BIREFRINGENCE, ANISOTROPIC SHRINKAGE AND LUMINANCE IN INJECTION MOLDED LIGHT-GUIDE PLATE: MODELING AND EXPERIMENT

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BIREFRINGENCE, ANISOTROPIC SHRINKAGE AND LUMINANCE IN INJECTION MOLDED LIGHT-GUIDE PLATE: MODELING AND EXPERIMENT

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ABSTRACT

Liquid crystal displays (LCDs) with edge-lit backlight system have been widely used in industry due to several advantages over traditional cathode-ray tubes (CRTs). The main component of the backlight system is the light-guide plate (LGP) which is designed to provide the highest possible degree of light concentration and luminance efficiency. However, the relationship between processing conditions in manufacturing and their optical performance have not been established. In addressing this issue, LGP moldings were made of optical grade polycarbonates (PCs) of low and high viscosity and a polystyrene (PS). The theoretical and experimental studies on the effect of the processing conditions on the anisotropic shrinkage, residual stresses and birefringence, and resulting luminance in the injection molded V-groove LGPs were carried out. The stress-optical coefficient and relaxation modulus functions of polymers were obtained by specially designed rheo-optical instrument. These functions were incorporated to the linear viscoelastic and photoviscoelastic constitutive equations to predict the thermal
birefringence in constrained, freely quenched plates and LGP moldings. The flow-induced birefringence and anisotropic shrinkage of LGPs were simulated by using a combination of a CV/FEM/FDM technique, a nonlinear viscoelastic constitutive equation, and orientation functions. The residual normal and transverse birefringence in LGPs along with shrinkages were measured. The predicted total birefringence was obtained by a summation of the predicted flow- and thermally-induced birefringence. Numerical results were compared with measurements at various processing conditions indicating a good agreement in the anisotropic shrinkage and a fair agreement in the residual birefringence. The luminance as a function of a viewing angle on the injection molded LGPs at various molding conditions was measured by means of the device that was built for this purpose. Strong effects from the processing conditions on optical performance were found. The results indicated that the LGPs made of low viscosity PC exhibited the best light concentration and the highest luminance while LGPs made of PS showed the lowest optical performance. Also, it was found that the luminance of LGPs showed a strong correlation with the depth of melt filling of the V-grooves and some correlation with the frozen-in birefringence.
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CHAPTER I
INTRODUCTION

Injection molding is one of the most widely employed polymer processing methods, being characterized by high degree of automation, high productivity and good dimensional stability of moldings. Molding of precise plastic optical parts such as compact disk (CD or DVD substrate) and light-guide plate (LGP) is one of the most important concerns in the industry today. In comparison with conventional optical glass parts, plastics offer several significant advantages including light weight and low cost. An additional benefit of injection molding is the ability to make the products with complicated shapes, such as various fitted-joints that can be molded in a one-shot process.

The injection molding process consists of heating the polymeric material to above its melting point, injecting the melt into a cold mold and packing extra melt to ensure the geometrical integrity of the part while cooling takes place. There are three fundamental
stages of the process: filling, packing and cooling. In the filling stage, a hydraulic pressure
generated by the machine unit, pushes a hot polymeric melt to rapidly fill a cold mold
having a cavity of the desired shape. During the holding or packing stage, extra material is
forced into the cavity in order to compensate for shrinkage during solidification. After a
certain time, the cavity entrance (gate) 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 to cool down to the room temperature.

Recently, substantial progress in simulation of injection molding has been made mostly
under the assumption of non-Newtonian viscous flow behavior. The simulation has
especially provided significant improvement to the mold design and subsequent process
optimization. Although the viscous flow simulation has served the immediate needs of the
injection molding industry, the molecular orientation cannot be considered as due to
viscous flow. Therefore, a viscoelastic flow simulation is required to compensate this
deficiency.

Due to a fast cooling of polymeric materials, injection molding process introduces
frozen-in molecular orientation or so called anisotropy which may significantly affect the
optical properties of plastic optical parts. The anisotropy, namely birefringence was recognized as contributions to the birefringence come from the sources of the flow and thermal-induced stresses. In amorphous polymers, it results from both mechanical and thermal history.

The flow-induced birefringence results from the flow stresses and based on the well-known stress-optical rule [1, 2]

$$\Delta n = C_\sigma \Delta \sigma$$ (1-1)

where $\Delta n$ is the birefringence, $\Delta \sigma$ is the principal stress difference and the $C_\sigma$ is the stress-optical coefficient of polymer in the melt state. However, the thermally-induced birefringence cannot be evaluated by Eq.(1-1) since it is not applicable in transition region from the rubbery to glassy state during cooling process due to the $C_\sigma$ exhibiting non-constant values in these states. Thus, the time and temperature dependence of mechanical and optical response along with the linear viscoelastic and photoviscoelastic equations are required in order to calculate the thermally-induced birefringence.

