much less effect on the inner peak values. As aforementioned, the outer peak is due to the deformation during the injection and compression stages and the subsequent relaxation of molecular orientation in the intermediate region and frozen-in orientation near the surface. This flow-induced birefringence peak near the wall becomes smaller at higher melt temperature since melt experiences lower shear stress at given volume flow rate, and faster stress relaxation after the injection and compression stages. Increasing the melt temperature the thermally-induced birefringence increased. Even though at a temperature well above $T_g$ the stress and birefringence relax very fast [1], above 240 °C, the contribution of the thermally-induced birefringence of PC was relatively important compared to that of the flow-induced birefringence differing from the contribution of the thermally-induced birefringence of PS, as shown in the previous section.
Figure 6-31 Measured (symbols) and predicted (lines) residual flow-induced birefringence $\Delta n^f$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks obtained in PC runs 4 and 5 in Table 6-5 corresponding to melt temperature of 240 °C (a) and 280 °C (b). The contribution of thermal birefringence was not included in the predicted birefringence.
By adding the residual thermally-induced birefringence to the residual flow-induced birefringence, according to Eq. (3.100), the better predicted total residual birefringence profiles at various radial positions was obtained qualitatively and quantitatively. These results are shown in Figure 6-29 (b), Figure 6-32 (a) and Figure 6-32 (b). It can be seen that increasing the melt temperature leads to a decrease of the flow-induced birefringence. The gapwise distribution of birefringence at a melt temperature of 280°C follows similar trends as those at melt temperatures of 240°C and 260°C. However, the magnitude of the total birefringence is reduced because of faster stress relaxation at higher temperature. Compared with the effect of mold temperature the change of the melt temperature has a larger effect on the gapwise flow-induced birefringence, due to high temperature sensitivity of PC melt viscosity.

As clearly indicated in Figure 6-29 (b), Figure 6-32 (a) and Figure 6-32 (b), as the melt temperature increases, the birefringence decreases especially near the wall region. The reason for this effect is that the frozen layer gets thinner and time available for stress relaxation gets longer as melt temperature increases. Compared with the melt temperature of 240°C, the birefringence decreases significantly as the melt temperature increase to 260°C due to the increase of stress relaxation. The gapwise distributions of the flow induced birefringence at different radial locations at the end of cooling for a melt temperature of 280°C follow similar trends of those for melt temperatures of 240°C and 260°C. Birefringence proportionally reduced with decreasing melt temperature. Similar to the effect of mold temperatures, a global birefringence maximum appears near the mold surface during the injection and switchover time. At the end of cooling, the birefringence at the core region completely relaxes. A maximum is observed about
$z/b = \pm 0.7-0.9$ near the surface. It is caused by the frozen–in chain orientation in the injection and compression stages and slower relaxation in the cooling stage. The maximum in the solidified layers has also decreased significantly with increasing the melt temperature.

On the other hand, the disadvantage of higher melt temperature is that the injection-compression cycle time gets longer, thereby resulting in the poor productivity. In this regard, among a variety of the processing conditions the melt temperature of the ICM is a crucial factor to decide what is more important the quality on ICM parts and the productivity.

In general, the simulation tends to underestimate the gapwise distribution of total residual birefringence. In particular, it is found that some differences between experimental and predicted birefringence are evident in the region between the location of maximum of $\Delta n$ and the center. Regardless, the predicted overall total values of $\Delta n$ are qualitatively in agreement with experimental results.

The average transverse birefringence, $<n_r - n_{s0}>$, as a function of radius at melt temperatures of 240 °C, 260 °C and 280 °C and a mold temperature of 60 °C is shown in Figure 6-33. As the melt temperature increases from 240 °C to 280 °C, the average transverse birefringence decreases significantly due to more stress relaxation at higher melt temperature. This birefringence also decreases in the radial direction [90,142]. Theoretical and experimental data on $<n_r - n_{s0}>$ of the present study are in contrast with experimental data reported by Chen et al. [10] indicating a minimum birefringence at some radial distances. The simulation and experimental results of the average transverse birefringence at all radial positions with melt temperatures of 240 °C, 260 °C
Figure 6-32 Measured (symbols) and predicted (lines) total residual birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the ICM disks obtained in PC runs 4 and 5 in Table 6-5 corresponding to melt temperature of 240 °C (a) and 280 °C (b). The contribution of thermal birefringence was included in the predicted birefringence.
and 280 °C are in good agreement. Some variation between the experimental data and simulated results may be attributed to various causes, such as the neglect of contribution to birefringence of flow in a delivery system consisting of contraction and expansion region [76] especially near the gate and the neglect of the fountain flow. It is also possible a source of this discrepancy that the stress-optical coefficient might not be a constant as used in the numerical simulation of flow birefringence. Nevertheless, the overall magnitude of the simulation result is a qualitative agreement with the experimental data.

Figure 6-33 Measured (filled symbols) and predicted (open symbols) average transverse birefringence $<n_{ss} - n_{θθ}>$ as a function of the radial position for PC runs 2, 4 and 5 (Table 6-5) corresponding to melt temperature of 240 °C, 260 °C and 280 °C.
6.2.4.4 The Effect of Compression Stroke

The ICM combining CIM and compression molding has been developed to incorporate the advantage of both molding processes. Despite of the advantages associated with this molding technique, it has introduced new processing parameters such as compression speed, compression stroke and switchover time. Therefore, it is of great importance to find effects of the compression stroke on the total birefringence in the molded parts. For this purpose, the compression stroke is considered as a parameter to affect the gapwise distribution of birefringence. During the injection stage, the melt is injected into a cavity of thickness which is initially larger by 1.0 to 2.0 mm than the final thickness of molding.

Figure 6-34 (a), Figure 6-29 (b) and Figure 6-34 (b) show the predicted and measured gapwise distributions of the total birefringence, $\Delta n$, at a mold temperature 60 $^\circ$C at various radial positions at the end of cooling stage for runs 6, 2 and 7 corresponding to at compression strokes of 1 mm, 1.5 mm and 2 mm, respectively.

Compared with a compression stroke of 1 mm, the birefringence decreases as the compression stroke increase to 1.5 mm because the resistance of polymer melt to flow under large compression stroke is less resulting in low pressure and lower birefringence value. The gapwise distributions of the total birefringence at different radial locations at the end of cooling for a compression stroke of 2 mm follow similar trends as those for compression strokes of 1 mm and 1.5 mm. The magnitude of birefringence proportionally reduced with an increase of the compression stroke. A maximum peak of birefringence appears near the surface as result of the frozen-in birefringence developed during the filling and switchover time and slow relaxation in the cooling stage. Its magnitude
depends on the compression strokes. In particular, the compression stroke of 1 mm showed higher global maximum birefringence than that of 2 mm. However, it should be noted that there is slight difference in birefringence between the compression strokes of 1 mm and 1.5 mm. This is due to the difference in switchover time. At longer switchover time more stress relaxation takes place. As the switchover time of 1.2 s was used for a compression stroke of 1 mm, the longer time for stress relaxation caused the lower global maximum birefringence compared with that at compression stroke of 1.5 mm with a switchover time of 1 s. At the end of cooling, the birefringence at the core region completely relaxes. The maximum has decreased with increasing the compression stroke.

From these results, one can conclude that as more cavity opening during the injection stage reduces the flow-induced stresses, resulting in smaller birefringence and the birefringence decrease with the radius increasing since thicker initial cavity lowers the velocity gradient and pressure during the injection stage.

The average transverse birefringence, \(< n_{ss} - n_{\theta\theta} >\), as a function of radius at compression strokes of 1 mm, 1.5 mm and 2 mm and a melt temperature of 260 °C and a mold temperature of 60 °C is shown in Figure 6-35. As the compression stroke increases from 1 mm to 2 mm, the average transverse birefringence, \(< n_{ss} - n_{\theta\theta} >\), decreases significantly because the polymer melt flows easier under large compression stroke resulting in low average transverse birefringence, \(< n_{ss} - n_{\theta\theta} >\), and birefringence, \(\Delta n\). This birefringence also decreases in the radial direction [90,142]. Theoretical and experimental data on \(< n_{ss} - n_{\theta\theta} >\) of the present study are in contrast with experimental data reported by Chen et al. [10] indicating a minimum birefringence at some radial
distances. The simulation and experimental results of the average transverse birefringence at all radial positions with compression stroke of 1 mm, 1.5 mm and 2 mm are in qualitative agreement. Some variation between the experimental data and simulated results may be attributed to various causes, such as the neglection of contribution to birefringence due to the flow in a delivery system consisting of contraction and expansion region [76] especially near the gate and neglection of the fountain flow.
Figure 6-34 Measured (symbols) and predicted (lines) total residual birefringence $\Delta n$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the PC ICM disks obtained in run 6 and 7 (Table 6-5) corresponding to the compression stroke of 1 mm (a) and 2 mm (b). The contribution of thermal birefringence was included in the predicted birefringence.
6.2.4.5 The Effect of Switchover Time

The switchover time in ICM process is also of great importance to the flow-induced birefringence. The switchover time means the response time delay for switching the injection-compression machine to the compression mode. Due to the limitation of control system, the switchover time in this work varied from 0.9 to 1.1 s.

Figure 6-26 shows the predicted gapwise residual flow birefringence $\Delta n$ distribution at various radial positions in PC ICM disks obtained in run 2 listed in Table 6-5. This data were directly compared with Figure 6-36 indicating result for the case of the ICM without the switchover time at a volume flow rate of 23 cm$^3$/s, a compression stroke of 0.15 cm and a compression speed of 0.4 cm/s. Figure 6-36 and Figure 6-26 are the simulated results for the switchover time is 0 s and 1 s, respectively.
During the switchover time, two competitive effects occur. They are stress relaxation in absence of flow along with cooling effect due to the heat transfer from the cold wall. Which effect is dominating during the switchover time totally depends on the duration of the switchover time. At the short switchover time relaxation effect is dominating over cooling leading to the final contribution to birefringence, because shorter switchover time induces less pressure and stress relaxation. On the other hand, at long switchover time of 1.1 s used in this work, the cooling is dominating effect in the contribution to birefringence, because cooling process takes place during this switchover time. Due to low temperature along the gapwise direction by the cooling effect, the flow-induced birefringence near the mold surface becomes higher due to higher stresses at the given compression speed and slower stress relaxation during the compression stage.

The simulated result in this work suggests that the switchover time is an important parameter for PC material. During the switchover time, the cooling process takes place faster than during the injection stage because the polymer melt is hot under flow with viscous heating. As result only stress relaxation occurs during the switchover time.

The simulation indicates the presence of a local minimum and a local maximum of the birefringence in Figure 6-36 at the switchover time of 0. When the switchover time was employed, this local maximum of $\Delta n$ is shifted further away from the outer wall and the global and local maximum birefringence is increased. This is due to the cooling effect causing the lower temperature along the gapwise direction leading to the increased viscosity of the polymer melts near the mold wall at nodes before the melt front at the end of injection. In turn, this leads to higher shear rate at the given compression speed resulting in higher shear stress.
Figure 6-36 Predicted residual flow-induced birefringence $\Delta n^f$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for the PC ICM disks without switchover time for run 2 (Table 6-5).

6.2.4.6 The Comparison between CIM and ICM

It is important to find effects of the compression stroke on the birefringence distribution $\Delta n$, and average transverse birefringence $\langle n_{ss} - n_{\theta\theta} \rangle$, in ICM parts. This is important in answering question how, when and whether to introduce the compression stage. Some experimental and simulation data will be presented here.

In contrast to ICM in CIM compression stage is absent. Therefore, it is also interesting to find the effect of the compression stage in ICM and difference that it introduces in comparison with CIM. In this regard, switchover time between injection and compression stages was intentionally avoided.
Figure 6-37 (a) shows the predicted gapwise residual flow birefringence, $\Delta n$, distribution at various radial positions at the end of cooling stage of CIM process without inclusion of the packing stage. This figure can directly be compared with Figure 6-37 (b) which depicts the corresponding result in the case of the ICM at the end of cooling stage without packing stage for the processing condition of PC run 2 listed in Table 6-5.

As seen from comparison of Figure 6-37 (a) and (b), birefringence is dramatically decreased in ICM, especially near the mold surface. In particular, the birefringence of the ICM increases and then decrease slightly with the increase of the radial position, whereas those of CIM continue to decrease significantly with the increase of the radial position. This trend in ICM and CIM is explained in detail by Kwon et al. [101]. The main reason for such a reduction of birefringence at a lower radius position of 2.948 cm compared with the radius of 3.704 cm is due to the fact that the velocity as well as the velocity gradient are proportionally increase with the radial position during the compression stage. In contrast in CIM, the velocity is proportionally decreased with the radial position.

From these results, one can conclude that the compression stage in the ICM certainly reduces the magnitude of the flow-induced birefringence most notably near the mold wall.
Figure 6-37 Predicted residual flow-induced birefringence $\Delta n^f$ distribution in the gapwise direction at various radial positions at the end of the cooling stage for CIM disks (a) and for ICM disks (b) for PC run 2 (Table 6-5) without switchover time and packing stage.
It is also interesting to find the difference in the average transverse birefringence in ICM and CIM moldings. The predicted and measured average transverse birefringence, \( <n_{ss} - n_{\theta\theta}> \) as a function of the radial direction for both CIM and ICM disks at the end of cooling is compared in Figure 6-38. In both cases this birefringence decreases in the radial direction [90,142]. It can be seen that the averaged transverse birefringence along the radial direction decreases with distance from the gate. The average transverse birefringence in the molding made by CIM is approximately twice as large as that made by ICM. Regardless, the overall predicted values of \( <n_{ss} - n_{\theta\theta}> \) are in qualitative agreement with the experimental results.

![Figure 6-38](image)

Figure 6-38 Measured (filled symbols) and predicted (open symbols) average transverse birefringence as a function of the radial position for PC run 2 (ICM) and run 8 (CIM) (Table 6-5).
6.3 Conclusion

A physical modeling and associated numerical analysis scheme were developed for two-dimensional flow in the ICM center-gated disk to predict the flow-induced residual birefringence and thermally induced birefringence and average transverse birefringence. Effects of various processing conditions on these birefringences were elucidated. The Control Volume/Finite Element/Finite Different (CV/FE/FD) numerical method was employed. The residual flow birefringence in the molded disk was calculated by considering the filling, compression, packing, and cooling stages of ICM by using a compressible nonlinear viscoelastic constitutive equation. To take into account the compressibility of polymeric melts, the Tait equation was introduced. The residual thermal birefringence in molded articles was calculated by using the viscoelastic and photoviscoelastic model [1,141,189] based on the free quenching approximation. Then, the total birefringence was calculated as a sum of the flow and thermal birefringence.

From the extensive simulation of the flow-induced birefringence for PS and PC, processing conditions affecting significantly birefringence were identified. The melt temperature, compression stroke and compression stage are the processing parameters that have strong effects on the birefringence and average transverse birefringence. As the melt temperature is increased the flow-induced residual birefringence and average transverse birefringence significantly decrease. The flow-induced residual birefringence and average transverse birefringence also decreases with an increase of the compression stroke but its effect is less than the effect of the melt temperature. In the ICM process without the switchover time and packing stage the maximum peak in the gapwise birefringence distribution significantly reduces compared to that in the CIM without the
packing stage. For the ICM with the switchover time of about 1 s, the flow-induced residual birefringence and average transverse birefringence are higher compared to those of ICM without a switchover time but they are lower compared to the CIM molding.

It was shown that the thermally-induced birefringence in the ICM process is mostly influenced by mold temperature. The residual thermally-induced birefringence in ICM molded parts was treated as that developed in freely quenched plates. The effect of melt temperature on residual thermally-induced birefringence is comparatively smaller than that of the mold temperature. The compression stroke and the compression stage did not make any effect on thermally-induced residual birefringence because the melt temperature and mold temperature are the same for the cases. The compression stage in the ICM process decreases the overall birefringence, but not on the thermally-induced residual birefringence. Therefore, one may conclude that ICM process is more useful for production of high quality optical parts than the CIM process.

It was found that the measured residual birefringence distribution showed a maximum near the outer wall of the mold and significant birefringence in the core region. Based on the experimental data of total residual birefringence and average transverse birefringence, the most important processing parameters that strongly influence the residual birefringence and average transverse birefringence in PS and PC ICM molding were the melt temperature and compression stroke. The processing parameter that exerted less influence on the residual birefringence and average transverse birefringence was the mold temperature.

The simulation results were compared with corresponding experimental data obtained at different processing conditions including variation of mold temperature, melt
temperature and compression stroke for PS and PC. Comparison with the experimental and theoretical results indicated that the theoretical results capture essential features of the gapwise flow birefringence, $\Delta n$, and average transverse birefringence, $<n_{zz} - n_{yy}>$, distributions.