This dissertation presents flow simulation on filling, packing and cooling stages of the injection molding process of LGPs. The analysis is based on a hybrid of finite
element/finite difference/control volume (FEM/FDM/CV) solution of a Hele-Shaw flow along with the non-linear Leonov constitutive equation. By introducing this nonlinear model, the shear and normal stresses are calculated and related to the flow-induced birefringence by using Eq. (1-1). The calculated pressures and temperature history were then used to predict the thermally-induced birefringence by using linear viscoelastic and photoviscoelastic constitutive equations. To carry out these calculations, the stress-optical coefficient function of polymers is required. Accordingly, a rheo-optical instrument with data acquisition was designed simultaneously to measure the mechanical and optical response of the polymer. To compare the simulation results with measurements in molding, a series of injection molding experiments on different polymers were conducted. In addition, to understand the relationship between the optical performance of molded LGPs and processing conditions, luminance measurements were carried out.

Chapter 2 gives an up-to-date literature review on the subject matter. Chapter 3 describes the details of the LGP injection molding experiments that include the material characterization, set up of data acquisition system, design of experiments, measurement of melt front propagation, birefringence and anisotropic shrinkage as well as the layout of the finite element mesh for LGP mold used in this study.
Chapter 4 introduces the linear viscoelastic and photoviscoelastic constitutive equations along with the free volume relaxation concept. To determine the stress-optical coefficient functions of different polymers, an experimental method for simultaneous measurements of the transient mechanical and optical responses was proposed and the suitable device was designed. The measured mechanical and optical responses were used to calculate the residual thermal birefringence in freely-quenched plates made of different grades of PCs. Subsequently, this algorithm was implemented to predict the thermally-induced birefringence in the injection molding process.

Chapter 5 describes the mathematical modeling of the flow analysis of molding process including filling, packing and cooling stages. A LGP cavity was discretized using certain numbers of finite element meshes. Transport equations were formulated based on a combination of one and two dimensional flow problems along with a nonlinear Leonov constitutive equation. The algorithm for molding of anisotropic shrinkage was also considered. The three components of flow-induced birefringence were calculated based on the stress-optical rule. The comparison of simulated and experimental results was made without consideration of thermally-induced birefringence. Then, by introducing the calculated pressure and temperature fields from the above flow analysis, a combination of constrained- and free-quenching was implemented to calculate the thermally-induced
birefringence of LGP moldings. The total residual birefringence was considered as a summation of the flow- and thermally-induced birefringences. The simulations were compared with the measurements.

Chapter 6 provides the results of measurements of the luminance as a function of viewing angle for LGPs made of two optical grade PCs and PS at various processing conditions. The depth of melt filling of the grooves in LGPs was measured at different locations selected based on the melt front propagation during the cavity filling. The dependences of luminance on the depth of melt filling, optical retardation and processing conditions were elucidated.

Consequently, this dissertation combined our earlier studies including the two dimensional CV/FEM/FDM in viscoelastic flow simulation and anisotropic shrinkage algorithms. In addition, a one dimensional viscoelastic flow algorithm was added to simulate the flow in the sprue and runner to investigate the gate freezing effect. Also, a constrained quenching was applied to unite the free quenching condition and forms a more realistic algorithm to predict the thermally-induced birefringence. Besides, various devices were designed to carry out required experiments.
CHAPTER II
LITERATURE REVIEW

2.1 Injection Molding Technology

Injection molding is one of the most widely employed technologies in the material processing industry. Besides well known high automation, production rate, and large volume production, injection molding technology also provides a high repeatability in dimensional specification making it unique technology.

2.1.1 Fundamentals of Injection Molding Technology

Although there are several limitations, injection molding provides many more advantages than other material processing methods. In modern injection molding, a polymer is heated up to its melt state in a screw extruder at a temperature above the glass transition temperature, $T_g$, for amorphous polymers or melting temperature, $T_m$, for semi-crystalline polymers and the screw is then used to pressurize the melted material and push it into a cold cavity at a temperature below $T_g$ or $T_m$ for amorphous or semi-
crystalline polymers, respectively. The polymeric melt is then solidified in the mold. After solidification the mold is opened and the part is ejected. A wide variety of parts with complicated shape can be made by this technology. Almost all thermoplastics and some thermosets can be injection molded [3]. Rubber compounds are also injection molded. In this case, the compound is injected into a hot mold and then vulcanized inside the mold. In addition, high percentages of solid powders, such as ceramic and metallic powders, can be mixed with thermoplastic and injection molded into a powder-polymer precursor for subsequent sintering. This is called powder injection molding [4]. In addition, injection molding can be used to make parts ranging from the large heavy duty parts to small MEMS (Micro-Electro-Mechanical Systems) scale parts. In the latter case, the process is called “micro molding” [5]. However, there is high cost in tooling and maintenance; difficulties in mold design, post-molding warpage and anisotropic shrinkage are the major disadvantages of this technology.

The injection molding cycle can be divided into three distinct stages including the cavity filling, packing (holding), and cooling (solidification) [3, 6]. In the filling stage, the pressure is provided to force the polymeric melt into the mold and fill the cavity. The packing stage is used to provide more material to compensate for the volume contraction caused by cooling of the polymer melt by applying a certain pressure for a period of time.
The packing stage is usually stopped once the gate is frozen. That means no more material can be added into the cavity. Then, the cooling stage takes place to allow the polymeric melt to be cooled down to a preset mold temperature. At this stage the pressure decays slowly. After cooling stage, the mold opens and the parts are ejected.