The simulation showed that for PS, the birefringence caused by thermally induced stresses was negligible compared with the flow induced birefringence because the stress-optical coefficient of PS in the glassy state is much lower than that in the melt state, while for PC, the thermally induced birefringence had a similar magnitude as the flow induced birefringence. The simulation showed that the gapwise residual flow birefringence is zero at the core due to a fast relaxation of stresses at high temperatures. A peak near the mold surface appears as a result of the combination of frozen-in chain orientation in the injection and compression stages and slow relaxation in the cooling stage. The nonzero concave shape of the residual birefringence in the core predicted and observed in moldings was shown due to the residual thermal birefringence. The magnitude of average transverse birefringence in CIM moldings is twice higher than that of ICM moldings. The following parameters in order of significance on the predicted and observed values of birefringence are melt temperature, mold temperature and compression stroke. To the best of our knowledge, the present study is the first investigation where the issues related to theoretical calculations of the frozen-in thermal and flow birefringence in ICM molded disks are treated. Although the theory does not fully describe experimental observations, the present approach is a significant step toward understanding complicated phenomena.
CHAPTER VII

SIMULATION AND EXPERIMENTAL STUDY OF RESIDUAL BIREFRINGENCE IN FREELY QUENCHED MULTILAYER PLATES

7.1 Introduction

During polymer processing, the polymer undergoes simultaneous mechanical and thermal influences in the fluid, rubbery, and glassy states. These effects introduce orientation, residual stresses and shrinkage in the products which in turn affect the physical, optical and mechanical properties, dimensional stabilities and appearance of the finished products. The frozen orientation manifests itself in the frozen-in birefringence phenomenon. Such induced residual stresses and birefringence in CIM, ICM and co-injection molding products can be attributed to two main sources. One is the flow-induced residual stresses including shear and normal stresses in nonisothermal flow. The other is the thermally induced residual stresses induced during the nonisothermal cooling process and inhomogeneous densitification [67,93,111,131,134,143,154]. It is desirable to predict and investigate the flow-induced and thermally-induced residual stresses and birefringence in the products obtained at different processing conditions.

The residual birefringence coming from the cooling process, namely, thermal birefringence, is not a linear function of the thermal stress, since the stress-optical or strain-optical coefficient shows photo-viscoelastic behavior and becomes a function of both time and temperature in the glass-to-rubber transition zone. Therefore, the memory
effect in the optical behavior of the polymer becomes significant and a photo-viscoelastic relation should be utilized in correlating the thermal birefringence with thermal stresses [124,172,189-191]. However, very little work is available in existing literature concerning this aspect.

Osaki and coworkers [192-195] performed the dynamic and stress relaxation measurements for PS and PC over the temperature range of 90-115 °C for PS and of 142-156 °C for PC. In the analysis of the data, they utilized a so-called modified stress-optical rule earlier developed by Read [196]. For PS, the master curves of the Young’s relaxation modulus at the reference temperature of 100 °C, as well as the strain-optical coefficient at the reference temperature of 115 °C were obtained. Shyu and Isayev [1] carried out the stress relaxation measurement over the temperature range of 22-123 °C for PS and 22-153 °C for PC to obtain the master curve of the strain-optical coefficient, the time dependent stress-optical coefficients and the shift factor of the strain-optical coefficient for both PS and PC.

The factors governing the development of thermal residual stresses and birefringence during the polymer processing have received much attention from many researchers over the years [76,124,126,127,133,134,141,197-203]. Isayev [76] and Isayev and Crouthamel [134] gave good reviews on the relevant theoretical works about the thermal stresses and birefringence in quenched amorphous polymers. The theories that have been tried up to now can be classified into two categories. One is based on the instant-freezing assumption [76,123,126,127,134,162,163,198,199,201]. The other is based on the viscoelastic relaxation assumption affected by rapid cooling [76,124,129,133,134,166,176,203-209]. Therefore, the thermal histories and viscoelastic
effects should be taken into account when the thermal stresses and birefringence of the final products are calculated. Also, thermal equilibrium is seldom attained in the polymer processing because of the existing temperature gradient and the rapid temperature change. Consequently, the nonequilibrium free volume should also be included in the Williams-Landel-Ferry (WLF) equation based on the free-volume approach [210]. In addition, the time-dependent volume relaxation [211,212] should be taken into account.

The present chapter presents measurement of the gapwise distribution of thermally-induced residual birefringence $\Delta n$ in free quenched multilayer plates of PS-PC-PS, PC-PS-PC, PS-PMMA-PS, PMMA-PS-PMMA, PMMA-PC-PMMA and PC-PMMA-PC. Furthermore, the simulations of the gapwise distribution of thermally-induced residual birefringence $\Delta n$ in freely quenched multilayer plates of PS-PC-PS and PC-PS-PC were carried out. The objective of the experiments and simulations was to elucidate the contribution of thermally induced birefringence on sequential co-injection moldings. For the simulation of the quenching experiment, as presented in Chapter IV, two models based on the viscoelasticity and photoviscoelasticity, accounting for the time and temperature dependence of mechanical and optical properties with the volume relaxation are considered. The volume relaxation is based on the first-order rate equation [141]. To verify the modeling, free quenching experiments was performed on thin multilayered plates with the six combinations using PS, PC and PMMA. The birefringence distributions along the thickness direction ($z$) of the plates were measured. The obtained data are compared with the results of a numerical simulation based on the viscoelasticity and photoviscoelasticity with volume relaxation included. Finally, the verified simulation
result will be incorporated in the modeling of coinjection molding process in Chapter VIII to determine the frozen-in birefringence in manufactured plastic articles.

7.2 Experimental

Free quenching experiments were carried out for multi-layered plates consisted of a variety of material combinations under quenching conditions, as listed in Table 7-1. In the quenching experiments thin plates of polystyrene (Styron 615-APR, Dow Chemical Co.), polycarbonate (PC123, General Electrical Co.) and polymethyl methacrylate (Perspex CP-51, INEOS Acrylics) were used to make multi-layered plates. The chemical structure of each polymer used in the free quenching experiment is shown in Figure 7-1.

Initial temperatures of 150, 160, 170 and 180 °C were employed for material combinations of PS-PC-PS, PC-PS-PC, PMMA-PC-PMMA and PC-PMMA-PC, and 110, 130, 150 and 170 °C for material combinations of PS-PMMA-PS and PMMA-PS-PMMA. A quenching temperature of 25 °C is used for all material combinations.

Large subplates of dimension 12×10×0.15 cm³ were made by compression molding at 185 °C for PS, 190 °C for PMMA and 225 °C for PC, followed by slow cooling for approximately 10 hr inside the compression molding to obtain stress-free subplates. These large subplates were selected based on the material combination used in this research and were stacked together to make multi-layered plate with a multi-layered structure in the rectangular mold with dimension 12×10×0.45 cm³. To attach stacked subplates in the mold, the mold put into vacuum oven for 45 min at a temperature of 225 °C for the PC and 210 °C for the PS or PMMA plates followed by slow cooling again.
These large multi-layered plates were then cut into small multi-layered plates of dimension $5 \times 5 \times 0.45$ cm$^3$ for quenching experiment. Before free quenching experiment, the birefringence measurement for one of the small multilayered plates was carried out showing that the birefringence of it was negligible (of the order of $10^{-7}$). For quenching in silicon oil, the sample were put in a larger beaker filled with silicon oil at the specified initial temperature for time of 5, 8, 15 and 90 min at 180, 170, 160 and 150 °C, respectively, for PS-PC-PS, PC-PS-PC, PMMA-PC-PMMA and PC-PMMA-PC, and 5, 15, 30 and 60 min for 170, 150, 130 and 110 °C, respectively, for PS-PMMA-PS and PMMA-PS-PMMA in order to attain thermodynamic equilibrium. The sample was then taken out of the beaker and immediately quenched in water at 25 °C.

Based on the magnitude of thermally induced birefringence of individual plate consisting of the multilayer plate, strips of width of 0.2 cm for PS-PC-PS and PC-PS-PC plates and strips of widths of 0.2 cm and 0.4 cm for PC or PS and for PMMA, respectively, for PMMA-PC-PMMA, PC-PMMA-PC, PS-PMMA-PS and PMMA-PS-PMMA plates were cut from the quenched plates by a low speed diamond saw (ISOMET low speed saw/BUECHLER). The birefringence distribution along the thickness direction was then measured by a polarizing microscope (Leitz Laborlux 12 POL/LEITZ WETZLAR) with a compensator (4th or 30th order, 1592K/LEITZ WETZLAR) within two to three days after quenching. Figure 7-2 shows the schematic diagram of the experimental procedure.
Figure 7-1 Chemical structures of PS, PC and PMMA
Table 7-1 Material Combinations and Quenching Conditions of the Free Quenching Experiments.

<table>
<thead>
<tr>
<th>Material combination</th>
<th>Initial Temperature</th>
<th>Quenching Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-PC-PS</td>
<td>Silicone oil</td>
<td>Water</td>
</tr>
<tr>
<td>PC-PS-PC</td>
<td>150 °C (90 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>160 °C (15 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>170 °C (8 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>180 °C (5 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td>PS-PMMA-PS</td>
<td>Silicone oil</td>
<td>Water</td>
</tr>
<tr>
<td>PMMA-PS-PMMA</td>
<td>110 °C (60 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>130 °C (30 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>150 °C (15 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>170 °C (5 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td>PMMA-PC-PMMA</td>
<td>Silicone oil</td>
<td>Water</td>
</tr>
<tr>
<td>PC-PMMMA-PC</td>
<td>150 °C (90 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>160 °C (15 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>170 °C (8 min)</td>
<td>25 °C</td>
</tr>
<tr>
<td></td>
<td>180 °C (5 min)</td>
<td>25 °C</td>
</tr>
</tbody>
</table>
**Figure 7-2 Free quenching experiments**

- Silicon oil
- Quenching
- Water
- Plate size: 5x5x0.45 cm³
- 0.45 cm
- Cut with a low speed diamond saw
- Sample thickness: 0.20-0.40 cm
- 0.20-0.40 cm
- Birefringence measurement by optical microscope with polarizer and compensator
7.3 Results and Discussion

The physical properties of PS and PC used in the numerical simulation are listed in Table 7-2. Young’s modulus $E$, strain-optical coefficient $C_\varepsilon$, stress-optical coefficient $C_\sigma$ functions with the corresponding shift factors, $\alpha_T$, used in the linear viscoelastic and photoviscoelastic constitutive equations. Their functions were obtained by Shyu [1,2] by performing tensile stress relaxation experiments. The master curves of Young’s relaxation modulus $E$, strain-optical coefficient $C_\varepsilon$, shift factors for Young’s modulus and strain-optical coefficient $\alpha_T$, and stress-optical coefficient $C_\sigma$ for PS are shown from Figure 7-3 to Figure 7-6, respectively. For PC these curves are shown from Figure 7-7 to Figure 7-10. The residual birefringence distribution in freely quenched samples measured two to three days after quenching are compared with the simulation results based on the viscoelasticity and photoviscoelasticity with volume relaxation (VPWV) model at time of $2 \times 10^5$ s after quenching. Since volume relaxation is considered in the VPWV model, aging which occurred during the two days following quenching is included in the simulation results.
Figure 7-3 Master curve of the Young’s relaxation modulus for PS at reference temperature of 97°C [2].

Figure 7-4 Master curve of the strain-optical coefficient for PS at reference temperature of 97°C [2].
Figure 7-5 Temperature dependence of the shift factors of $E$ and $C_\varepsilon$ for PS [2].

Figure 7-6 Master curve of the stress-optical coefficient for PS at reference temperature of 97°C [2].
Figure 7-7 Master curve of the Young's relaxation modulus for PC at reference temperature of $147.5^\circ$C [2].

Figure 7-8 Master curve of the strain-optical coefficient for PC at reference temperature of $147.5^\circ$C [2].
Figure 7-9 Temperature dependence of the shift factors of $E$ and $C_\varepsilon$ for PC [2].

Figure 7-10 Master curve of the stress-optical coefficient for PS at reference temperature of 97°C [2].
Table 7-2 Physical Properties of PS and PC Used in the Simulation.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PS</th>
<th>Ref.</th>
<th>PC</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta_i )</td>
<td>0.00021</td>
<td>[213]</td>
<td>0.0002</td>
<td>[198]</td>
</tr>
<tr>
<td>( \beta_T )</td>
<td>0.000066</td>
<td>[213]</td>
<td>0.00067</td>
<td>[198]</td>
</tr>
<tr>
<td>( \alpha ) \text{ (m}^2\text{/s)}</td>
<td>6.13\times10^{-8}</td>
<td>[213]</td>
<td>7.31\times10^{-8}</td>
<td>[213]</td>
</tr>
<tr>
<td>( h ) \text{ (J/s} \cdot \text{m}^2 \cdot \text{K)}</td>
<td>490</td>
<td>[2]</td>
<td>490</td>
<td>[2]</td>
</tr>
<tr>
<td>( \tau_r ) \text{ (s)}</td>
<td>0.04</td>
<td>[2]</td>
<td>0.3</td>
<td>[2]</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.33</td>
<td>[214]</td>
<td>0.41</td>
<td>[214]</td>
</tr>
<tr>
<td>WLF equation: ( C_1 )</td>
<td>10.6</td>
<td>[2]</td>
<td>8.82</td>
<td>[2]</td>
</tr>
<tr>
<td>( C_2 ) \text{ (K)}</td>
<td>57.0</td>
<td>[2]</td>
<td>40.2</td>
<td>[2]</td>
</tr>
<tr>
<td>( T_s ) \text{ (K)}</td>
<td>370.0</td>
<td>[2]</td>
<td>420.5</td>
<td>[2]</td>
</tr>
<tr>
<td>( T_r ) \text{ (K)}</td>
<td>370.0</td>
<td>[2]</td>
<td>420.5</td>
<td>[2]</td>
</tr>
</tbody>
</table>
7.3.1 PS-PC-PS Plates

In order to understand the complicated orientation phenomenon that develops during the co-injection molding process of polymers, a first step is to consider the frozen-in birefringence introduced by the fast cooling process itself. In particular, such a cooling process gives rise to thermal birefringence in multilayer plates. Experiments have shown that no birefringence appears when light is passed perpendicular to the thickness of the strip consisted of skin and core layers of sandwich structure, thus indicating that the values of birefringence in the other two planes are equal.

The measured and simulated thermally-induced residual birefringence distributions along the thickness direction of PS-PC-PS plates quenched in water at constant quenching temperature of 25°C from different initial temperatures are shown in Figure 7-11.

For PC core layer, the value of $C_σ$ is always positive of +5600 Brewsters from the tensile creep experiment, and +4800 to +5500 Brewsters from the shear creep experiment for the melt [190] and +100 Brewsters at room temperature [2]. Therefore, the birefringence of the PC core layer is always positive throughout the cross section because of the positive value of stress-optical coefficient $C_σ$ for the melt and at room temperature of PC as well as the tensile stresses in the PC core layer of quenched sample of PS-PC-PS plates. The thermally-induced birefringence of PC core layer increases with an increase of the initial temperature and always positive in this layer.

For PS skin layer at initial temperature below 160 °C, the birefringence is negative throughout the cross section. An increase in the initial temperature leads to its positive value at the surface and negative value at the interface. At an initial temperature
of 150 °C, no zero birefringence is observed in the PS skin layer. It is due to the fact that when the stresses in PS skin layer of quenched PS-PC-PS plates are compressive in the surface region and tensile in the core region, as shown in Figure 7-6 the stress-optical coefficient $C_{\sigma}$ of PS change from positive to negative after short elapsed time. For example, as shown in Figure 7-11, compressive stress near the surface and the positive stress-optical coefficient $C_{\sigma}$ of PS in quenched PS-PC-PS plates produces negative birefringence in the case of initial temperature of 150 °C. Moreover, compressive stress near the surface and the negative stress-optical coefficient $C_{\sigma}$ of PS after short quenching time produces negative birefringence for the case of above 160 °C. On the other hand, for the core region of PS skin layer, tensile stress and the negative stress-optical coefficient $C_{\sigma}$ of PS after long quenching time produces negative birefringence for all the cases as shown in Figure 7-11. Therefore, the sign for the stress-optical coefficient $C_{\sigma}$ of PS results in the sign reversal in the birefringence for the PS skin layer compared with the PC showing the positive values of $C_{\sigma}$ for the melt and at room temperature.

As the initial temperature increases further, zero birefringence appears near surface. The difference between birefringence distribution for the PC and PS layers can apparently be attributed in large part to the corresponding stress-optical coefficient $C_{\sigma}$ for each of these polymers. It is well known that the value of $C_{\sigma}$ for PS is time- and temperature-dependent and, negative and positive above and below $T_g$, respectively. Its value for the melt is -5200 Brewsters [2] and +10 Brewsters at room temperature [215].
The stress-optical behavior of polystyrene can be explained in the following way [216]. The birefringence of PS is mainly caused by the orientation of the phenyl groups and the polarizabilities of the phenyl group are very close to those for toluene. The polarizabilities of toluene are $15.64 \times 10^{-30}$ and $13.66 \times 10^{-30}$ m$^3$/molecule in the in-plane directions of the benzene ring, and $7.48 \times 10^{-30}$ m$^3$/molecule in the normal direction of the benzene ring [217]. Upon deformation in the glassy state, polymer chains cannot move around and the phenyl groups are tilted toward the stretching direction, resulting in a positive birefringence. In the rubbery state, polymer chains, to some extent, are able to move and tend to align along the stretching direction, rendering the plane of the phenyl groups to lie preferentially perpendicular to the stretching direction and, therefore, leading to a negative birefringence. In the above, only the contribution of tilting of phenyl groups to the positive birefringence in the glassy state was considered. However, other factors influencing the birefringence in the glassy state should also be mentioned. Pick and Lovell [218] showed that the anisotropic local electric field effect resulting from change in interchain spacing in directions perpendicular to and parallel to the extension direction always gives rise to negative birefringence and should be the underlying reason for the observed negative birefringence of PMMA in the glassy state. For PS the effect of anisotropic local electrical field effect is smaller than that of tilted phenyl groups since the birefringence is positive in the glassy state.