Molding variables such as shot size (injection volume), injection speed (flow rate), melt and mold temperatures, packing (holding) pressure and time have strong influences on the development of pressure, temperature, physical properties and final dimensions of parts. Therefore, frozen-in molecular orientation, residual stresses, polymer degradation, shrinkage, and warpage are all influenced by these variables. In addition, in the case of injection molding of semi-crystalline polymers, the processing conditions also strongly affect the crystallization and microstructure development in moldings, which can influence their final performance and characteristics.

2.1.2 Evolution of Injection Molding Technology

In 1868, John Wesley Hyatt modified a metal die casting machine and became the first to inject hot celluloid into a mold to produce billiard balls [7]. He and his brother Isaiah patented a ram injection molding machine in 1872 [8]. Subsequently, the process did not draw much attention until 1926 [9], when the first plunger type ram injection molding machine was manufactured in Germany by Eckert and Ziegler. For the following
decades, many improvements were made to improve this technology. A major expansion among these improvements was the invention of the screw injection molding machine in 1943 by H. Beck [10]. This invention is being used until nowadays.

The injection molding machine (press) consists of two parts, an injection unit and a clamping unit. Injection molding machine can fasten the molds in either a horizontal or vertical orientation. The majority of machines are horizontally oriented but vertical machines are used in some applications such as insert molding, allowing the machine to take advantage of gravity [11]. In addition, there are many ways to fasten the molds to the platens, the most common being manual clamps. However, when fast mold changes are required, hydraulic and magnetic clamps are used. Injection molding machines can be classified primarily by their type of driving systems, such as hydraulic, electric or hybrid. Hydraulic machines have historically been the only option available until Nissei Plastic Industrial Co., LTD introduced the first version of electric injection molding machine of model MM-5 in 1983 [12]. The mechanical mechanism of electric version of injection molding machine is similar to the hydraulic version, but an AC servo motor, ball screw, gear and timing belt were used to replace the conventional hydraulic elements. Therefore, the electric press reduced operation costs by cutting energy consumption and also addresses some of the environmental concerns surrounding the hydraulic machine. The
electric presses have been shown to be quite, faster, having a higher accuracy in controlling movements of machine. However, a higher cost of this type of machine is a concern. The hybrid injection molding machines [13] take advantage of the best features of both hydraulic and electric systems. In addition, a robotic arm is often used to remove moldings either by side or top of the machine. But collecting parts through a container or a continuously moving conveyor is still taking the advantage of cost saving.

Furthermore, a co-injection molding machine was introduced to allow multiple resins to be injected into one mold and make a single part. It requires separated screw barrels for each resin to be injected. The materials are injected either simultaneously or sequentially so that one material forms a skin and the other forms a core [14].

For massive production, a manifold hot runner system of injection molding was implemented [15]. In this technique, the material stays in a reservoir inside the mold section called manifold. The manifold is used to redirect the material into multiple runners which can be in number more than a hundred. This technology certainly requires a high tonnage injection molding press leading to significant cost increase.

Almost all the modern machine equipped with sophisticated computer and data acquisition system to monitor every injection molding sequence. The most recent
development includes microprocessor technology applied to the machine with upstream and downstream auxiliary equipments [16].

2.2 Simulation of Injection Molding Process

Extensive theoretical investigations of the injection molding process have been reported over the past several decades. Such theoretical simulations typically require: (1) description of mold cavity geometry; (2) governing equations to describe the non-isothermal flow dynamics of the polymeric melt; (3) constitutive equation to describe the rheological behavior; (4) the equation of state to describe the thermodynamics properties of polymeric melt; (5) numerical algorithm to solve the above equations.

The first fundamental research on the modeling of injection molding process was reported by Spencer and Gilmore [17-20] in the early 1950’s at Dow Chemical and later on the Ballman and his co-workers [21, 22] at Monsanto in late 1950’s. Continuation of these pioneering studies has received considerable attention for processing thermoplastics, elastomers, and thermosets. The numerical simulation of melt filling in injection molding started in the sixties and seventies. Pearson [23], Kamal and Kenig [24, 25], Gogos et al. [26, 27] and Stevenson et al. [28-31] have studied one-dimensional flow in a center-gated
disc. Toor et al. [32], Harry and Parrott [33] and Load and Williams [34] analyzed the filling of thin rectangular cavities by means of a one-dimensional flow representation. Williams and Lord [35] and Nunn and Fenner [36] considered one-dimensional flow in a circular tube whereas Hieber et al. [37] proposed a simple approximation for polymer flow in a non-circular tube under non-isothermal conditions. Detailed theoretical studies of two-dimensional filling in an arbitrary planar thin cavity based on a Hele-Shaw type of flow [38], have been carried out by Richardson [39], White [40], Kamal et al. [41, 42], Tadmor et al. [43-45], Hieber et al. [46, 47] and Isayev et al. [48, 49]. Practical application of the above mathematical models to a more complex geometry was developed by means of the flow analysis network (FAN) [43-45, 50, 51]. The approach determines the melt front pattern relative to a mesh configuration consisting of rectangular elements. In the mid-eighties, Wang et al. [52] combined the control volume (CV) with the finite element method (FEM) and finite difference method (FDM) to handle melt front advancement in three-dimensional thin geometry. However, it has to be noted that all of the above studies have been based on the assumption that the polymeric melt is incompressible.