In the simulation no single volume relaxation time can give overall satisfactory predictions of the residual birefringence in freely quenched PS and PC plates [2]. Simulation results based on relaxation times $\tau_v$ of 0.04 s at 97 °C for PS and 0.3 s at 147.5 °C for PC for volume relaxation process were obtained. It was found to fit all
measured residual birefringence well [2]. Heat transfer coefficient that best fit the experimental results was 490 J/s·m²·K for quenching in water [2].

It should be noted that in the present case of symmetric quenching the birefringence profile is not balanced, that is \( \int_{-b}^{b} \Delta n dz \neq 0 \). The unbalance of birefringence is due to the fact that the stress-optical coefficient is not a constant, but a function of both time and temperature. The simulated result predicted by the VPWV model gives qualitatively comparable predictions.

The predicted residual stress distributions in PS-PC-PS material combination quenched in 25°C water from different initial temperatures are plotted in Figure 7-12. As shown in this figure, the residual stresses in the PC core region are always positive (tensile) and lower than that in PS skin region. For PS skin region, the residual stresses is positive (tensile) near the interface but they are negative (compressive) near the surface. Higher initial temperatures result in slightly higher absolute values of residual stresses both in the PC core and PS skin regions. However, as the initial temperatures are increased, the increase of residual stresses for PC core region is larger than that of PS skin region except for the surface layer. In general, the residual stresses change with initial temperatures for both regions is not very large. The fact that the effect of high initial temperatures on residual stresses was not significant is in agreement with earlier study [134]. The position of zero residual stress moves slightly toward the surface as the initial temperature increases.

To get a better understanding of how the residual stresses and birefringence are built up, the transient responses should be investigated. The evolution of actual and
effective temperatures for quenching of PS-PC-PS slab in 25°C water from \( T_0 \) of 170°C is shown in Figure 7-13. Above 145°C, volume relaxation of PC happens so fast that the effective temperature in the PC core region is virtually identical with the actual temperature. Volume relaxation of PS skin region is accelerated above 95°C and the effective temperature in PS skin region is virtually same as the actual temperature. Below 145°C, when the actual and effective temperatures for PC core region are compared, the difference becomes more and more prominent as the actual temperature drops down. For PS skin region, the difference between them become bigger and bigger as the actual temperature decreases. After 44 s after quenching, the gapwise distribution of the effective temperature in PC core region is uniform but in PS skin region the effective temperature is still decreased toward the surface. After 440 s after quenching, the effective temperatures in both PC core and PS skin regions are practically uniform and still decreases slowly with time, resulting in the aging phenomenon.
Figure 7-11 Residual birefringence distributions along the thickness direction in PS-PC-PS plates quenched in 25°C water from different initial temperatures.
Figure 7-12 Predicted residual stress distribution in PS-PC-PS plates quenched in 25°C water from different initial temperatures.
Figure 7-13 Predicted evolution of the actual (a) and effective (b) temperature profiles during quenching. Quenching conditions: $T_i=170^\circ C$, $T_\infty = 25^\circ C$
7.3.2 PC-PS-PC Plates

Figure 7-14 shows the measured and simulated residual birefringence distributions along the thickness direction of PC-PS-PC plates quenched in water at 25°C from different initial temperatures.

In contrast with the PS-PC-PS plates freely quenched from the high initial temperature, the residual birefringence in freely quenched PC-PS-PC plates is always negative throughout the PS core layer. This is because even though the stresses in quenched sample are tensile in the core region, the stress-optical coefficient $C_\sigma$ for the melt of PS is negative. Higher initial temperature leads to larger value of the birefringence. As one can see, no zero birefringence is observed in this layer.

For PC skin layer, the sign of birefringence changes from positive near the interface to negative at the surface. It is due to the fact that there is no sign reversal of the birefringence of PC because its stress-optical coefficient $C_\sigma$ for the melt and at room temperature of PC is positive. The stresses in quenched sample are compressive in the surface region and tensile in the core region of PC skin layer. The position of zero birefringence changes with the initial temperature in a peculiar way. At high initial temperature, it is close to the surface and moves toward the interface as the initial temperature decreases. The higher initial temperature results in higher absolute values of residual birefringence both in the surface and near the interface. Volume relaxation times $\tau_v$ and heat transfer coefficient used in the simulation are the same as in the case of PS-PC-PS.
The residual birefringence profile predicted by the VPWV model is in qualitative agreement with the experimental data.

Figure 7-14 Residual birefringence distributions along the thickness direction in PC-PS-PC plates quenched in 25°C water from different initial temperatures.
7.3.3 PS-PMMA-PS Plates

The residual birefringence distributions along the thickness direction of PS-PMMA-PS plates quenched in water at 25 °C from different initial temperatures are shown in Figure 7-15. The difference between birefringence distribution for the PMMA and PS layers can be attributed in large part to the corresponding stress-optical coefficient $C_\sigma$ for each of these polymers. It is well known that the value of $C_\sigma$ for PS is time- and temperature-dependent and, negative and positive above and below $T_g$, respectively, with the value of -5200 Brewsters for the melt [2] and +10 Brewsters at room temperature [215]. On the other hand, for PMMA the stress optical coefficient $C_\sigma$ changes sign from negative to positive at high temperature above the glass transition temperature [219-223].

Similar to the PS-PC-PS plates freely quenched from the high initial temperature, the residual birefringence distribution in freely quenched PS-PMMA-PS plates is always positive throughout PMMA core layer with its value being very low. It is due to the fact that the stresses in quenched sample are tensile in the core region with the positive sign of stress-optical coefficient of PMMA core layers for the melt in the PS-PMMA-PS plates. However, as the stress-optical coefficient of PC is much larger than that of PMMA, the birefringence of PMMA core layer in PS-PMMA-PS plates is more than one order magnitude smaller than that of PC core layer in PS-PC-PS. Higher initial temperature leads to larger value of the birefringence but the effect is not significant.

In PS skin layer the position of zero birefringence moves toward the surface with increasing initial temperature. For PS skin layer, the residual birefringence has negative
values near the interface and in the extensive region away from the interface of PS layer, and positive values at the surface, respectively. As shown for the case of PS skin layer in PS-PC-PS plates in Section 7.3.1, the sign for the stress-optical coefficient $C_\sigma$ of PS result in the sign reversal in the birefringence for the PS skin layer compared with the PMMA core layer showing no sign reversal by the tensile stress combined with positive values of $C_\sigma$ for the melt state of PMMA core layer. The position of zero birefringence changes with the initial temperature in a peculiar way. At high initial temperature, it is close to the surface and moves toward the interface as the initial temperature decreases. In regards to unequal areas of the positive and negative regions of PMMA core region and PS skin region, the difference between these areas is seen to increase with increasing initial temperature.

Moreover, significant difference of the magnitude of birefringence between PMMA and PS region is due to the fact that the stress optical coefficient of the PMMA is approximately one order magnitude lower than that of PS [224].
Figure 7-15 Residual birefringence distributions along the thickness direction in PS-PMMA-PS plates quenched in 25°C water from different initial temperatures.
7.3.4 PMMA-PS-PMMA Plates

Figure 7-16 shows the residual birefringence distributions along the thickness direction of PMMA-PS-PMMA plates quenched in water at 25°C from different initial temperatures. In contrast with the PS-PMMA-PS plates and similar to the PC-PS-PC plates freely quenched from the high initial temperature, the residual birefringence in freely quenched PMMA-PS-PMMA plates is always negative throughout the PS core layer with value being substantially higher compared with that of PMMA skin layer. This is because even though the stresses in quenched sample are tensile in the core region, the stress-optical coefficient $C_\sigma$ for the melt of PS is negative. Therefore, the magnitude and the pattern of the birefringence in PS core layer in PC-PS-PC plates and PMMA-PS-PMMA plates are similar to each other. Higher initial temperature leads to larger value of the birefringence. No zero birefringence is also observed in this layer.

For PMMA skin layer, the sign of birefringence changes from positive near the interface to negative at the surface with the position of zero birefringence slightly moving toward the surface with increasing initial temperature in PMMA skin layer. It is due to the fact that the sign of stress-optical coefficient of PMMA for the melt state and at room temperature is totally opposite to that of PS. However, as the stress-optical coefficient of PS is larger than that of PMMA, the birefringence of PMMA skin layer in PMMA-PS-PMMA plates is less than that of PS skin layer in PS-PC-PS plates.

It is noted that areas of the positive and negative regions for PMMA skin layer and PS core layer are not balanced. Moreover, the difference between areas of positive and negative birefringence of it increases at higher initial temperature. The value of $C_\sigma$
for PS is negative and positive above and below $T_g$, while that of PMMA is positive for the melt and negative at room temperature. The sign change of $C_\sigma$ for PMMA was discussed by Tsvetkov and Verkhotina [225] and Read [226]. According to Kock and Rehage [222], positive sign of birefringence of PMMA for the melt state is associated with a continuous transition from hindered rotation of free rotation of the ester side group. In other words, the optical anisotropy of a PMMA monomer unit is mainly caused by the ester side group. The contribution of the ester group to the optical anisotropy of a statistical segment depends on the orientation of the –COO- plane with respect to the axis of the segment. Calculations of the optical anisotropy by Tsvetkov and Verkhotina [225] and Read [226] based upon the additivity of bond polarizabilities show that the values of the optical anisotropy differ for different positions of the –COO- plane. In the case of a fixed trans-position where the –COO-plane is perpendicular to the axis of the segment the optical anisotropy of a monomer unit is negative. In the case of free rotation the calculations show that the optical anisotropy is positive. Free rotation means that there is no preferred position of the -COO-plane with respect to the axis of the segment. Thus a temperature dependent change of the mean position of the –COO-plane can explain the temperature dependence of the optical anisotropy as well as the change of the sign.

The stress-optical coefficient $C_\sigma$ of the PMMA is approximately one order magnitude of lower than that of PS. It can explain the enormous difference between birefringence distributions of the PMMA and PS layers, as shown in Figure 7-16.
Figure 7-16 Residual birefringence distributions along the thickness direction in PMMA-PS-PMMA plates quenched in 25°C water from different initial temperatures.
7.3.5 PMMA-PC-PMMA Plates

The residual birefringence distribution along the thickness direction of PMMA-PC-PMMA plates quenched in water at 25°C from different initial temperatures is shown in Figure 7-17.

It is well known that the value of $C_\sigma$ for PC has a positive value of +5600 Brewsters from the tensile creep experiment, and +4800 to +5500 Brewsters from the shear creep experiment for the melt [190] and +100 Brewsters at room temperature [2]. Similar to PC core layer in the PS-PC-PS plates freely quenched from the high initial temperature, the residual birefringence distribution of PC core layer in freely quenched PMMA-PC-PMMA plates is always positive throughout the layer with very high value compared with that of PMMA layer. Higher initial temperature leads to larger value of the birefringence.

However, opposite to the case of PS skin layer in PS-PC-PS plates, in PMMA skin layer of PMMA-PC-PMMA plates the sign of residual birefringence changes from positive on the interface to negative on the surface with the position of zero birefringence slightly moving toward the surface with increasing initial temperature in PMMA skin layer. It is due to the fact that the sign of stress-optical coefficient of PMMA in PMMA-PC-PMMA plates changes at high temperature above the glass transition temperature [219-223]. This trend is the opposite to the sign of stress-optical coefficient for the melt state and at room temperature of PS in PS-PC-PS plates. Therefore, the pattern of the birefringence distribution in PMMA skin layer of PMMA-PC-PMMA plates and in PS skin layer of PS-PC-PS plates is totally opposite to each other.
For the magnitude of birefringence of PC core and PMMA skin layer, the birefringence of PC core layer is more than one order magnitude larger than that of PMMA skin layer because the stress-optical coefficient of PC is much larger than that of PMMA. With the parabolic shape of birefringence of PMMA and PC layers and unequal areas of the positive and negative regions for PMMA-PC-PMMA plates, the difference between these areas is seen to increase with initial temperature.

Figure 7-17 Residual birefringence distributions along the thickness direction in PMMA-PC-PMMA plates quenched in 25°C water from different initial temperatures.
7.3.6 PC-PMMA-PC Plates

Figure 7-18 shows the residual birefringence distributions along the thickness direction of PC-PMMA-PC plates quenched in water at 25 °C from different initial temperatures.

The difference between birefringence distribution for the PMMA and PC layers can be attributed in large part to the corresponding stress-optical coefficient $C_\sigma$ for each of these polymers. It is well known that the stress-optical coefficient of $C_\sigma$ for PMMA is time- and temperature-dependent and changes sign from negative to positive at high temperature above the glass transition temperature [219-223]. On the other hand, the value of $C_\sigma$ for PC has a positive value of +5600 Brewsters from the tensile creep experiment, and +4800 to +5500 Brewsters from the shear creep experiment for the melt [190] and +100 Brewsters at room temperature [2].

Similar to the PC core layer in PS-PC-PS plates, the residual birefringence distribution of PMMA core layer in PC-PMMA-PC plates is always positive throughout PMMA core layer with its value being very low compared to PC skin layer in PC-PMMA-PC plates. It is due to the fact that combining the tensile stresses in the core layer of quenched sample the positive sign of stress-optical coefficient of PMMA for the melt in the PC-PMMA-PC plates is the same sign of stress-optical coefficient of PC for the melt in the PS-PC-PS plates. However, as the stress-optical coefficient of PMMA is much smaller than that of PC, the birefringence of PMMA core layer in PC-PMMA-PC plates is more than one order magnitude smaller than that of PC core layer in PS-PC-PS. Higher
initial temperature leads to larger value of the birefringence but the effect is not significant.

The sign of birefringence of PC skin layer changes from positive near the interface to negative at the surface with the position of zero birefringence moving toward the surface with increasing initial temperature from the interface in PC skin layer. It is due to the fact that the stress-optical coefficient $C_\sigma$ of PC for the melt and at room temperature is positive and the stresses in quenched sample are compressive in the surface region and tensile in the core region of PC skin layer. The position of zero birefringence between positive birefringence near the interface and negative birefringence near the surface changes with the initial temperature in a peculiar way. The position moves closer to the surface with an increase in the initial temperature. The higher initial temperature results in higher absolute values of residual birefringence both in the surface and near the interface. The stress optical coefficient $C_\sigma$ of PMMA is much smaller than those of PC. This can explain why there is tremendous difference between birefringence values of the PMMA and PS layers, as shown in Figure 7-18.
Figure 7-18 Residual birefringence distributions along the thickness direction in PC-PMMA-PC plates quenched in 25°C water from different initial temperatures.
7.4 Conclusions

Methodology was developed to calculate the thermal residual birefringence for the material combination of PS-PC-PS and PC-PS-PC based on the measured mechanical and optical relaxation functions of PS and PC from the reference by Shyu et al. [1].

Free quenching experiments from the different initial temperatures into the water of 25 °C were carried out on three layers slabs including PS-PC-PS, PC-PS-PC, PMMA-PC-PMMA, PC-PMMA-PC, PS-PMMA-PS and PMMA-PS-PMMA layers. The thermal residual birefringence distribution along the thickness direction of the multi-layered plates was measured.

For PC core domain of PS-PC-PS combination, the residual thermal birefringence is always positive with its value slightly increasing with the initial temperature. For PS skin domain, the residual thermal birefringence is negative throughout the PS layer at an initial temperature of 150 °C. Higher initial temperature leads to positive birefringence at the surface and negative at the interface.

For PS core domain of PC-PS-PC combination, the residual thermal birefringence is always negative with its value slightly increasing with the initial temperature. For PC skin domain, the thermal residual birefringence is negative near the surface and positive near the interface. The position of zero thermal residual birefringence is shifted toward the surface with an increase of the initial temperature.

For PMMA core domain of PS-PMMA-PS combination, the residual thermal birefringence is always positive with its values slightly increasing with the initial temperature. For PS skin domain, the residual birefringence has positive values at the
surface and negative values near the interface. With increase of the initial temperature the position of zero birefringence moves close to the surface.

For PS core domain of PMMA-PS-PMMA material combination, the residual thermal birefringence is always negative with its value being significantly higher compared with that of PMMA layer. Higher initial temperature leads to the larger absolute value of the birefringence. For PMMA skin domain, the thermal residual birefringence has negative value at the surface and positive values near the interface. The position of zero birefringence changes with the initial temperature in a peculiar way. With an increase of the initial temperature, it moves slightly closer to the surface.

For PC core domain of PMMA-PC-PMMA material combination, the residual thermal birefringence is always positive with its value being significantly higher compared with that of PMMA layer. Higher initial temperature leads to larger absolute value of the birefringence. For PMMA skin domain, the thermal residual birefringence has negative values at the surface and positive values near the interface. The position of zero birefringence changes with the initial temperature in a peculiar way. With an increase of the initial temperature, it moves slightly close to the surface.