On the other hand, the theoretical modeling has also been extended to the post filling stage by introducing the compressibility behavior of polymeric melts. The earliest work
in the analysis of the packing stage was reported by Spencer and Gilmore [20]. In addition to the assumption of Poiseuille flow, they proposed a modified van der Waals equation of state to describe the compressibility of the polymeric melts. Subsequently, this linear, single domain equation of state has been employed by several researchers [3, 53-55]. Chung et al. [53-55] solve the generalized Hele-Shaw equation numerically with the polymeric melt being assumed a Newtonian fluid under isothermal conditions. Later, Schmidt and Menges [56] solved the post filling stage pressure variation based on a modified Spencer-Gilmore equation of state. In 1988, Titomanlio et al. [57] analyzed the mass entering the mold during the post filling stage based on a simple model in which a solidification crystallization index is employed as a fitting parameter. In addition, Huilier [58] have further studied the post filling stage by introducing the double domain Tait equation of state [59]. The Tait equation is an empirical equation of state proposed by Tait to model the experimental specific volume data of various polymers. This equation provides another option, other than Spencer-Gilmore equation of state [60], for researchers to describe their PVT data.

Results of the flow simulation give the pressure, temperature and velocity fields and propagation of the melt front during the melt filling stage, the weld line formation and the shrinkage of molded parts for specified processing variables.
2.2.1 Flow Analysis Network (FAN)

The flow analysis network (FAN) method was originally developed by Tadmor and co-workers [43-45] to analyze melt filling in a rectangle cavity. The FAN technique is a method for tracking flow front location in fluid dynamics involving flow with a free surface. In contrast to algorithms that track flow front location using remeshing schemes, the FAN allows for approximate tracking of the flow front by using a fixed mesh. The FAN solves the generalized Hele-Shaw flow for thermoplastic injection molding using a simplified version of FEM. The method associates a control volume and a filling factor, \( f \), with each node at each time step. The pressure distribution was found from solving the discretized equations. Then the pressure and mesh geometry are used to find flow rates between the nodal control volumes. The flow front is advanced by updating the nodal filling factors from the flow rates and a time step. The FAN scheme enables conservation of mass, even for highly distorted element shapes, and also allows elements of different dimension to be simultaneously used in a single simulation. Besides, the FAN reduced the problem to the solution of a set of linear equations. It imposes no restrictions as to the complexity of the boundaries. The FAN proves effective at modeling flat, constant thickness cavities, including parts with holes and knit lines, as well as various types of extrusion problems [61].
2.2.2 Control Volume / Finite Difference Method (CV/FDM)

Finite difference method (FDM) originated in the 1930’s for hand calculation. Its use expanded rapidly with the development of digital computers. However, it becomes complicated while a non-equally space domain is involved. The FDM still represents the most developed and best understood numerical procedure for solving partial differential equations. It also plays the role that forms the basis of more contemporary finite element method, which can handle a wide variety of complex domain problems.

There are several ways to derive the finite difference equations [62-64]. The control volume approach derives finite difference equations not by discretizing the governing partial differential equations, but by applying conservation principles directly to a macroscopic control volume [65, 66]. The practical value of the control volume approach lies in analyzing domains with a complex geometry which requires irregular node spacing. Conservation principles can be applied to each element to obtain a set of linear algebraic equations containing unknown variables within each control volume. An analysis of this type of application requires careful manipulation of the variables at the element boundaries in case of mold filling. Tracking the location of advancing melt front is required in the simulation of cavity filling. Beside, tracking of free surface and moving boundary are necessary in other polymer processing [67-69]. An iterative scheme called
the pressure correction technique, using a CV based FDM suggested by Patankar [66] has received widespread application in the numerical solution on both compressible and incompressible flows [66, 68].

2.2.3 Control Volume / Finite Element Method (CV/FEM)

The finite element method originated in the 1960’s as a technique for structural analysis. It has now developed into a powerful tool for the solution of a wide range of different equations arising in engineering and science. A major advantage of this method is its geometrical flexibility and easiness in carrying out solutions on domains of irregular shape. Boundary conditions are treated in a convenient way, especially those involving flux or derivative conditions. The mold flow simulations of a complex geometric part are typically based on Hele-Shaw type of flow with a combination of control volume finite element method (CV/FEM) and finite difference method (CV/FEM/FDM) [46-49, 70-76].

Control volume method has long been used in the numerical solution for fluid mechanics, especially with finite difference method [65, 66]. The early use for mold filling analysis is the flow analysis network (FAN) method of Tadmor and co-workers [43-45]. The control volume scheme of FAN was then combined with a finite element representation of the cavity geometry by Hieber and Shen [46, 47] to model injection
mold filling. Using a finite element data structure allows three-node triangular elements to be combined in any geometry, for which the generalized Hele-Shaw formulation is valid. Since CV/FEM constructs a finite element mesh in the entire flow domain, no computational effort is needed for remeshing during the analysis. This makes the numerical scheme robust and more user-friendly than the conventional finite element method to solving moving boundary problems. Another major characteristic of CV/FEM is its ability to easily track flow fronts in complex parts. This makes the method very attractive in dealing with real molding process. In fact, the CV/FEM has become the most popular way to simulate injection molding process involving complex geometries.

2.3 Constitutive Equations

Constitutive equations are mathematical relationships that allow computing of the stresses in a liquid for a given flow history. They are often derived from constitutive models, which imply a set of assumptions and idealizations about the molecular or structural forces and motions producing stress.

2.3.1 Viscous Models

A purely viscous model has been used to describe the shear viscosity of the polymeric fluid for the flow simulation, although viscoelastic effects cannot be neglected
in juncture-flow area [77]. A viscous model provides a good prediction [3, 58] of the filling and post-filling stages on pressure evolution since the shear viscosity of the polymeric fluid is the most important property in flow analysis. In addition, the viscous model provides a direct solution for viscosity as long as the shear rate is calculated. Therefore, it provides a rapid solution for industrial needs. In fact, most of the commercial softwares such as MOLDFLOW, CMOLD, were developed based on the viscous model.

Among the viscous models, the power law model for shear viscosity has been shown a good comparison with experimental data during the filling stage [24-26, 46]. However, the power-law model is only valid for certain materials which shear thin at relatively low shear stress levels [3, 52]. For polymers whose viscosity shear thins at much higher shear stress levels, the power-law model would overestimate the shear viscosity at low shear rate region. In particular, it has been shown by Hieber et al. [3, 78] that a modified-Cross model [79] gives a good fit to the shear viscosity data for a broad variety of polymeric materials. The modified-Cross model gives the relationship between viscosity, $\eta$, and shear rate, $\dot{\gamma}$

$$\eta(\dot{\gamma}, T, p) = \frac{\eta_b(T, p)}{1 + \left(\frac{\eta_b \dot{\gamma}}{\tau}\right)^{1-n}}$$

(2-1)
where $n$ denotes the power law index, $\eta_0$, zero-shear viscosity, and $\tau^*$ being the characteristic stress.

2.3.2 Viscoelastic Models

Unlike the viscous model, the main difficulty in utilization of viscoelastic models is that shear rate is coupled with time derivatives resulting in a set of elliptic partial differential equation. Therefore, an iterative process between the governing equations and the constitutive equation is required to reach a satisfied convergent criterion in calculation of shear rate at each time step. This process is very time-consuming even performing with the most modern personal computer.

Although the viscous model has been widely used to provide a quick solution in simulation of injection molding, all components of stress tensor are not considered. As mentioned, the juncture-flow regions are usually encountered during injection molding in the gate, runner system and in the cavity with contraction and expansion areas [77]. To handle such flows, it is important that the viscoelastic properties of materials be considered. Besides, to predict the flow-induced stresses, molecular orientation and birefringence in all planes, the viscoelastic model is required [80, 81].

Isayev and Hieber [80] were among the first who proposed theoretical approach relating the nonlinear viscoelastic model to predict the development of frozen-in
birefringence in injection molding. The use of nonlinear viscoelastic models in simulation of injection molding is blooming since then. Among the differential version of viscoelastic model, the Leonov model [82, 83] has drawn much attention and provided a good prediction for many materials used in injection molding simulation. The Leonov multi-mode viscoelastic constitutive equation was used to describe flow of polymer melts. The governing equation is:

\[
\dot{\mathbf{C}}_k + \frac{1}{2\theta_k} \left[ \mathbf{C}_k^2 + \frac{1}{3} (\mathbf{I}_C^k - \mathbf{I}_C^1) \mathbf{C}_k - \mathbf{I} \right] = 0 \quad (2-2)
\]

where \( \mathbf{C}_k \) is the elastic strain tensor for the \( k \)th relaxation mode, \( \theta_k \) the relaxation time of the \( k \)th relaxation mode, \( \dot{\mathbf{C}}_k \), the Jaumann derivative of the elastic strain tensor, \( \mathbf{I} \), the unit tensor, \( \mathbf{I}_C^k \) and \( \mathbf{I}_C^1 \), the first and second invariant of the elastic strain tensor.

Sobhanie and Isayev [48, 49] used Leonov model to predict the stress components and cavity pressures for injection molded rubber compound. Baaijens [84] and Flaman [85] used the compressible Leonov model to simulate the injection molding cycle and predict the residual flow stresses for a strip mold. Shyu [86] implemented CV/FEM/FDM scheme along with the compressible Leonov model to predict the residual flow stresses and birefringence for an injection molded center-gated disk made by PS and PC. Guo and Isayev [87] extended this algorithm to semicrystalline polymers by additional contribution of crystallization kinetics. Lee et al. [88] developed a numerical analysis...
using a finite difference method and studied the distribution of birefringence in a center-gated disk obtained by injection molding and injection/compression molding processes using Leonov model. Chen et al. [89] employed the Leonov model combined with the modified CV/FEM method to simulate flow stresses during injection/compression molding of a center-gated disk. Kwon et al. [90, 91] developed a finite difference algorithm based on Leonov model to simulate anisotropic shrinkage in amorphous and semicrystalline polymers for an injection molded strip cavity. Isayev and Lin [92] combined the earlier developed algorithms from ref. [86, 90] to simulate the residual flow-induced stresses and birefringence of optical grade PCs by a combination of one-dimensional delivery system with two-dimensional gate and LGP cavity along with the multimode Leonov model.