For PMMA core domain of PC-PMMA-PC material combination the residual thermal birefringence is always positive with its value being low compared with that of PC layer. Higher initial temperature leads to slightly larger value of the birefringence in PMMA core layer. For PC skin domain, the thermal residual birefringence has negative values at the surface and positive values near the interface. The position of zero birefringence changes with the initial temperature in a peculiar way. With an increase of the initial temperature, it moves closer to the surface.
The birefringence data from the material combination of PS-PC-PS and PC-PS-PC were compared with the results of a numerical simulation based on the linear viscoelastic and photoviscoelastic constitutive equations and the first-order rate equation for volume relaxation. The effect of the initial temperature was evaluated. For the material combination of PS-PC-PS, as the initial temperature increases, the residual thermal birefringence of PC core layer increases. For PS skin domain, higher initial temperature leads to positive birefringence at the surface and negative at the interface. For the material combination of PC-PS-PC, as the initial temperature increases, the residual thermal birefringence of PS core layer increases. For PC skin domain, the residual thermal birefringence distribution shows positive value at the surface and negative value at the interface. As the initial temperature increases, the position of zero thermal residual birefringence is shifted toward the surface. These observations are in fair agreement with predicted data.
CHAPTER VIII
SIMULATION AND EXPERIMENTAL STUDY OF CO-INJECTION MOLDING OF AMORPHOUS POLYMERS

8.1 Introduction

In this chapter, a two-dimensional viscoelastic simulation of the flow- and thermal-induced birefringence developed during the filling, packing and cooling stages of the sequential co-injection molding of a center-gated disk by using hybrid finite element method (FEM) and finite difference method (FDM) was carried out. The physical modeling to predict interface development and skin/core distribution of multi-layer flow during multi-component molding, based on the kinematics and dynamics of interface evolution was developed in Chapter V. Experimental studies of the flow-rate controlled sequential injection molding were also carried out. The compressible nonlinear viscoelastic model for the filling and packing stages was used to calculate the flow stresses for skin and core melts. For the flow birefringence, the linear stress-optical rule [145] was used. To calculate the thermal stresses and the thermal birefringence, the linear viscoelasticity and photoviscoelasticity [1,141] for multilayer plates developed in Chapter IV were employed. Although the coupling effects between the flow birefringence and thermal birefringence were neglected in calculations of the total birefringence, the present study shows that the thermal birefringence contribution is significant. The PVT equation [151] by Tait was employed to calculate flow during the packing stage.

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8.2 Experiments and Simulation

To carry out the study on experiments and simulation, it was necessary to choose material pairs based on their rheological properties.

8.2.1 Materials and Their Characterization

Three different polymers in Table 8-1 were used in the experiments: polystyrene (Styron 615-APR), polycarbonate (PC123) and polymethyl methacrylate (Perspex CP-51). These thermoplastics were supplied by Dow Chemical Company, General Electrical Company and INEOS Acrylics, respectively. In Table 8-2, the material combinations used in the experiments are summarized. Throughout this study the core material is written first. The shear viscosity ratio at $\dot{\gamma}=0$ s$^{-1}$ and at $\dot{\gamma}=10^2$ s$^{-1}$ are also given. The thermal properties of these materials are assumed to be constant and independent of temperature. The densities of melts in the filling stage are also taken to be constant. The physical properties of polymers are listed in Table 6-1.

Figure 8-1 through Figure 8-3 show the experimental and fitted shear-rate dependent viscosity at different temperatures for PS, PC and PMMA, respectively. The experimental viscosity data of PS 615 at temperature of 160, 180, 200$^\circ$C over a wide range of shear rate were taken from Lee [186]. The rheological characterization of PC and PMMA was performed at temperatures of 260, 273.3, 286.7 and 300$^\circ$C, and 204, 219, 234 and 249$^\circ$C, respectively, over a range of shear rates using an Advanced Capillary Rheometer (RH7). In order to determine the number of modes $N$, rheological parameter $s$, the viscosity $\eta_k$, and the relaxation time $\theta_k$ for each mode of the Leonov equation
which are required in the sequential co-injection molding process simulation, the six relaxation modes for PS, PC and PMMA were used. The viscosity data at different temperature were fitted by means of nonlinear regression fitting [185].

The lines in Figure 8-1 to Figure 8-3 represent the nonlinear regression fit of the experimental data (symbols) to Leonov model. The parameters obtained from the best fit are listed in Table 8-4 with the constants in the Arrhenius temperature-dependent equation. For the calculation of melt compressibility of each polymer melt, P-V-T equation of state by Tait [151] is used and its parameters taken from reference are listed in Table 8-5.

Table 8-1 Characteristics of Materials.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Source Grade</th>
<th>Zero shear viscosity at 230°C [Pa·s]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Dow Chemical Co. STYRON 615APR</td>
<td>4.00×10^2</td>
</tr>
<tr>
<td>PC</td>
<td>General Electrical Co. PC123</td>
<td>46.95×10^2</td>
</tr>
<tr>
<td>PMMA</td>
<td>INEOS Acrylics CP-51</td>
<td>14.75×10^2</td>
</tr>
</tbody>
</table>

*Zero shear viscosities at 230°C were obtained from extrapolation of fitted data.
Table 8-2 Material Combinations.

<table>
<thead>
<tr>
<th>System (Core/Skin)</th>
<th>Zero shear viscosity ratio ($R^*$)</th>
<th>Viscosity ratio at $\dot{\gamma}=10^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/PS</td>
<td>11.74</td>
<td>16.46</td>
</tr>
<tr>
<td>PMMA/PS</td>
<td>3.69</td>
<td>4.81</td>
</tr>
<tr>
<td>PC/PMMA</td>
<td>3.18</td>
<td>3.42</td>
</tr>
</tbody>
</table>

$*R=\frac{\eta_{core}}{\eta_{skin}}.$

Table 8-3 Physical Properties of Polymers.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PS</th>
<th>PC</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho^0 \times 10^3$ (Kg/m$^3$)*</td>
<td>1.04 [186]</td>
<td>1.16 [187]</td>
<td>1.16 [184]</td>
</tr>
<tr>
<td>$\rho \times 10^3$ (Kg/m$^3$)*</td>
<td>0.984 [186]</td>
<td>1.06 [187]</td>
<td>1.06 [184]</td>
</tr>
<tr>
<td>$C_p$ (J/Kg $\cdot$ K)</td>
<td>1420 [186]</td>
<td>2150 [187]</td>
<td>2363 [184]</td>
</tr>
<tr>
<td>$k$ (W/m $\cdot$ K)</td>
<td>0.17 [186]</td>
<td>0.234 [187]</td>
<td>0.23 [184]</td>
</tr>
</tbody>
</table>

$*\rho^0$ at T=25 $^\circ$C and $\rho$ at T=180 $^\circ$C.
Figure 8-1 Measured (symbols) and fitted (curves) shear rate dependence of the viscosity for PS. Experimental data were taken from [186]. Six modes were used in fitting.
Figure 8-2 Measured (symbols) and fitted (curves) shear rate dependence of the viscosity for PC. Six modes were used in fitting.
Figure 8-3 Measured (symbols) and fitted (curves) shear rate dependence of the viscosity for PMMA. Six modes were used in fitting.
Table 8-4 Material Constants of PS, PC and PMMA Used in the Sequential Injection Molding Simulation.

<table>
<thead>
<tr>
<th>Material constants</th>
<th>PS</th>
<th>PC</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Arrhenius-type equation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_b$ (K)</td>
<td>16593</td>
<td>11593</td>
<td>16900</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>434.15</td>
<td>533.15</td>
<td>462.15</td>
</tr>
<tr>
<td><strong>Leonov model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s$</td>
<td>0.002</td>
<td>0.001</td>
<td>0.0001</td>
</tr>
<tr>
<td>$A_1$ (Pa·s)</td>
<td>$2.634 \times 10^{-13}$</td>
<td>$1.221 \times 10^{-8}$</td>
<td>$1.174 \times 10^{-12}$</td>
</tr>
<tr>
<td>$A_2$ (Pa·s)</td>
<td>$9.372 \times 10^{-13}$</td>
<td>$3.481 \times 10^{-10}$</td>
<td>$2.471 \times 10^{-12}$</td>
</tr>
<tr>
<td>$A_3$ (Pa·s)</td>
<td>$6.291 \times 10^{-13}$</td>
<td>$1.452 \times 10^{-7}$</td>
<td>$1.534 \times 10^{-14}$</td>
</tr>
<tr>
<td>$A_4$ (Pa·s)</td>
<td>$4.297 \times 10^{-14}$</td>
<td>$2.787 \times 10^{-7}$</td>
<td>$9.437 \times 10^{-14}$</td>
</tr>
<tr>
<td>$A_5$ (Pa·s)</td>
<td>$2.709 \times 10^{-14}$</td>
<td>$2.472 \times 10^{-8}$</td>
<td>$2.602 \times 10^{-14}$</td>
</tr>
<tr>
<td>$A_6$ (Pa·s)</td>
<td>$2.564 \times 10^{-17}$</td>
<td>$2.472 \times 10^{-8}$</td>
<td>$3.409 \times 10^{-14}$</td>
</tr>
<tr>
<td>$B_1$ (s)</td>
<td>$2.308 \times 10^{-15}$</td>
<td>$3.602 \times 10^{-10}$</td>
<td>$1.577 \times 10^{-16}$</td>
</tr>
<tr>
<td>$B_2$ (s)</td>
<td>$1.794 \times 10^{-16}$</td>
<td>$3.772 \times 10^{-11}$</td>
<td>$1.500 \times 10^{-17}$</td>
</tr>
<tr>
<td>$B_3$ (s)</td>
<td>$1.395 \times 10^{-17}$</td>
<td>$3.950 \times 10^{-12}$</td>
<td>$1.858 \times 10^{-18}$</td>
</tr>
<tr>
<td>$B_4$ (s)</td>
<td>$1.085 \times 10^{-18}$</td>
<td>$4.136 \times 10^{-13}$</td>
<td>$5.614 \times 10^{-19}$</td>
</tr>
<tr>
<td>$B_5$ (s)</td>
<td>$8.433 \times 10^{-20}$</td>
<td>$4.331 \times 10^{-14}$</td>
<td>$1.117 \times 10^{-19}$</td>
</tr>
<tr>
<td>$B_6$ (s)</td>
<td>$6.557 \times 10^{-21}$</td>
<td>$4.535 \times 10^{-15}$</td>
<td>$4.980 \times 10^{-20}$</td>
</tr>
</tbody>
</table>

| **Stress-optical coefficient in melt state** |               |               |                |
| $C_\sigma^\theta$ (Pa$^{-1}$) | $-5.2 \times 10^9$ [2] | $5.6 \times 10^9$ [2] | $1.0 \times 10^{10}$ [223] |
Table 8-5 Material Constants in Tait Equation.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_{1,i}$ (m³/Kg)</td>
<td>970.8</td>
<td>862.8</td>
<td>862.07</td>
</tr>
<tr>
<td>$b_{2,i}$ (m³/Kg·K)</td>
<td>0.5788</td>
<td>0.549</td>
<td>0.600</td>
</tr>
<tr>
<td>$b_{3,i}$ (Pa)</td>
<td>$1.555\times10^8$</td>
<td>$1.565\times10^8$</td>
<td>$2.042\times10^8$</td>
</tr>
<tr>
<td>$b_{4,i}$ (K⁻¹)</td>
<td>$3.019\times10^{-3}$</td>
<td>$2.738\times10^{-3}$</td>
<td>$5.44\times10^{-3}$</td>
</tr>
<tr>
<td>$b_{5,i}$ (m³/Kg)</td>
<td>970.8</td>
<td>862.8</td>
<td>862.07</td>
</tr>
<tr>
<td>$b_{2,i}$ (m³/Kg·K)</td>
<td>0.2429</td>
<td>0.2229</td>
<td>0.2126</td>
</tr>
<tr>
<td>$b_{3,i}$ (Pa)</td>
<td>$2.008\times10^8$</td>
<td>$2.65\times10^8$</td>
<td>$2.73\times10^8$</td>
</tr>
<tr>
<td>$b_{4,i}$ (K⁻¹)</td>
<td>$1.38\times10^{-3}$</td>
<td>$2.78\times10^{-3}$</td>
<td>$4.289\times10^{-3}$</td>
</tr>
<tr>
<td>$b_5$ (K)</td>
<td>360.2</td>
<td>422.2</td>
<td>388.65</td>
</tr>
<tr>
<td>$b_6$ (K/Pa)</td>
<td>$3.20\times10^{-7}$</td>
<td>$5.00\times10^{-7}$</td>
<td>$2.27\times10^{-7}$</td>
</tr>
</tbody>
</table>
8.2.2 Sequential Injection Molding Experiments and Measurements of Birefringence and Interface Distribution

An experimental study has been performed in order to test the influence of processing parameters including the mold temperature, melt temperature and volume ratio between the two polymer melts on the residual birefringence distribution and the interface distribution in a center-gated disk mold by the sequential injection molding. A sequential co-injection molding apparatus has been designed and constructed by the author. The experiment was carried out on Hull Hydraulic Transfer Molding Press to deliver the two polymer melts sequentially to the mold. A schematic drawing of ram-type sandwich injection molding apparatus used in this study is shown in Figure 8-4. The machine is a vertical type injection unit with mechanical clamping system actuated by hydraulic pressure. The diameter and thickness of the center-gated disk are 12.7 cm and 0.29 cm or 0.3175, respectively, as shown in Figure 8-5. The data acquisition system is connected to the sequential co-injection molding machine and records the pressure and the plunger position to measure the flow rate by means of linear velocity displacements transducer (LVDT). The pressure was monitored by one Dynisco PT435A pressure transducer mounted at center position of the mold. The sequential co-injection molding experiments were carried out the following manner. PS, PMMA and PC were respectively dried at 80 °C for PS and PMMA and 105 °C for PC for 4 hours under vacuum conditions. The exact amount of PS, PMMA and PC to fill the delivery system and cavity are used. Chips were made by compression molding under the temperature of 200 °C for PS and PMMA and 230 °C for PC, respectively.
By placing the chips into the cylinder of injection-compression molding, the ICM experiments were conducted under different processing conditions with varying mold temperatures, melt temperatures, the volume of first-injected skin melt, mold thickness and material properties.

Table 8-6 lists the material combinations and various processing parameters used in this study. Experiments were carried out for all runs except for Run #1. In addition, simulations were carried out for all runs. As shown in Table 8-6, the processing temperatures were chosen to avoid the solidification of PS and PMMA during injection thereby minimizing possibility of a short shot.

Experiments and simulation of sandwich molded parts and flow visualization investigations of the sequential co-injection molding process show that it is sensitive to differences in the rheological properties of the skin and core melts. In sequential co-injection molding the equality of normal and shear stresses on both sides of an interface during filling stage should be satisfied. The normal stress is generally dominated by pressure, whose gradient along the flow direction is proportional to the viscosity. Difference in the pressure gradients induced by different viscosities of skin and core melts causes the interface deformation during sequential co-injection molding. The core melt injected enters from the gate into the central part of the cavity away from the walls. It generally takes the path of least resistance to penetrate the skin displacing skin melt at the hot core to completely fill the cavity. For both skin and core melts to flow and fill the mold together, the equality of normal stress or pressure between skin and core melts must be consistent. This is only possible if the skin melt has a lower viscosity than the core melt. If the first melt has a much higher viscosity, its flow rate in response to a pressure
gradient will be low and the second melt with low viscosity will move fast to penetrate the skin further and fill the entire mold resulted in breakthrough phenomena. Therefore, if skin-core sandwich structured parts are to be produced to measure the residual birefringence of skin and core layers, the first skin melt injected must possess a lower viscosity than the second core melt.

When the skin melt (PC) possesses much higher viscosity than the core melt (PS or PMMA) or PMMA as a skin melt possess much higher viscosity than the core melt (PS), the flow front of the core material overtakes that of the skin melt, and the breakthrough phenomenon occurs, and consequently a defective part appears. Therefore, the material combinations showing the breakthrough phenomenon were not chosen since the measurement of the residual birefringence was needed. The material combinations were selected based on these arguments and are shown in Table 8-6.

Strips of width of 0.1 cm for PS-PC-PS plate and strips of widths of 0.1 cm and 0.3 cm for PMMA-PC-PMMA and PS-PMMA-PS plates were respectively cut from the sandwich injection molded disk by a low speed diamond saw (ISOMET Low Speed Saw/BUECHLER). The gapwise distribution of interface and birefringence $\Delta n$ along the flow direction is measured using a polarizing microscope (Leitz Laborlux 12 POL/LEITZ WETZLAR) with a tilting compensator (4th or 30th order, 1592K/LEITZ WETZLAR). The detailed cutting procedures for obtaining the specimens for the interface distribution and birefringence measurement are shown in Figure 8-6. The obtained data were compared with the simulated results. As the interface distributions of PS-PC-PS, PMMA-PC-PMMA or PS-PMMA-PS is easily observable. Therefore, no
black master batch to facilitate the monitoring of skin or core melt was needed in this study.