In addition, since earlier nineties the simulation of injection molding by using the nonlinear integral type of viscoelastic models has been developed. Among the integral viscoelastic models, the K-BKZ model has been mostly implemented in injection molding. Douven [93] developed an algorithm to predict the residual stresses and birefringence for injection molded amorphous thermoplastics by using the multimode Leonov model and the K-BKZ model [94]. This later model was simplified by Wagner
by neglecting the Cauchy strain term in the original K-BKZ model. In case of non-isothermal, the compressible K-BKZ (Wagner) model was given as [93]

\[
\sigma = -p(\rho, T)I + \int_{-\infty}^{t} M(t-\tau, T) h(I_1, I_2) C^{-1}_{1}(\tau)d\tau
\]  

(2-3)

The memory function \(M(t-\tau, T)\) can be obtained by measurement of linear viscoelastic material functions only. It represents the time derivative of shear relaxation modulus given by a discrete relaxation spectrum. The function \(h\), called the damping function must be obtained by measurements in the non-linear region. Various forms of \(h\) can be found in [97]. The \(I_1\) and \(I_2\) are the first and second invariants of the Finger strain tensor, \(C^{-1}_{1}(\tau)\).

Yu et al. [98] developed mathematical models to predict birefringence, residual stress and density distribution in a freely quenched compression molded samples as well as in the injection molded samples by using the K-BKZ model. Fan et al. [99] applied the algorithm from Douven [93] to predict the flow-induced birefringence of an injection/compression molded disk.

2.4 Residual Thermal Stresses and Birefringence

Residual stresses in an injection molding part can be attributed to two main sources. The first is due to the shear and normal stresses that develop during the non-isothermal flow of the polymer in mold cavity [2, 3, 100]. These stresses do not completely relax due
to a rapid increase of relaxation time during cooling. Such stresses will eventually be frozen into the injection molding parts termed residual flow-induced stresses. The second type of the residual stresses arises while temperature of moldings drops down to the no-flow temperature (solid state) \([3, 101]\) during cooling. The linear viscoelastic behavior of the polymer during its passage through the glass transition temperature, \(T_g\), coupled with non-equilibrium free volume changes result in the development of thermally-induced (cooling) stresses that become residual after demolding. The flow- and thermally-induced stresses are always coupled since they were developed within a molding cycle. There is no single constitutive equation which is able to describe the formation of flow- and thermally-induced stresses in fluid, rubbery and solid states. However, in theoretical modeling, a separate treatment of flow- and thermally-induced stresses was normally adopted to handle this problem.

2.4.1 Flow- and Thermally-induced Stresses

The experimental determination of residual stresses in injection-molded parts has been performed mostly based on the layer-removal method of Treuting and Read \([102]\). Coxon and White \([103]\) investigated the effect of crosslinking on residual stresses in injection molded HDPE. The result showed that the residual stresses are compressive near surface, with a subsurface compressive maximum, and tensile in the interior. This
profile for the crosslinked specimen was similar in shape to that of the uncrosslinked specimen, with a slightly greater compressive stress maximum. Thus, the characteristic shape of the residual stress profile was determined by the molding conditions, and subsequent crosslinking only slightly increasing the level of compressive stress maximum. In addition, the same tendency of residual stress profile has been observed from several experiments on semi-crystalline and amorphous polymers [104-107].

Flow stresses appear mostly as a result of the cavity filling stage due to strong contribution of velocity. High shear rates in the melt during injection introduce shear stresses and the first and second normal stresses differences [70, 100]. Flow stresses develop when the polymer is in the fluid and rubbery states, i.e., above the glass transition temperature. Therefore, the theoretical modeling of flow stresses is directly related to modeling of the cavity filling as mention in Section 2.2. However, the effort in modeling thermally-induced stresses is associated with use of the constitutive equation applied in solid state. In addition, to produce a residual thermally-induced stresses, free quenching experiments of a particular geometry were normally conducted.

The area of modeling thermal stresses in polymers has paralleled similar developments about thermal stresses in inorganic glasses. The first theoretical treatment of thermal stresses was based on the “instant freezing” theory proposed by Bartenev [108]
in the late forties. He postulated that above the solidification temperature, the glass can be treated as an ideal fluid bearing no stress. Below this temperature, glass is solidified and behaves like an elastic material with no stress relaxation due to a high viscosity of glass.

This introduces the assumption that the temperature gradient was frozen in at $T_g$. A detail review of the instant freezing theory and its evolution was given by [3, 86, 109]. However, it has to be noted that the instant freezing theory is too rough to describe the time-temperature behavior of polymeric materials in the transition zone. Accordingly, a time-temperature dependent linear viscoelastic constitutive equation is required to describe such a behavior.

Morland and Lee [110] proposed a linear viscoelastic constitutive equation for thermorheological simple material which can be applied to a transient temperature field:

$$
\sigma_{ij} = \int_0^{\xi} \left\{ 2G(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{ij} - \frac{1}{3} \varepsilon_{kk} \delta_{ij} \right] + \delta_{ij} K(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{kk} - 3\varepsilon_{rr} \right] \right\} d\tau
$$

(2-4)

$$
\xi = \int_0^{\tau} \frac{d\tau}{a_{T}[T(\tau)]}
$$

(2-5)

where $\sigma_{ij}$ and $\varepsilon_{ij}$ are the stress and strain tensor, $G$ the shear relaxation modulus, $K$ the bulk relaxation modulus, $a_T$ the empirical shift factor, and $\xi$ is the reduced time. Muki and Sternberg [111] solved Eqs. (2-4) and (2-5) for a quenching sphere and a slab with complete lateral restraint and thus zero lateral strain during cooling (constrained quenching). Lee and coworkers [112, 113] have subsequently modified and solved the
equation of Muki and Sternberg [111] numerically for that of an infinite slab with free lateral expansion and lateral resultant force (free quenching). Narayanaswamy and Gardon [114] have applied the theory from Lee and coworkers [112, 113] to calculate the transient and residual stress during quenching of inorganic glass by using linear piecewise expansion of the convolution integral. It was found that much larger time steps can be used and more accuracy was obtained by their approximation. In addition, their prediction shows a good agreement with experiments on glass quenched from high initial temperatures but deviation was observed for initial temperatures close to the $T_g$.

The above studies consider the shift factor only a function of temperature. In fact, the shift factor is determined by the free volume [115]. It means that the shift factor can be determined by the temperature only in the equilibrium state. However, more free volume was introduced during a rapid cooling leading to so called nonequilibrium state. The additional free volume will accelerate the relaxation process. Therefore, the linear viscoelastic model should be modified with inclusion of effect of the nonequilibrium free volume. Accordingly, a concept of fictive temperature, $T_f$, was proposed by Tool [116]. Tool [116] expressed the thermal strain, $\varepsilon_T$, at any time and the rate of approaching equilibrium state according to

$$\varepsilon_T = \beta_1 (T_f - T_0) + \beta_2 (T - T_f)$$   \hspace{1cm} (2-6)
\[
\frac{dT_t}{dt} = \frac{T - T_t}{\tau}
\]  

(2-7)

where $\beta_l$ and $\beta_g$ are thermal expansion coefficients at the liquid and glassy state, respectively. The $T_0$ is the initial temperature of a quenching article and $\tau$ is the relaxation time which depends on both $T$ and $T_t$. Therefore, the $T_t$ can be considered as the temperature from which the quenching process can produce corresponding volume, $V$, at the time $t$, $V(t)$.

For polymers at temperatures between $T_g$ and $T_g + 100^\circ$C, many material properties, such as relaxation modulus, can be well described by the WLF equation [117]:

\[
\log a_T = \frac{-C_1(T - T_r)}{C_2 + T - T_r}
\]  

(2-8)

where $C_1$ and $C_2$ are material constants and $T_r$ is the reference temperature. Rusch [118] studied volume and stress relaxation of PMMA and PS and concluded that WLF equation can be applied to temperature below $T_g$ by using the effective temperature, $T_{\text{eff}}$ (which is analogous to the fictive temperature) in place of the real temperature $T$. Shyu and Isayev [119], simulated the residual thermal stresses in freely quenched PS and PC plates by using the linear viscoelastic constitutive equation proposed by Morland and Lee [110] along with the equilibrium form of Eq. (2-7) and Rusch’s effective temperature [118] in the WLF equation. They found that with inclusion of the volume relaxation effect, the predicted residual thermal stresses are about 30% less than that without considering the
volume relaxation effect. Guo and Isayev [87] have followed the same approach but combined the flow-induced crystallization kinetics to modeling of the semi-crystalline isotactic polypropylenes.

2.4.2 Photoviscoelasticity

The development of stresses during deformation is caused by the modulus of material whereas the development of birefringence during deformation is caused by the stress- and strain-optical coefficients of material [120]. The stress-optical coefficient, obtained from creep experiments, and the strain-optical coefficient, obtained from stress relaxation experiments vary not only with temperature but with time as well. This field of study is referred as photoviscoelasticity. Photoviscoelastic phenomena can be clearly observed in the glass to rubber transition zone. Brecic [121] gave a clear explanation of the phenomenological theory of photoviscoelasticity, and interested readers could refer to this book.

Gurnee et al. [122] investigated the time dependent stress-optical coefficients of PS by tensile stress relaxation and creep tests. Later, Rudd and Gurnee [123] performed tensile stress relaxation experiments on five narrow and two broad molecular weight of PS to study the effects of molecular weight and molecular weight distribution on the birefringence of PS in temperature range corresponding to the glass transition zone. The
absolute value of birefringence versus log time curves was observed to pass through a maximum. The magnitude of the birefringence is independent on molecular weight over 15400. The maximum of birefringence became larger with increase of temperature and the curves at different temperatures can not be superimposed by shifting.