Figure 8-4 Schematic diagram of sequential injection molding apparatus.
Figure 8-5 The coordinate system and dimensions of the center-gated disk cavity.
Figure 8-6 Cutting procedure for preparing a specimen from an sequential co-injection molded sample used for measurement of the interface distribution (a) and birefringence measurement (b).
Table 8-6 Processing Conditions for Sequential Injection Molding Experiments and Simulations.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Material combination</th>
<th>Melt temp. core/skin (°C)</th>
<th>Mold temp. (°C)</th>
<th>Volume flow rate (cm³/s)</th>
<th>Packing pressure (psi)</th>
<th>Vol. of skin melt (%)</th>
<th>Thickness of mold (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PC/PS 250/250</td>
<td>40</td>
<td>30</td>
<td>2100</td>
<td>72.5</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PC/PS 250/250</td>
<td>60</td>
<td>32</td>
<td>2300</td>
<td>72.5</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PC/PS 250/250</td>
<td>80</td>
<td>32</td>
<td>2360</td>
<td>72.5</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PC/PS 230/230</td>
<td>60</td>
<td>33</td>
<td>2220</td>
<td>72.5</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>PC/PS 270/270</td>
<td>60</td>
<td>28</td>
<td>2180</td>
<td>72.5</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PC/PS 250/250</td>
<td>60</td>
<td>28</td>
<td>2180</td>
<td>62.5</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>PC/PS 250/250</td>
<td>40</td>
<td>30</td>
<td>2100</td>
<td>72.5</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>PMMA/PS 230/230</td>
<td>60</td>
<td>50</td>
<td>2170</td>
<td>72.5</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>PC/PMMA 230/230</td>
<td>60</td>
<td>26</td>
<td>2250</td>
<td>72.5</td>
<td>3.18</td>
<td></td>
</tr>
</tbody>
</table>
To graphically illustrate experimental errors, the standard deviations are shown using error bars in Figure 8-7 for the material combination of PS-PC-PS under the processing condition of run 4. All experimental data are average values of at least three data points. Due to the small standard deviations and for clarity of the remaining grapes error bars are not shown, but all are similar as shown in Figure 8-7.

Figure 8-7 Standard deviations of measured total residual birefringence ($\Delta n$) distribution using error bars in the gapwise direction at various radial direction for the sequential co-injection molding for the material combination of PS-PC-PS under the processing conditions of run 4.
8.3 Numerical Analysis Techniques

In this study, a center-gated disk mold was used in the sequential co-injection molding simulation.

8.3.1 Mesh Generations

To simulate the molding process, a schematic of discretized finite-element triangle meshes for a quarter of the disk cavity in two-dimensional planar surface is shown in Figure 8-8. Due to the symmetrical flow occurring in the process, only a quarter of disk cavity and half thickness have been considered for the cavity filling to reduce the computation times. In finite element modeling, a finer mesh typically results in a more accurate solution. However, as a mesh is made finer, the computation time increases. For the current simulations the disk mold was divided into 315 elements and 184 nodes in the planar direction based on the previous work of Shyu [2] and Li [161] who balanced mesh size with computation time as well as initial trials that showed a significant increase in computation time with minimal increases in elements and nodes. With these meshes, the CPU time to carry out calculations for one processing condition was 8-24 hours on Pentium IV 3 GHz PC.
Figure 8-8 A schematic of discretized finite-element triangle mesh for a quarter of the disk cavity in 2-D planar surface.
8.3.2 Sequential Co-injection Molding Process Simulation

The flow mechanism depends on the corresponding rheological properties of both skin and core materials. Due to the dynamic coupling of mass, heat and momentum equation for two polymers and the difference in their rheological and thermal properties during the sequential co-injection molding process, the rules used for the traditional single-phase injection molding process design may not always be suitable for sequential co-injection molding. The numerical simulation should be able to differentiate the materials at any instant and location in the cavity. Therefore, in order to track the interface shape and predict the flow-induced birefringence, tracing individual components is required during the entire molding process.

In the present implementation for the sequential co-injection process, each polymer obeys the governing equations for generalized Hele-Shaw flow of nonlinear viscoelastic fluids under the non-isothermal conditions. The coordinate system used in the simulation for sequential co-injection molding is shown in Figure 8-5. The transport equations for 2D sequential co-injection molding are given by Eqs. (5.23) to (5.25). The boundary and initial conditions are given by Eqs. (5.27) to (5.30). Typically, for flow rate controlled sequential co-injection molding, both skin and core flow rates at the entrance are specified, thus

\[
Q = Q_{ent} \quad \text{and} \quad Q_c = Q_{ent}^c \quad \text{and} \quad Q_s = Q_{ent}^s
\]  

(8.1)

It is assumed that the fluids are not miscible at the interface. The kinematics and dynamics conditions of interface require that the force and velocities are continuous as presented by Eqs. (5.15) and (5.21), and the thermal boundary conditions are given by Eq. (5.22). A time-dependent moving interface must follow trajectories in the normal
direction and no mass can cross the moving interface, as described by Eq. (5.12). The governing equations for pressure development and interface evolution then follow Eqs. (5.66) and (5.67), (5.62) and (5.64). These governing equations are coupled with Leonov viscoelastic constitutive equation, Eq. (5.31), and numerically presented by Eqs. (5.95) and (5.97). These equations were solved using the hybrid control-volume finite element and finite difference method (CV/FEM/FDM) with successive under-relaxation iterations.

Initial computations of the interface distribution determined that division of half of the gapwise direction into 39 nodes was sufficiently accurate. Figure 8-9 contrasts the simulated interface distribution at 19, 39 and 79 nodes along the gapwise direction for the material combination of PS-PMMA-PS under the processing condition of run 8. Computation times for the increasing mesh sizes were 4, 8 and 20 hous, respectively. It is important to mention that the simulated interface distribution using 19 nodes along the gapwise direction showed instability near the gate even though the computation time was short. This instability can be reduced by refining the mesh as observed. Comparison between the mesh sizes of 39 and 79 showed almost no difference in the interface distribution at the positions of radial direction measured in this work and there was a time saving over 70%. Therefore, further division was not considered and the calculations were carried out using 39 nodes along the gapwise direction and 184 nodes along the radial direction of the mold.
Figure 8-9 Simulated interface distribution with three mesh sizes for the material combination of PS-PMMA-PS under the processing conditions of run 8.
8.3.3 Pressure Profiles

The experimental and simulation results for pressure traces were obtained for the sequential injection molding conditions of run 7 carried out for material combination of PS-PC-PS, a melt temperature of 250/250°C, a mold temperature of 40°C, a volume flow rate of 30 cm$^3$/s, a packing pressure of 2100 psi, a volume of skin melt of 0.725 and a mold thickness of 2.92 cm.

The measured pressure trace obtained from a pressure transducer directly under the sprue at the center of cavity is shown in Figure 8-10 with simulated pressure data. In this figure symbols represent the recorded pressure at the entrance node and line represents the corresponding predicted pressure traces. The simulated pressure trace during the filling and at the beginning of the packing stage is in a good agreement with the experimental data. It can be seen that the pressure trace from the experiment increases monotonically during the filling and takes off at the beginning of the packing stage and then the packing pressure is maintained during the packing time. In the packing stage, the measured pressure trace recorded by the pressure transducer under the sprue is taken as the entrance pressure. Time of 1.228 s marks the end of the filling stage and the beginning of the packing stage. The cooling stage is started right after the packing time ends. The pressure decreases abruptly due to the release of the packing pressure and cooling. The filling, packing and cooling stages of pressure change can be easily distinguished based on the displacement data in this figure. The simulation results indicate that at the start of the packing stage, the cavity pressure jumps up within 0.8 s, while the measurements show a slower pressure rise.
Figure 8-10 Measured (symbols) and simulated (solid line) pressure and measured displacement (dashed line) trace during sequential co-injection molding of material combination of PS-PC-PS in run 7 at melt temperature of 250/250°C, a mold temperature of 40°C, a volume flow rate of 30 cm³/s, a packing pressure of 2100psi, a volume of skin melt of 0.725 and a thickness of mold of 2.92 mm.
8.4 Results and Discussions

The predicted and measured total birefringence at various radial positions was compared to investigate the effect of processing conditions for the material combination of PS-PC-PS and the effect of material properties.

8.4.1 The Birefringence of PS in Injection Molding Process

Birefringence development in injection molded atactic PS was first studied by Ballman and coworkers [174,227]. Their studies revealed that PS exhibits dog-eared birefringence profiles across the thickness of the injection-molded parts with the maximum of the birefringence being at intermediate regions close to the mold wall. The center of injection-molded samples exhibited typically little or no birefringence due to rapid relaxation of stresses and chain-orientation as a result of slow cooling. There are two main sources for birefringence developed in an injection molded amorphous polymers. One is the flow-induced birefringence arising as a result of preferential orientation of the chains in flow direction, and the other is the thermally-induced birefringence caused by the non-equilibrium density change during inhomogeneous rapid cooling through the glass transition temperature [76].

A birefringence minimum has sometimes been observed between the mold surface and the maximum value and in the core [111,137]. Birefringence is influenced by melt temperature, injection speed, mold temperature and packing pressure. Generally increasing the melt temperature decreases the maximum birefringence. This is a result of reduction of the relaxation time of melts with increasing the melt temperature. Therefore, it creates favorable conditions for the relaxation of stresses and birefringence after the
cavity filling. Decreasing the injection speed increases the value of maximum birefringence. According to [228] increasing the flow rate leads to truncation of the long-term tail of the relaxation spectrum of the polymer melt, thus decreasing the effective relaxation time. The second reason is that at the high flow rate, thermal convection dominates over thermal conduction to the cold mold surface, thus also creating the favorable conditions for the relaxation process and retarding the growth of the frozen-in layer.

The effect of the mold temperature on the maximum birefringence is considered in the same manner as the effect of the melt temperature. Increasing the mold temperature creates a favorable condition for stress and birefringence relaxation leading to decrease in the value of maximum birefringence. The packing pressure also plays an important role in creating a second birefringence maximum close to the core. While the birefringence maximum near the wall is formed during the cavity filling, the second maximum of birefringence is developed as a result of a rise in normal stresses in the hot core region in the packing stage. The development of normal stresses in layers adjacent to the frozen-in layer in the packing stage is retarded owing to the long relaxation time.

Due to the high levels of birefringence detected in the PC core, the following studies were devoted to comparison of the predicted flow-induced and thermally-induced birefringence with the measured birefringence in moldings.

8.4.2 Comparison between Numerical Simulations and Experiment

Birefringence behavior is explained by the effect of the processing conditions affecting the skin and core melt front movement in the mold. It can be imagined that there
are two distinct fronts - flow front along the flow direction and temperature front along the gapwise direction- established during filling stage in the co-injection molding. The melt front moves with the given volumetric flow rate along flow direction. The temperature front defines the solid-liquid boundary, which moves towards the interior of the molded part along gapwise direction. The speed of the temperature front defined by the temperature gradient along gapwise direction is primarily governed by the local heat flux vector which is primarily controlled by the difference of mold temperature and melt temperature. The spatial profile of the solid-liquid boundary throughout the part at the end of the filling stage defines the thickness of the frozen-in layer at that time. This layer defines the boundary beyond which the built-up stresses relax. The regions toward the core remain molten being further deformed when the PC core is injected. This is expected to have a significant influence on the flow-induced birefringence distribution developed in the PS skin layer as well as the PC core regions near the interface of the two polymers.

The development of the gapwise distribution of the birefringence is determined by the combined effect of variation of shear rate and temperature decay. The former is caused by the shear flow during the filling stage and subsequent packing stage due to the compressibility of the material. The latter greatly increases the shear viscosity and relaxation time of the polymer. During filling, the velocity and shear rate decrease near the mold wall because of the solidification effect, narrowing the available cross sectional area of the channel for polymer melt flow. As a result, the velocity and shear rate increase in the PS skin region far from the mold wall, with the peak shear rate occurring just outside the solidified region. This behavior of the shear rate, coupled with viscosity
increase caused by cooling, determines the gapwise distribution of the total residual birefringence along the radial direction of the disk.

The predicted gapwise flow-induced birefringence distributions during the sequential co-injection molding in run 2 (Table 8-6) for PS-PC-PS material combination is discussed below. This run was carried out at a melt temperature of 250 °C / 250 °C, a mold temperature of 60 °C, a volumetric flow rate of 32 cm³/s, a packing pressure of 2300 psi and volume of skin melt of 0.725.

The evolution of the predicted gapwise flow-induced gapwise birefringence distribution at various radial positions at different times during the injection stage of the skin melt and during the injection stage of core melt are shown in Figure 8-11 and Figure 8-12. It is seen that birefringence continues to build up with time during the injection stages of skin and core melts due to the development of the shear stresses and the first normal stress differences.

The maximum birefringence in PS skin occurred at \( \frac{z}{b} = \pm 0.8-0.9 \). The peaks of transient birefringence during the injection of PS skin and PC core melts continually decreased in magnitude with increasing radial position from the gate. It is due to the fact that during the injection stage of PS skin melt, the velocity and shear stress decreases with the radial position in the disk because the velocity is inversely proportional to the radius so that the birefringence near the gate is larger than that in the downstream nodes.

The predicted gapwise flow birefringence distribution at the end of the filling stage at the various radial positions is shown in Figure 8-13. At the end of the filling stage, maximum peak of the birefringence in PS skin region appears near the surface of the disk. The peak is due to the dominant effect of the first normal stress difference by deformation.
and orientation of long chain polymer molecules during filling stage. While, in the PC core region, the flow-induced birefringence distribution due to deformation and orientation of PC molecules varies monotonically with $z/b$.

The predicted gapwise flow birefringence distributions at the end of packing stage with a packing pressure of 2300 psi are shown in Figure 8-14. Like the birefringence distribution at the end of filling stage, there is one birefringence maximum in PS skin region near the surface produced in the filling stage with slightly decreased value of $\Delta n_l$. It is also noted that the shape of birefringence distribution is not changed even though the magnitude of birefringence is reduced due to the stress relaxation during the packing stage. This is because the packing pressure of 2300 psi is not high enough to retard this stress relaxation and to fully compensate the volume shrinkage of polymer.

The predicted residual flow birefringence distribution at the end of cooling stage is given in Figure 8-15. At the end of the cooling stage, the birefringence distribution along the gapwise direction near the wall is almost the same as the birefringence distribution at the end of packing stage, shown in Figure 8-14. But the birefringence in the core region including a part of PS skin layer and the whole PC core layer becomes smaller due to the stress relaxation of the chain orientation immediately after completion of the packing stage, since the temperature in this region is not reached to the glass transition temperature at this stage.
Figure 8-11 Predicted flow-induced birefringence ($\Delta n^f$) distribution in the gapwise direction at various radial positions during filling stage of skin material at $t=0.45$ s (a), 0.64 s (b) and 0.88 s (c) for the sequential co-injection molding with combination of PS-PC-PS under the processing condition of run 2.
Figure 8-11 Predicted flow-induced birefringence ($\Delta n^b$) distribution in the gapwise direction at various radial positions during filling stage of skin material at $t=0.45$ s (a), 0.64 s (b) and 0.88 s (c) for the sequential co-injection molding with combination of PS-PC-PS under the processing condition of run 2 (continued).
Figure 8-12 Predicted flow-induced birefringence ($\Delta n_f$) distributions in the gapwise direction at various radial positions during filling stage of core material at $t=1.14$ s (a) and 1.21 s (b) for the sequential co-injection molding with combination of PS-PC-PS under the processing condition of run 2.
Figure 8-13 Predicted flow-induced birefringence ($\Delta n^f$) distributions in the gapwise direction at various radial positions at the end of the filling stage $t=1.22$ s for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 2.

Figure 8-14 Predicted flow-induced birefringence ($\Delta n^f$) distributions in the gapwise direction at various radial positions at the end of the packing stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 2.
8.4.3 The Effect of Mold Temperature

The effect of mold temperature on the interface distribution and birefringence distribution under non-isothermal viscoelastic flow is quite complex. The mold temperature affects the cooling of skin and core layers in sequential injection-molded parts. As skin melt is injected into a mold, it is quenched and solidifies instantaneously near the wall. The development of the solidified layer in the filling stage depends on the mold temperature. The thickness of the solidified layer determines the cross sectional area for the flow of the skin and core polymer melts. Higher mold temperature reduces the cooling rate of the skin and core layer, resulting in more uniform cooling through the thickness.
The predicted gapwise distribution of the residual flow birefringence $\Delta n^\beta$ at a mold temperature of 40°C in run 1 is shown in Figure 8-16. The predicted and measured gapwise distribution of the residual flow birefringence $\Delta n^\beta$ and measured gapwise distributions of the total residual birefringence at different mold temperatures of 60 and 80 °C corresponding to runs 2 and 3 with a melt temperature of 250 °C at various radial positions at the end of cooling stage are shown in Figure 8-17 and Figure 8-18, respectively.

Each figure represents the results corresponding to three different mold temperatures. The birefringence first increases, shows a maximum and then decreases towards the inner region. In most cases, the birefringence decreases rapidly in radial direction of disk due to a decrease of flow velocity. The development of the gapwise distribution of the birefringence is determined by the combination of the effects of shear rate and temperature history during the sequential co-injection of PS skin and PC core melts. The shear rate history is caused by the shear flow during the injection stage of PS skin and PC core melts followed by the packing stage due to the compressibility of the polymer melts. Changes of the temperature history in the polymer melt are due to the effect of mold temperature in this case. The maximum birefringence is evident in the PS skin. A global maximum birefringence in a PS skin region appears at $z/b=\pm 0.8-0.9$ near the outer wall. This results from frozen–in chain orientation in the filling stage of sequential injection of skin and core melts and slow relaxation in the cooling stage, since the relaxation time increases quickly and the stresses become frozen-in. The values of residual birefringence in molding obtained in Runs 1 to 3 are relatively low. This is due to the high melt temperature of 250 °C used during sequential co-injection molding. In
single component injection molding, fast relaxation of chain orientation occurs immediately after completion of the filling stage in the core, since the temperature in this region is still high. However, the latter is not always true for two-component injection molding because skin and core materials have totally different glass transition temperature, $T_g$. The predicted residual flow birefringence distributions in the PC core are lower for runs 2 and 3 than that for run 1. One of the interesting features shown by Figure 8-16 is that the predicted residual flow birefringence distributions in the PC core are not small. This phenomenon occurs in the cooling stage of coinjection molding process with PS skin and PC core components having the different glass transition temperatures. For these polymers, difference in $T_g$ is approximately 50°C. If one assumes that the temperature at the interface is 140°C, then in PS skin layer close to the interface the stress relaxation process continues till glass transition temperature of PS is achieved, while relaxation does not occur any more in the PC core layer close to the interface. Experimental data shows the presence of birefringence in the PC core. Evidently, the thermally-induced birefringence dominates in the core region.

A single nonlinear constitutive equation can not describe the rheological behavior of a polymer in the glassy, rubbery and fluid states and in particular, in the transition region between them. In injection, packing, and cooling stages of sequential co-injection molding the dominant terms in the dynamic equations are also different. Therefore, it was assumed that the coupling effects between the flow- and thermally-induced stresses are negligible, such that they can be evaluated independently.

One of the interesting features in Figure 8-17 and Figure 8-18 is that measured residual birefringence in the PC core are similar magnitude compared to that in the PS
skin region. Therefore, the residual thermal birefringence was calculated including the interface position along the radial direction based on the linear viscoelasticity and photoviscoelasticity with the volume relaxation effects included [1,141] as described in Chapter IV. Figure 8-19, Figure 8-20, Figure 8-21 show the simulated gapwise distribution of the thermally-induced birefringence, $\Delta n^h$ for PS-PC-PS material combination quenched from an initial temperature of 250 °C at different quenching temperatures of 40, 60 and 80 °C, respectively. For PC core, thermally-induced birefringence is always positive throughout the cross section for the case of quenching temperature of 40 and 60 °C. However, for a quenching temperature of 80 °C the sign of birefringence varies from positive in the center to negative at the interface. Moreover, it is found that the birefringence decreases with an increase of the quenching temperature. For PS skin, the birefringence varies between positive at the surface and negative at the interface for all quenching temperatures.

When the thermally-induced birefringence $\Delta n^h$ was added to the corresponding flow-induced birefringence, $\Delta n^f$, the simulated total birefringence provided a better quantitative and qualitative description of the measured birefringence in sequential co-injection moldings. The predicted gapwise total residual birefringence distributions at various radial positions at the end of cooling stage are calculated and given in Figure 8-22 for a mold temperature of 40°C. The predicted and measured gapwise total residual birefringence distributions at various radial positions at the end of cooling stage are given in Figure 8-23 and Figure 8-24 for different mold temperatures of 60 and 80°C corresponding to runs 2 and 3, respectively, and a melt temperature of 250 °C. Simulations showed that, for the case of PS skin, total residual birefringence $\Delta n$
was mainly caused by flow, since the magnitude of the thermally-induced birefringence \( \Delta n^h \) at this domain was significantly lower than the corresponding flow-induced birefringence, \( \Delta n^f \). Therefore, the flow-induced birefringence \( \Delta n^f \) in PS skin was not significantly changed when the predicted thermally-induced birefringence \( \Delta n^h \) was added. On the contrary, the total residual birefringence of core PC was mostly caused by thermal stresses generated during cooling. Even though the predicted residual flow-induced birefringence in the PC core are not small because the difference in \( T_g \) of PS skin and PC core materials is approximately 50\(^\circ\)C, the flow-induced birefringence relaxed faster than the thermally-induced birefringence in this domain when the flow stopped. It is noted that measured total residual birefringence \( \Delta n \) in PC core was comparable to that in PS skin. The measured residual birefringence \( \Delta n \) in PC core was possible to describe by the simulated thermally-induced birefringence \( \Delta n^h \) with addition of the contribution of simulated flow-induced birefringence, \( \Delta n^f \).

An increase of the mold temperature, creating a favorable condition of birefringence relaxation decreases the value of maximum birefringence in PS skin. The gapwise position of the maximum, which is built up during the cavity filling stage, moves towards the mold wall with increasing mold temperature. This occurs primarily as a result of a decrease in cooling rates upon the increase of the mold temperature, which decreases the melt relaxation time. The birefringence level in the core also decreases with mold temperature. As the mold temperature decreases, more cross sectional area is covered by of the frozen polymer near the gate, locally increasing the thickness of PS frozen layer, and thereby moving the birefringence maximum away from the mold wall. It is primarily
a result of an increase in cooling rates upon decrease of the mold temperature that cause an increase in the relaxation time. This observation was in agreement with the results obtained by Kadota et al. [42] in coinjection molding. They observed that a decrease of the mold temperature increases the birefringence throughout the thickness with the peak position of birefringence moving slightly away from the mold surface.

The possible reasons for the discrepancy observed between the measured and simulated total residual birefringences were the negligence of the fountain flow of the skin and core melts and the delivery system. In particular, some differences between measured and predicted birefringence were evident in the region between the center and the location where the maximum of $\Delta n$ is build up. This is because the contribution of flow in a delivery system consisting of contraction and expansion regions was neglected [76]. The flow in these regions provides an additional contribution to birefringence. Therefore, the predicted birefringence underestimates the measured one. This discrepancy is present in all experimental data of sequential co-injection moldings in this work. The predicted overall total values of $\Delta n$ were in fair agreement with experimental results.

Based on the present studies, it can be concluded that the position of solidified layer and magnitude of the flow-induced birefringence maximum at the end of cooling stage do correlate in an explainable manner with the mold temperature.
Figure 8-16 Predicted residual flow-induced birefringence ($\Delta n^f$) distribution in the gapwise direction at various radial positions at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 1.
Figure 8-17 Measured (symbols) and predicted (lines) residual flow-induced birefringence ($\Delta n^\theta$) distribution in the gapwise direction at various radial positions at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 2.
Figure 8-18 Measured (symbols) and predicted (lines) residual flow-induced birefringence ($\Delta n^R$) distribution in the gapwise direction at various radial positions at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 3.
Figure 8-19 Predicted thermally-induced birefringence ($\Delta n_{th}$) distributions in the gapwise direction at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 1.
Figure 8-20 Predicted thermally-induced birefringence ($\Delta n^{th}$) distributions in the gapwise direction at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 2.
Figure 8-21 Predicted thermally-induced birefringence ($\Delta n^{th}$) distributions in the gapwise direction at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 3.
Figure 8-22 Predicted total residual birefringence ($\Delta n$) distribution in the gapwise direction at various radial positions with the contribution of thermal birefringence at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 1.
Figure 8-23 Measured (symbols) and (lines) predicted (lines) total residual birefringence ($\Delta n$) distribution in the gapwise direction at various radial positions with the contribution of thermal birefringence at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 2.
Figure 8-24 Measured (symbols) and (lines) predicted (lines) total residual birefringence ($\Delta n$) distribution in the gapwise direction at various radial positions with the contribution of thermal birefringence at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 3.
The influence of the mold temperature on the phase distribution was first investigated by Young et al. [30], for the material combinations of HDPE-PS-HDPE and PS-HDPE-PS injected isothermally into a mold at temperatures of 120, 150 or 180 °C. They found that depending upon the material combination employed, the tendency for encapsulation may either be favorable or unfavorable. If a good encapsulated core/skin sandwiched structure is obtained isothermally and PS is injected first, the tendency to form good encapsulated parts deteriorates with decreasing mold temperature. Also the effect of mold temperature on the tendency to form core/skin parts reinforces the view that the viscosity ratio rather than the normal stress is the dominating parameter.

In the present study, the simulation and experiments were carried out at different mold temperatures under non-isothermal conditions for the material combination of PS-PC-PS. First, PS was injected to fill the mold partially and then PC was injected. In order to observe the interface distribution of PS skin and PC core materials, a part of the sample from the disk sample is cut-off in the flow direction. The location of the PC core material is measured as a function of distance from the gate. The predicted normalized gapwise interface distributions as a function of radial direction for a mold temperature of 40°C is shown in Figure 8-25. The predicted and measured normalized gapwise interface distribution as a function of radial direction for a mold temperature of 60 °C and 80°C corresponding to runs 2 and 3 at a melt temperature of 250 °C at the end of cavity filling are shown in Figure 8-26 and Figure 8-27, respectively. Symbols represent experimental data, and lines are results from simulation. It is seen in Figure 8-25 through Figure 8-27 that the interface distribution exhibits a blunt flow front with larger accumulation of the PC core near the gate. In the case of runs 1 to 3 corresponding to the mold temperature of
40, 60 and 80 °C, slight increase of the measured thickness of the PC core is observed with an increase of the mold temperature. The slight decrease of the measured degree of penetration of the PC core melt into the PS skin melt is also observed. Conversely, the lower mold temperature results in slightly increased degree of penetration of the PC core melt into PS skin melt along the flow direction. These effects are due to the rate of heat conduction from the wall to the PS skin depending on the mold temperature. As a skin material is injected first, a part of the skin melt near the cavity wall freezes and forms the solidified layer while the rest of PS skin melt flows down a central hot channel. When the PC core melt is injected it displaces the PS skin melt in the center of the channel by pushing the PS skin in front. As the PS skin melt flows, it continues to solidify on the wall producing the solidified PS skin layer. The thickness of the solidified PS layer is determined by the mold temperature because the rate of thermal conduction is proportional to the temperature gradient. At the lower mold temperature, higher rate of thermal conduction occur leading to the thicker solidified layer. Therefore, the cross sectional area of the total channel for the core melt available to push the skin melt ahead to the central region decreases. In this study, this effect is not significant because the injection rate is high enough to reduce this effect. Due to this phenomenon, high velocity gradient can be developed along the gapwise direction in the PC core region. It causes slightly increased penetration of the PC core melt into the PS skin melt along the flow direction. It can be seen that increasing the mold temperature leads to a slight increase of the thickness of the PC core melt.

Since three samples, obtained at the three mold temperatures discussed in this section, have the same volume ratio of the material combination of PS-PC-PS, thicker PS
skin at a given location means thinner PC core at the same location. An increase in the mold temperature thus leads to a slight decrease in the thickness of the solidified layer at the end of cooling and therefore to a slight decrease of birefringence in PS skin at the surface. As explained earlier, two fronts develop simultaneously during the injection stage: the flow front and the solid-liquid front. As the solid-liquid front moves towards the interior, the effective cross-sectional area, through which the polymer flows, continuously decreased. This results in increased local fluid velocities for a given volumetric flow rate imposed by the injection unit [42]. However, in the present study, this effect is not significant because the injection rate is high enough to decrease this effect. As a result, the low mold temperature forces the PC core to move slightly more in the flow direction than the case of high mold temperature since at the low mold temperature the frozen layer slightly advances inward and decreases the cross-sectional area. As a result, the PC core advances forward. The present results agree with the observation made by Kadota et al. [42], Yang et al. [229] and Selden [41]. In particular, Kadota et al. [42] observed that the thickness variation of core melt at different mold temperatures at the same injection speed is less significant even though the degree of penetration of the core melt does not change. Yang et al. [229] also found that the mold temperature influences the flow pattern of skin and core melts very slightly such that the flow front of a high mold temperature is blunter than that of a low mold temperature. Selden [41] studied the effect of molding parameters on the material distribution in sequential co-injection molded plates using experimental design. This statistical analysis showed that the injection speed, core temperature, and core content were the most
significant parameters in affecting skin/core distribution in comparison with the mold temperature.

This relationship between the degree of penetration and the thickness of the core melt is valid based on the mass conservation equation of PS skin and PC core melts. The results of the numerical simulations and the measurements are found to be in good agreement. It can be recommended that in order to obtain more uniform distribution of the PC core material, a low mold temperature can be employed. Similar effects can also be obtained by increasing the viscosity of the PS via reducing its melt temperature. However, this was not done in the present study.

Figure 8-25 Predicted gapwise position of interface at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 1.
Figure 8-26 Measured (symbols) and predicted (line) gapwise position of interface at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 2.
Figure 8-27 Measured (symbols) and predicted (line) gapwise position of interface at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 3.
8.4.4 The Effect of Melt Temperature

The effect of melt temperature on the residual birefringence distribution and the interface distribution in co-injection molding is more complicated. The increase of the melt temperature decreases the viscosity of both skin and core melts and speeds up their relaxation behavior. A magnitude of the effect on residual birefringence and interface distribution depends on activation energies of components during viscoelastic flow. Figure 8-28, Figure 8-17 and Figure 8-29 show experimental and simulated results of the gapwise distributions of the residual birefringence at several radial locations at three different melt temperatures of 230°C, 250°C and 270°C corresponding to runs 4, 2 and 5 at the end of cooling stage where the PS skin and the PC core have same melt temperatures. The residual birefringence is more sensitive to variation of the melt temperature than that of the mold temperature. The experimental and predicted residual gapwise distribution of the birefringence at the end of cooling for melt temperature of 270 °C shows similar trend as that at a melt temperature of 230 °C with significantly different magnitude of birefringence in both skin and core regions. High value of the birefringence peak is seen at lowest melt temperature. As mentioned before, the outer peak is due to the deformation of the skin melts during the filling and the subsequent relaxation of molecular orientation in the intermediate region and frozen-in orientation near the surface. Such a flow-induced outer peak in the residual birefringence become smaller with higher melt temperature since at higher temperature lower shear and normal stresses are generated due to low viscosity and shear rate for the given volumetric flow rate. Also, at a higher melt temperature faster stress relaxation occurs.
The predicted residual flow birefringence distributions at the end of the cooling stage in the core region is very low due to the low relaxation time and chain orientation immediately after the completion of the filling state at the higher melt temperature, since the temperature in the core region is still high. On the contrary to the prediction, the experimental data shows the presence of significant birefringence in this region. Evidently, the thermally-induced birefringence dominates in the core region. The magnitude of experimental birefringence at the PC core region is similar as shown in Figure 8-28 and Figure 8-29, which indicates that the effect of the melt temperature on the thermally-induced birefringence is insignificant if a melt temperature is well above the glass transition temperature of PC core. By including the interface distribution along the radial direction based on the simulation in Chapter V, the thermally-induced residual birefringence was calculated based on the approach described in Chapter IV.

With the assumption that the coupling effects between the flow- and thermally-induced stresses are negligible, the predicted and measured gapwise total residual birefringence distributions at various radial positions at the end of cooling stage are given in Figure 8-30, Figure 8-23 and Figure 8-31 for different melt temperatures of 230, 250 and 270 °C corresponding to runs 4, 2 and 5, respectively and a mold temperature of 60 °C. The experimental and predicted total residual birefringence increases significantly as the melt temperature decreases from 270 °C to 230 °C. Higher shear and normal stresses are developed from high viscosity and shear rate at lower melt temperature for the given volumetric flow rate. Also the relaxation of the polymer orientation was retarded at lower melt temperature. The overall predicted residual birefringence shows fairly good agreement with the experimental data.
Figure 8-28 Measured (symbols) and predicted (lines) residual flow-induced birefringence ($\Delta n^\parallel$) distribution in the gapwise direction at various radial positions at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 4.
Figure 8-29 Measured (symbols) and predicted (lines) residual flow-induced birefringence ($\Delta n^*$) distribution in the gapwise direction at various radial positions at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 5.
Figure 8-30 Measured (symbols) and (lines) predicted (lines) total residual birefringence ($\Delta n$) distribution in the gapwise direction at various radial positions with the contribution of thermal birefringence at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 4.
Figure 8-31 Measured (symbols) and (lines) predicted (lines) total residual birefringence ($\Delta n$) distribution in the gapwise direction at various radial positions with the contribution of thermal birefringence at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 5.
The effect of melt temperature on the interface distribution in sequential co-injection molding is quite complex since increasing the melt temperature decreases the viscosity of both skin and core melts. However, the effect on the melt temperature depends on rheological behavior of individual polymer components and their activation energies of viscous flow.

The effect of melt temperature on interface distribution is shown in Figure 8-32, Figure 8-26 and Figure 8-33 which show the measured and predicted PS-PC-PS interface distribution with respect to the distance from the gate entrance at the melt temperature of 230 °C, 250 °C and 270 °C corresponding to runs 4, 2, and 5, respectively. Increasing the melt temperature of both PC core and PS skin melts at a constant mold temperature of 60 °C leads to a decrease in the thickness of the PC core and an increase in the penetration length of the PC core. Even though increasing the melt temperature induces a larger relative decrease of viscosity of PS than that of PC, as shown in Figure 8-1 and Figure 8-2, the net change in viscosity of PC is much more greater than the change in viscosity of PS leading to the increased penetration and thinner PC core. Figure 8-34 shows calculated viscosity of PC and PS as a function of shear rate at high temperatures similar to the melt temperature in sequential co-injection molding. It is seen that PC has viscosity there is more than one order of magnitude greater than PS and is more shear thinning. It is concluded that there is a reduction of the core thickness and an increase of the penetration length with increased melt temperature.

These observations were in good agreement with the experimental data of Lee [186] and numerical simulation of Li [161]. They carried out an experimental and theoretical simulation study for the effect of melt temperature on the interface distribution
in simultaneous co-injection molding. They found that increasing the melt temperature of both PS skin and PC core melts led to decrease in the thickness of core melt and an increase in its degree of penetration.

Figure 8-32 Measured (symbols) and predicted (line) gapwise position of interface at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 4.
Figure 8-33 Measured (symbols) and predicted (line) gapwise position of interface at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 5.
Figure 8-34 Comparison of the calculated viscosity of PC and PS as a function of shear rate at the same temperatures similar to the melt temperature in sequential co-injection molding.
8.4.5 The Effect of the Volume of Skin Melt

From the experiments and simulation on the effect of the mold temperatures and the melt temperatures, it is observed that encapsulation is possible for sequential co-injection molding using a material combination of PS-PC-PS with core/skin viscosity ratio greater than 1 when a certain amount of skin melt is injected prior to the sequential injection of a set amount of the core melt. In order to obtain skin/core sandwich structure by sequential co-injection molding, one of the major tasks is to control the flow fronts by finding the proper volume of first-injected skin melt.

The predicted gapwise distribution of the flow-induced residual birefringence $\Delta n^R$ and measured gapwise distribution of the total birefringence with respect to the distance from the gate entrance for the volume of first injected skin melt of 72.5 % and 62.5 %, respectively, at the end of cooling stage are shown in Figure 8-17 and Figure 8-35. The rest of the processing conditions were constant as a mold temperature of 60°C and a melt temperature of 230°C as shown for runs 2 and 6 in Table 8-6. However, for run 2, the volumetric flow rate for both skin and core melts were 32 cm$^3$/s and the packing pressure was 2300 psi, while for run 5 the volume flow rate for both skin and core melts were 28 cm$^3$/s, and the packing pressure was 2180 psi.

As shown in Figure 8-17 and Figure 8-35, when the volume of first-injected PS skin melt is decreased from 72.5% to 62.5% corresponding to runs 2 and 6, both of simulation and experiments indicate that the maximum of flow-induced birefringence and total birefringence near the wall decreases with increasing the volume of first-injected PS skin melt. This is because if the volume of first-injected PS skin melt is decreased, more core material is injected into the cavity. It means longer shearing of high viscosity core
melt occurs. This effect can give higher flow-induced residual birefringence and higher measured total residual birefringence near the wall.

On the other hand, as shown in Figure 8-17 and Figure 8-35, measured residual birefringence $\Delta n$ distribution in PC core indicates the presence of significant birefringence even though the predicted flow-induced birefringence in the PC core is very low due to the faster stress relaxation. This discrepancy is due to neglect of the thermally-induced birefringence in calculation. Accordingly, the residual thermally-induced birefringence in sequential co-injection molding parts are treated as those developed in freely quenched multilayer plates. This birefringence was added to the predicted frozen-in birefringence. The coupling effect between the flow- and thermally-induced residual stresses was neglected. Thus, the residual thermally-induced birefringence was calculated independently by including the predicted interface distribution and based on the approach described in Chapter IV.

The predicted gapwise total residual birefringence distributions at various radial positions at the end of cooling stage are calculated and given in Figure 8-23 and Figure 8-36 corresponding to runs 2 and 6, respectively. It is found that the magnitude of measured and simulated total birefringence at the PC core region is similar because the processing condition for run 2 and 6 is exactly the same, except for the volume of the first-injected PS skin melt. For the influence of the volume of first-injected skin melt on the total residual birefringence, the experimental and predicted total residual birefringence increases as the volume of first-injected skin melt decreases from 72.5% to 62.5%. The less is the volume of the first-injected PS skin melt is, the more is the amount of the core melt injected into the cavity. It means the shearing of high viscosity core melt
can be lasted longer. The overall predicted residual birefringence shows good agreement with the experimental data. However, comparing the experimental data with the predicted result in the region between the peak of global maximum birefringence and the interface, some deviation is evident because the contribution of flow in delivery system consisting of contraction and expansion regions is neglected.

Figure 8-35 Measured (symbols) and predicted (lines) residual flow-induced birefringence ($\Delta n^p$) distribution in the gapwise direction at various radial positions at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 6.
Figure 8-36 Measured (symbols) and (lines) predicted (lines) total residual birefringence ($\Delta n$) distribution in the gapwise direction at various radial positions with the contribution of thermal birefringence at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 6.
One of the most important processing conditions in sequential co-injection molding is the volume of the first-injected skin melt. If a large amount of skin melt is injected before the injection of core melt, short core penetration is observed because there is less volume available for the core melt to penetrate. On the contrary, if the initial amount of skin melt in the mold is insufficient, the core melt front may overtake the skin melt front and breakthrough phenomenon will take place. Differing from the other processing, the effect of the volume of first-injected skin melt on the interface evolution between skin and core melts was more evident. Less skin melt in the cavity resulted in higher volume occupied by the core melt. It is noted that the volume of first-injected skin melt was one of the most critical factors to determine the interface distribution.

The effect of the volume variation of first-injected skin melt on the interface distribution can be observed from Figure 8-26 and Figure 8-37 corresponding to runs 2 and 6, where results of simulation are shown for the case of variation of the volume of the first-injected skin melt only. Figure 8-26 and Figure 8-37 show experimental and simulated results of the effect of the volume ratio of first-injected skin melt of 72.5% and 62.5% on the interface shape at the end of cooling stage. It can be seen that increasing the volume of first-injected skin melt leads to an insignificant change in the thickness of the core melt and a significant increase in the penetration length of the core melt front. As more core material is injected into the cavity the core penetrates deeper inside the skin melt. Core penetration changes mostly in the flow direction and not in the thickness direction as the filling during the core injection occurs mostly in this direction. This is due to the fact that the core melt always take the path of least resistance to penetrate the skin displacing skin melt at the hot core exhibiting with the low flow resistance to
completely fill the whole cavity. We conclude that there is a slight increase of the core thickness and a significant increase of the penetration length due to a decrease in the volume of the first-injected skin melt. These observations were in agreement with the numerical study carried out by Li [161] who noted that the volume of first-injected skin melt significantly affected the length of penetration in the flow direction, but did not affect the core layer thickness. As shown in Figure 8-26 and Figure 8-37, the overall predicted interface distribution is in good agreement with the experimental data.

![Graph](image)

**Figure 8-37** Measured (symbols) and predicted (line) gapwise position of interface at various radial positions for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 6.
8.4.6 The Effect of Thickness of the Mold

The effect of the mold thickness in the sequential co-injection moldings on the predicted gapwise distributions of the residual flow birefringence $\Delta n^f$ was studied. A mold thickness of 3.18 mm and 2.92 mm was used in runs 1 and 7, respectively. The predicted flow birefringence $\Delta n^f$ and measured birefringence $\Delta n$ at a mold thickness of 3.18 mm and 2.92 mm for runs 1 and 7 at various radial positions at the end of cooling stage is shown in Figure 8-16 and Figure 8-38. The rest of the processing conditions were held constant: melt temperature of 250 $^\circ$C, mold temperature of 40 $^\circ$C, volumetric flow rate of 30 cm$^3$/s, packing pressure of 2100 psi and volume of first-injected skin melt of 72.5%.

Similar to the birefringence distribution for the different processing conditions discussed early, the simulated flow-induced and measured total birefringence shown in Figure 8-16 and Figure 8-38 first increases at each radial position showing a maximum and then decreases towards the inner region. The birefringence decreases rapidly with increasing radius. In general, the simulated and measured birefringence decreased slightly when the mold thickness got thicker. This is because the skin and core melts flow easily with thicker mold leading to low pressure and low total birefringence value. This generated lower shear rate and reduced normal stresses during filling stage.

One of the interesting features in Figure 8-38 is that measured residual birefringence in the PC core is not small. When the thermally-induced birefringence $\Delta n^t$ was considered with the corresponding flow-induced birefringence, $\Delta n^f$, the simulated total birefringence provided a better description of the measured birefringence in sequential co-injection moldings.
The predicted gapwise total residual birefringence distributions at various radial positions at the end of cooling stage are calculated and given in Figure 8-22 and Figure 8-39 at different mold thickness of 3.18 mm and 2.92 mm, respectively, with the rest of the processing conditions being held the same. It is noted that measured total residual birefringence $\Delta n$ in PC core was comparable to that in PS skin. Simulated total residual birefringence $\Delta n$ showed that the birefringence in the PC core of the moldings was mainly caused by thermal stresses. On the contrary, the flow-induced birefringence $\Delta n^f$ in PS skin was not significantly changed when the thermally-induced birefringence $\Delta n^t$ was added.

For the influence of the mold thickness on the total residual birefringence, simulations and measurements showed that the maximum of birefringence in PS domain decreased when the mold thickness increased, as shown in Figure 8-16 and Figure 8-38. This is attributed mainly to the effect of the flow-induced birefringence because the thermally-induced birefringence was not affected by the change of mold thickness. The flow-induced birefringence decreases when the mold thickness is thicker because decrease of the mold thickness means the decrease of the available cross-sectional area in the channel for flow of skin and core melts during the filling stage. Therefore, the skin and core melts are easier to flow in a thicker mold resulting in low pressure and lower total birefringence value. This led to a lower shear and normal stresses during filling stage. It is found that the predicted results are in qualitatively good agreement with experimental data.

Figure 8-25 shows the predicted normalized gapwise interface distribution as a function of radial direction for a mold thickness of 3.18 mm with a mold temperature of
40 °C and a melt temperature of 250 °C at the end of cavity filling. The predicted and measured normalized gapwise interface distribution as a function of radial direction for a mold thickness of 2.92 mm with a mold temperature of 40 °C and a melt temperature of 250 °C at the end of cavity filling is shown in Figure 8-40. From Figure 8-25 and Figure 8-40 for the case of run 1 and 7, respectively, it is noted that when the thick mold was used, an increase in the experimental data on thickness of the PC core was observed. This is the increase of thickness of the PC core phase near the gate. Thin mold results in increase of the degree of penetration of the PC core melt into PS skin melt along the flow direction due to decrease of thickness of the PC core phase near the gate. This is the result of combined effects of heat conduction from the wall and velocity gradient in PC core. It is because of the rate of heat conduction from the wall to the PS skin depending on the mold thickness. As the PS skin melt is injected first into the cavity, the PS skin melt near the cavity walls freezes and forms the solidified layer and the rest of skin melt flows down a central channel. When the core melt is injected, it displaces the skin melt in the center of the channel by pushing it forward. As the skin melt flows ahead, it continues to solidify on the wall producing solidified skin layer. The thickness of solidified layer is determined by the thickness of mold because the rate of heat conduction is proportional to the temperature gradient. In the thin mold, the higher is the rate of thermal conduction, the thicker is the solidified layer. Since solidified layer is thick in the case of thin mold, the cross section of the total channel for core melt to push the skin ahead in the central region decreases. It is found that there is good agreement between results of the numerical simulations and the measurements.
Figure 8-38 Measured (symbols) and predicted (lines) residual flow-induced birefringence ($\Delta n^\theta$) distribution in the gapwise direction at various radial positions at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 7.
Figure 8-39 Measured (symbols) and (lines) predicted (lines) total residual birefringence ($\Delta n$) distribution in the gapwise direction at various radial positions with the contribution of thermal birefringence at the end of the cooling stage for the sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 7.
Figure 8-40 Measured (symbols) and predicted (line) gapwise position of interface at various radial positions for sequential co-injection molding with combination of PS-PC-PS under the processing conditions of run 7.
8.4.7 The Effect of Material Properties

The residual birefringence distribution and the interface distribution of skin and core melts in sequential co-injection molding depend on the rheological behavior of individual components under non-isothermal viscoelastic flow. To study the effect of material properties of skin and core materials on gapwise birefringence distribution, three material combinations of PS-PC-PS, PS-PMMA-PS and PMMA-PC-PMMA are employed for runs 4, 8 and 9. Figure 8-28, Figure 8-41 and Figure 8-42 show the gapwise distribution of measured birefringence $\Delta n$ and simulated total or flow-induced residual birefringence $\Delta n^t$ at various radial positions at the end of cooling stage in sequential co-injection molding for three material combinations of PS-PC-PS, PS-PMMA-PS and PMMA-PC-PMMA, respectively, at skin and core melt temperature of 230°C and a mold temperature of 60°C. The other processing conditions are listed in Table 8-6.

Compared to Figure 8-28 and Figure 8-41 for the material combinations of PS-PC-PS and PS-PMMA-PS, respectively, the predicted flow-induced birefringence for the PS skin shows that the birefringence first increased, reached a maximum and then decreases towards the inner part of PS skin region. Even though the volumetric flow rate for the material combination of PS-PMMA-PS is higher than that of PS-PC-PS, the maximum values of the birefringence near the outer wall of $z/b=\pm 0.8-0.9$ in PS skin region were similar to each other. This is due to significantly different rheological behavior of PC and PMMA as core materials, as shown in Figure 8-2 and Figure 8-3. The viscosity of PC core is higher than that of PMMA. The high viscosity of PC core region led to development of high shear and normal stresses. The distribution of shear rate of PC core region has a direct influence on the shear rate of the skin melt that is already injected.
Through this effect PC core also induces shearing to PS skin region. Therefore, the difference of viscosity between PC core and PMMA core may compensate the effect of volumetric flow rate on the maximum of birefringence in PS skin region between the material combinations of PS-PC-PS and PS-PMMA-PS.

On the other hand, the simulation of flow-induced birefringence for the PC core for the material combination of PS-PC-PS and for the PMMA core for the material combination of PS-PMMA-PS resulted in birefringence distribution showing a maximum at the interface and then decreasing to zero towards the center of the PC and PMMA core region. It is noted that the flow-induced residual birefringence of PC core for the material combination of PS-PC-PS is not small compared with PMMA core for the material combination of PS-PMMA-PS even though the fast relaxation of chain orientation after completion of the filling stage takes place. It is because PS skin and PC core components have the different glass transition temperatures. The glass transition temperature $T_g$ of PC core is approximately 50°C higher than that of PS. When the temperature at the interface is 140°C, then in PS skin layer close to the interface the stress relaxation process continues till glass transition temperature of PS is achieved, while PC core layer close to the interface relaxation does not occur any more. On the contrary, for PC core in the material combination of PS-PMMA-PS the flow-induced residual birefringence is small because the PS skin and PMMA core have similar glass transition temperature and the fast relaxation of chain orientation developed in PMMA core after completion of the filling stage.

For the material combinations of PS-PC-PS and PMMA-PC-PMMA, the core material is PC, but PS and PMMA are employed as skin materials, respectively. As
shown in Figure 8-30 and Figure 8-42, the simulation of total residual birefringence for the PC cores show similar magnitudes and patterns of birefringence distribution. On the other hand, as shown in Figure 8-28 and Figure 8-42 the simulation of flow-induced birefringence for the PS skin of PS-PC-PS and for the PMMA skin of PMMA-PC-PMMA shows that the birefringence distribution developed in the same fashion at the end of cooling stage at the different skin material showing a maximum and then decreases towards inner part of skin region. However, the magnitude of the simulated flow-induced birefringence is significantly different. It is because the stress-optical coefficient of PS being negative is much higher than that of PMMA being positive as shown in Table 8-4. Therefore, the flow-induced birefringence with negative sign of PS skin region for the material combination of PS-PC-PS is higher than that with positive sign of PMMA skin region for the material combination of PMMA-PC-PMMA.

It is noted that the discrepancy between the experimental data and simulated results was found especially in the PC core region of PMMA-PC-PMMA. It is due to neglecting of the contribution of thermally-induced birefringence arising through inhomogeneous densification of the skin and core melts and the change in viscoelastic properties. Thus, the better qualitative and quantitative prediction of residual birefringence in sequential co-injection moldings requires both the contribution of the flow-induced and thermally-induced birefringence. The thermally-induced birefringence coming from the cooling process is not a linear function of the thermal stress because the stress-optical or strain-optical coefficient shows photoviscoelastic behavior and becomes a function of both time and temperature in the glass-to-rubber transition zone. Therefore, the memory effect in the optical behavior of the polymer becomes significant, and a
photoviscoelastic relation should be used in correlating the thermal birefringence with thermal stress [124,172,189,191,223]. Unfortunately, experimental data on Young’s relaxation modulus and the strain-optical coefficient of PMMA is not available in the literature. It should be noted that PMMA behavior is complicated because the value of the stress optical coefficient changes sign at 144°C [223] with its value being negative below that temperature, as frequently cited in the literature [219-221].

If the contribution of the thermally-induced birefringence is considered, it is expected that simulated total residual birefringence would provide a better qualitative and quantitative description of the measured birefringence in the material combinations of PS-PMMA-PS and PMMA-PC-PMMA in sequential co-injection molding.
Figure 8-41 Measured birefringence ($\Delta n$, symbols) and predicted residual flow-induced birefringence ($\Delta n^\prime$, lines) distribution in the gapwise direction at various radial positions at the end of the cooling stage in sequential co-injection molding with combination of PS-PMMA-PS under the processing conditions of run 8.
Figure 8-42 Measured gapwise birefringence ($\Delta n$, symbols) and predicted total gapwise residual birefringence ($\Delta n$, line) distribution in PC core and predicted gapwise residual flow-induced birefringence ($\Delta n''$, lines) distribution in PMMA skin layer at various radial positions at the end of the cooling stage in sequential co-injection molding with combination of PMMA-PC-PMMA under the processing conditions of run 9.
Interface distribution in sequential co-injection molding is very sensitive to the viscosity ratio, as first indicated by White and Dee [28]. They suggested that it is necessary for the normal and shear stresses to be equal on both sides of an interface during flow. The normal stress is generally dominated by pressure with gradient in the direction of flow being proportional to the viscosity and a viscous resistance to interface deformation. Differing pressure gradients induced by different viscosities cause interface deformation during extrusion with high viscosity melts moving into lower shear stress region. They also found that in sequential co-injection molding very different phase distributions could be induced by reversing the order of injection of PS and polyethylene melt of grossly different rheological properties. Later Young et al. [30] observed that in sequential co-injection, shear viscosity plays a predominant role in influencing the mode of penetration of the mold and the interface distribution in the molded part. They concluded that the most uniform skin/core structure is obtained when the second melt has a higher viscosity than the skin polymer.

As stated by White et al. [29,31], the viscosity ratio represents the dominant factor influencing the interface shape during an isothermal cavity filling. They found that if two polymer melts were injected into a mold in the form of an annular ring and a core, the configuration of the interface was stable only if the annulus contained a low viscosity melt. If the annulus contained a higher viscosity melt, a phase inversion may occur. Viscosity ratio between the skin and core ($\eta_{\text{core}}/\eta_{\text{skin}}$) should be between 0.2 and 2 for optimum mold filling, i.e. the core should have a similar or slightly higher viscosity than the skin [32,33,45,47,57].
Figure 8-32, Figure 8-43 and Figure 8-44 show numerical and experimental interface distribution for sequential co-injection molding of material combination of PS-PC-PS, PS-PMMA-PS and PMMA-PC-PMMA having zero shear viscosity ratio of 11.74, 3.69 and 3.18 respectively, at the end of cavity filling in runs 4, 8 and 9. Symbols represent experimental data, and lines are simulated results. It is noted in Figure 8-32 and Figure 8-43 that when the higher viscosity PC core melt is injected into PS and PMMA skin melt, respectively, the viscosity ratio represents the dominant factor influencing the degree of penetration and the thickness of core melt. It is found that as the viscosity ratio is increased from 3.18 for the material combination of PMMA-PC-PMMA to 11.74 for that of PS-PC-PS, the degree of penetration of the core melt becomes less and the thickness of core melt becomes increasingly less uniform.

On the contrary, as shown in Figure 8-43 and Figure 8-44 for the material combination of PS-PMMA-PS and PMMA-PC-PMMA with close viscosity ratio of 3.18 and 3.69, respectively, the interface distribution such as the degree of penetration and the thickness of core melt for the material combinations showed similar result.

It is observed that the numerical simulations on interface distribution were in fair agreement with the measurements. As shown in Figure 8-43 and Figure 8-44, the simulated result showed somewhat less penetration and thicker core melt than the experimental data of the interface distribution. One of the reasons for the discrepancy observed in the degree of penetration and the thickness of core melt for the material combinations of PS-PMMA-PS and PMMA-PC-PMMA was due to the different behavior of shear rate-dependent viscosity of skin and core materials, coupled with the effect on
rheological behavior of skin and core materials when the contribution of flow in a
delivery system consisting of contraction and expansion regions was not considered.

Figure 8-43 Measured (symbols) and predicted (line) gapwise position of interface at
various radial positions for the sequential co-injection molding with
combination core/skin of PS-PMMA-PS under the processing conditions of
run 8.
Figure 8-44 Measured (symbols) and predicted (line) gapwise position of interface at various radial positions for the sequential co-injection molding with combination core/skin of PMMA-PC-PMMA under the processing conditions of run 9.
8.5 Conclusions

Numerical and experimental studies of a two-dimensional non-isothermal transient two-phase flow in the sequential co-injection molding process have been performed. The physical modeling and associated numerical simulation of interface distribution and flow-induced residual stresses and birefringence of amorphous polymers in sequential co-injection molded center-gated disks were carried out for two-dimensional viscoelastic simulations based on the Hele-Shaw approximation, combined with the kinematics and dynamics of the time-dependent moving interface. The CV/FE/FD numerical method was employed. The residual flow birefringence in the molded disk was calculated by considering the filling, packing, and cooling stages. A compressible nonlinear viscoelastic constitutive equation was used. To take into account the compressibility of polymeric melts, the Tait equation in the packing stage was introduced. The residual thermal birefringence in molded articles was calculated by using the viscoelastic and photoviscoelastic model with volume relaxation [23] based on the free quenching approximation, shown in Chapter IV. The total birefringence was then calculated as the sum of the flow-induced and thermally-induced birefringence.

The simulation results were compared with corresponding experimental data, indicating that the theoretical results capture essential features of the gapwise flow birefringence distribution. The simulation also showed that the gapwise residual flow-induced birefringence was very low at the core layer due to the fast relaxation of stresses at high temperatures in this region. A peak near the mold surface in the skin layer appeared as a result of the combination of the frozen-in chain orientation in the filling stage and slow relaxation in the cooling stage. Needless to say, the skin and core
materials have similar viscosity ranging of viscosity ratio from 3 to 4 such as PS-PMMA-PS and PMMA-PC-PMMA, the simulated and measured results of total residual birefringence and interface distribution have shown that material combinations with different viscosities of such as PS-PC-PS might be utilized in this process if the viscosity of core melt is higher that that of the skin melt. For the material combination of PS-PC-PS the melt temperature exhibited the strongest effect on total residual birefringence as well as the interface distribution and thickness of core melt phase. The volume of first injected skin melt had a significant effect on the penetration length of a core melt into a skin melt in the flow direction. However, the variation of mold temperature showed only a slight effect on the total residual birefringence and the interface distribution. For the effect of material properties, as the viscosity ratio increased the core melt phase tended to get thicker and showed less penetration of the core melt. The skin uniformity also followed the general observation that there was an increasing difficulty in obtaining its uniformity as the viscosity ratio increases. Breakthrough phenomena were mainly determined by the volume of initially injected skin melt and the rheological properties of material combination.

To the best of our knowledge, the present study is the first investigation where the issues related to theoretical calculations of the frozen-in thermal and flow birefringence in sequential co-injection-molded disks are treated. Although the theory does not fully describe experimental observations, the present approach is significant step toward understanding the complicated phenomena from the rheological point of view. For more accurate predictions of the residual thermal birefringence and stresses in molded parts, improvement of simulations is desirable. It is especially desirable to understand the
case of pressurized constrained quenching that possibly occurs during co-injection molding and the role of geometric constraint of the mold on the boundary conditions.
CHAPTER IX
SUMMARY

ICM for manufacturing of plastic optical parts such as lenses, disk substrates and other optical components and two-component molding process, such as co-injection molding for the production of sandwich components are playing an increasingly large and important role in the processing of plastics. It is seen that these polymer processes offer numerous advantages over CIM. However, the main disadvantage in dealing with the ICM and multi-component injection molding is that the processes are difficult to control. In particular, the procedures used for the single-phase injection molding are not applicable for two-component molding like sequential co-injection molding. There are no science-based rules for setup of the two-component molding variables to obtain successful moldings for the optical and mechanical performance.

Since in ICM and co-injection molding, polymer has to melt and flow, a viscoelastic model for the melt stage has to be employed for the simulation of the transient or residual flow stress and birefringence development in products. In addition, the compressibility of the polymer melt should be taken account in the packing stage.

Measurements and viscoelastic simulations of the gapwise distribution of the birefringence component, $\Delta n$, and the average transverse birefringence, $<n_{rr} - n_{\theta\theta}>$, along radial direction were carried in PS and PC ICM moldings obtained under various processing conditions. Viscoelastic simulations of the thermally-induced birefringence
component were carried out in freely quenched PS and PC slabs. A viscoelastic numerical scheme was developed to calculate the flow-induced birefringence and average transverse birefringence using a hybrid numerical scheme based on control volume/finite element method/finite difference method (CV/FEM/FDM). The flow-and thermally-induced residual stresses were calculated using nonlinear and linear viscoelastic theories, respectively. The flow-induced birefringence was calculated from the flow-induced stresses using the stress-optical rule. The thermally-induced birefringence was calculated using a photoviscoelastic theory. The simulated total residual birefringence and average transverse birefringence based on combination of the flow-induced birefringence and thermally-induced birefringence on the assumption of no coupling effect between them were compared with the measurements.

The simulation was verified with the experimental measurements of pressure traces, gapwise residual birefringence distribution and average transverse birefringence in center-gated disk mold. The simulation also shows similar trends as experimental observations on the effect of various processing parameters, such as mold temperature, melt temperature, compression stroke and compression stage on birefringence in moldings. In the literature, a few experimental studies [100,109,230] have investigated the residual birefringence distribution experimentally. Moreover, in the literature, the viscoelastic model for polymer melt was applied to the injection-compression molding. In ICM molding this work showed that

1. The residual flow birefringence profile is zero in the core due to fast relaxation at high temperature and shows a peak near the surface as a result of chain freezing in the injection and compression stages and slow relaxation at
low temperature in the cooling stage. The measured nonzero birefringence
distribution of the residual birefringence in the core is derived from the
thermally-induced birefringence. The residual thermal birefringence in the
injection-compression molded part was considered to arise from that in a
freely quenched plate. The simulation results were compared with
corresponding experimental data, indicating that the theoretical results capture
essential features of the gapwise residual birefringence distribution.

2. For the polystyrene (PS) and polycarbonate (PC), the strongest effect among
the various processing parameters on the total residual birefringence as well as
the average transverse birefringence is the melt temperature and compression
stroke. However, the variation of mold temperature shows only a slight affect
on the total residual birefringence and the average transverse birefringence.

This research is the first attempt to study the birefringence development in co-
injection molded parts by investigating the basic underlying principles such as the rheo-
optical behavior of amorphous polymers in the glass-to-rubber transition zones with the
effect of volume relaxation in nonisothermal process. The final goal was to consider the
contribution of the thermally-induced birefringence for the simulation of total residual
birefringence in the sequential co-injection molding process.

To understand the development of birefringence and stresses in molded parts, the
underlying mechanical and optical properties of PS and PC materials were used. In
particular, the obtained information on the photoviscoelastic behavior of PS and PC was
used for calculating the residual birefringence and stresses in multi-layered plastic
products. Free quenching experiments were performed on multi-layered plates consisted
on PS, PC and polymethyl methacrylate (PMMA). The thermal residual birefringence distribution along the thickness direction of the multi-layered plates was measured. The measured data were compared with results of a numerical simulation based on the linear viscoelastic and photoviscoelastic constitutive equations for the mechanical and optical properties, respectively, and the first-order rate equation for volume relaxation.

The effect of the initial temperature on the development of the residual thermal birefringence was evaluated experimentally and numerically.

1. For the material combination of PS-PC-PS, the residual thermal birefringence in PC domain is always positive and increases at higher initial temperature, while in PS domain the residual thermal birefringence is typically negative throughout the PS layer. However, higher initial temperature leads to positive birefringence at the surface and negative at the interface. When the order of each plate is reversed like in case of PC-PS-PC, the residual thermal birefringence for PS domain is always negative and increases with an increase initial temperature, while, for PC domain, thermal residual birefringence is negative near the surface and positive near the interface. It is noted that the position of zero thermal residual birefringence is shifted toward the surface as the initial temperature increase.

2. For the material combination of PS-PMMA-PS, the residual thermal birefringence for PMMA domain shows small positive value compared to the PS domain and increases with an increase of the initial temperature, while the residual birefringence for PS domain has positive values at the surface and negative values near the interface showing that the position of zero
birefringence is close to the surface at high initial temperatures and moves toward the interface as the initial temperature decreases. If the order of each plate is reversed like in case of PMMA-PS-PMMA, for PS domain the residual thermal birefringence is always negative throughout the layer with its value being high compared with that of PMMA layer. Higher initial temperature leads to larger value of the birefringence. For PMMA domain, the thermal residual birefringence has negative values at the surface and positive values near the interface. The position of zero birefringence changes with the initial temperature in a peculiar way. At high initial temperatures, it is close to the surface and moves toward the interface as the initial temperature decreases.

3. For PC domain in the material combination of PMMA-PC-PMMA, the residual thermal birefringence is always positive throughout the layer with its value being very high compared with that of PMMA layer. Higher initial temperature leads to larger value of the birefringence. For PMMA domain, the thermal residual birefringence has negative values at the surface and positive values near the interface. The position of zero birefringence changes with the initial temperature in a peculiar way. At high initial temperatures, it is close to the surface and moves toward the interface as the initial temperature decreases.

For the reversed order of material combination like in case of PC-PMMA-PC, the residual thermal birefringence of PMMA domain is small and positive in value compared with PC skin domain showing large and positive in value. Higher initial temperature leads to larger value of the birefringence. For PC domain, the thermal residual birefringence has negative values at the surface
and positive values near the interface. The position of zero birefringence changes with the initial temperature in a peculiar way. At high initial temperatures, it is close to the surface and moves toward the interface as the initial temperature decreases.

4. A methodology was developed to calculate the thermally-induced birefringence for multi-layered plates. It was based on the mechanical and optical relaxation functions from the literature. The model predictions capture fairly well experimental data regarding the effect of the initial temperature.

In polymer processing operations of amorphous polymers, molecular orientation and inhomogeneous density change inherently occur under nonisothermal flow conditions, thus playing a major role in determining resultant residual stresses and end-use physical and optical properties. This research is the first attempt to study the residual birefringence development as affected by the flow and thermal history during the sequential co-injection molding process.

Numerical analysis was carried out to develop a viscoelastic model and process simulation of sequential co-injection molding of a center-gated disk. It was based on the kinematics and dynamics of the time-dependent moving interface, as well as Hele-Shaw approximation. The numerical model was based on dynamics and process physics rather than on an empirical approach. The residual flow birefringence in the sandwich-molded disk was calculated by considering the filling, packing, and cooling stages of sequential co-injection molding by using a compressible nonlinear viscoelastic constitutive equation. To take into account the compressibility of polymeric melts, the Tait equation was introduced. The transient gapwise interface development during the two-component
molding was described by the interface evolution equation formulated in this research. The material distribution was accurately determined by enforcing the local mass conservation at each fluid sub-domain, apart from the global conservation of mass at the whole cavity domain. Both core and skin melt front advancements are tracked by employing the volume of fluid (VOF) model. A hybrid CV/FEM/FDM is employed to solve the formulated governing equations for pressure and interface distribution coupled with nonlinear viscoelastic constitutive equation. The residual thermal birefringence in sandwich-molded parts was calculated by using the viscoelastic and photoviscoelastic model and based on the free quenching approximation. Then, the total residual birefringence was calculated as a sum of the flow-induced and thermally-induced birefringence.

Based on this developed numerical model, simulations of sequential co-injection molding of amorphous polymers using a center-gated disk cavity were carried out. The simulation results and experimental data were compared. In general, qualitatively good agreement was found between them. In addition, the effects of material combinations and processing parameters on the residual birefringence and interface distribution were evaluated. It is believed that this dissertation provided invaluable insight into the design of multi-component molding application as well as a better understanding of the process.

The simulation and experimental studies for 2-D transient two-layer flow in the flow-rate controlled sequential co-injection molding were performed. Material combinations with a broad range of viscosities were employed in this process. For a material combination of PS-PC-PS, the melt temperature exhibited strongest effect on the total residual birefringence as well as the interface distributions and thickness of core
melt. The volume of first-injected skin melt has a significant effect on the penetration length of the core melt into the skin melt in the streamwise direction, but no effect on the interface position. A smaller volume of initial injection of skin melt may cause a breakthrough phenomena, while a larger volume of first injection of skin melt leads to a less penetration of core melts and non-uniform skin/core sandwich structure.

Breakthrough phenomena are mainly determined by the volume of melt in initial single phase injection and rheological properties of material combinations. If the core melt has a higher viscosity than the skin melt, an encapsulated sandwich structure can be achieved. In the reverse case, where the core melt has a lower viscosity than the skin melt, breakthrough phenomena is very likely.

Finally, to the best of our knowledge, this study is the first successful attempt to simulate the sequential co-injection molding of viscoelastic melts under flow rate controlled conditions.

9.1 Recommendations for the Future Work

Based on theoretical and experimental findings made in the present study, the following future studies could be recommended:

(1) More accurate model to take into account the fountain flow effect, the frozen layer effect, and pressure decay effect for injection-compression molding and co-injection molding processes.

(2) Residual stress and birefringence distribution within the skin and core materials in simultaneous co-injection molding.
(3) Crystallization and microstructure development within the skin and core materials along with the interface evolution in co-injection molding process.

(4) Residual stress and birefringence distribution within the skin and core materials of semi-crystallizing polymer along with the interface evolution in co-injection molding.

(5) Interface instability and fingering effects in co-injection molding.

(6) 3-D interface evolution to predict the interface distribution and residual birefringence in the planar direction as well as in the gapwise direction for co-injection molding process.

(7) The interface adhesion between the two polymer and the long term mechanical properties of two-component molded parts.

(8) More accurate and plausible model to incorporate the constraint quenching approximation instead of the free quenching approximation into the flow simulation for the thermally-induced residual birefringence in injection-compression molding and co-injection molding processes.

(9) More accurate model to take into account flow in the delivery system consisting of contraction and expansion region taking place in injection-compression molding and co-injection molding processes.

(10) Tensile stress-relaxation experiments for PMMA with simultaneous measurements of the Young’s relaxation modulus and the strain-optical coefficient to verify the universality of the thermal birefringence simulation for multi-layered plates.
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