Stein et al. [124] measured the dynamic birefringence of LDPE film in oscillating deformation, which showed a decrease of the strain-optical coefficient with increasing frequency. Later, Takeuchi and Stein [125] applied the time-temperature superposition to the real and imaginary parts of the dynamic birefringence at various temperatures. Onogi et al. [126] carried out the stress relaxation experiment for annealed and quenched LDPE. The curves of the strain-optical coefficient versus log time and relaxation modulus versus log time below a certain temperature can be superposed well by a horizontal shift along the abscissa. The optical shift factor obeys the WLF equation while the mechanical shift factor is much larger than the optical one. Later, Onogi et al. [127] applied the time-temperature superposition to time dependent curves of the birefringence and relaxation modulus of annealed and quenched isotactic PP at various temperatures. As in case of LDPE, the mechanical shift factor generally gives larger activation energy than the optical shift factor.
Similar to linear viscoelastic constitutive equation, the linear photoviscoelastic constitutive equation was used to describe optical response while deformation takes place. The first mathematical treatment of photoviscoelasticity was given by Mindlin in the later forties [128]. He used a four element mechanical model and assumed that the material is incompressible and only the spring parts (elastic) of the model contributes to birefringence. He obtained

\[
E - n_0^{-2} \delta = R \sigma + 2S \varepsilon + C_\epsilon \theta \delta
\]

(2-9)

where $E$ is the dielectric tensor, $n_0$, the refractive index in the unstrained state, $R$, $S$, linear differential operators of time, $\sigma$, the deviatoric stress tensor, $\varepsilon$, the deviatoric strain tensor, $C_\epsilon$, the strain-optical coefficient and $\theta$, the mean stretch. Then the mechanical-optical relationship is

\[
n_1 - n_2 = C_\sigma(t)(\bar{\sigma}_i - \bar{\sigma}_2) = C_\varepsilon(t)(\bar{\varepsilon}_i - \bar{\varepsilon}_2)
\]

(2-10)

where $n_1$ and $n_2$ are principal refractive indices, and $\bar{\sigma}_i$ and $\bar{\varepsilon}_i$ are the spatial parts of the principal stress and strain, respectively. The $C_\sigma(t)$ and $C_\varepsilon(t)$ are the stress- and strain-optical coefficient as a function of time, respectively.

Read [129-131] applied molecular theory of viscoelasticity to describe optical behavior of polymers. He derived for the oscillating strain

\[
C_\sigma^* = \frac{\Delta n^*}{\varepsilon^*} = C_\sigma^* + iC_\sigma^-
\]

(2-11)
\[ C_\sigma^+ = C_\sigma \sum_{i=1}^{v} \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \] (2-12)

\[ C_\sigma^- = C_\sigma \sum_{i=1}^{v} \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \] (2-13)

\[ C_\sigma = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} 6\pi N \frac{\alpha_\parallel - \alpha_\perp}{45} \] (2-14)

\[ C_\varepsilon^* = \frac{\Delta n^*}{\varepsilon^*} = C_\varepsilon^- iC_\varepsilon^+ \] (2-15)

where \( \Delta n^* , \varepsilon^* , \sigma^* , C_\sigma^* , C_\varepsilon^* \) are the complex birefringence, strain, stress, strain- and stress-optical coefficient, respectively, \( \omega \), the frequency, \( \tau_i \), the relaxation time of the \( i^{th} \) relaxation mode, \( \alpha_\parallel \) and \( \alpha_\perp \), the polarizability along and perpendicular to chain direction, respectively, \( \bar{n} \), the mean refractive index, \( N \), the number of molecules per unit volume. According to Read, this analysis is valid only at sufficiently low frequencies and high temperature. At high frequency and low temperature the distortional mechanism becomes significant and the theory is not applicable.

Dill [132] considered the refraction index tensor \( n_{ij} \) to be a functional of the strain (or stress) tensor. For the case of a small strain, an expansion of the functional in power series and an application of the time-temperature superposition lead to the following constitutive equation for linear photoviscoelastic materials:

\[
\begin{align*}
n_{ij} \frac{n_{kk}}{3} \delta_j &= \int_0^\tau C_\sigma(\zeta - \tau) \frac{\partial}{\partial \tau} \left[ \sigma_{ij} - \frac{\sigma_{kk}}{3} \delta_j \right] \, d\tau \\
&= \int_0^\tau C_\varepsilon(\zeta - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{ij} - \frac{\varepsilon_{kk}}{3} \delta_j \right] \, d\tau
\end{align*}
\] (2-16)
where $C_\sigma$ and $C_\varepsilon$ are the stress- and strain-optical coefficient function, respectively, $\delta_{ij}$ the unit tensor, $\sigma_{ij}$ the stress tensor, $\varepsilon_{ij}$ the strain tensor and $\xi$ is the reduced time defined by Eq. (2-5). To apply Eq. (2-16), measured stress- or strain-optical coefficient functions are required.

Later, Coleman and Dill [133] derived the relationship between the strain and refractive tensor of a “simple fluid”, of which the strain and refractive tensor are functional of the history of the deformation gradient. Priss et al. [134] proposed a mechanical model for description of viscoelastic properties of polymers in the transition zone. In their model, the elastic (distortional) and entropic (orientational) elements are connected serially. Then the nonequilibrium birefringence $\Delta n(t)$ equals to the sum of distortional $\Delta n_d(t)$ and orientational $\Delta n_{or}(t)$ contributions. The stress-optical rule [1] was assumed to be valid and generates

$$\sigma(t) = \sigma_d(t) \quad (2-17)$$

$$\Delta n(t) = \Delta n_d(t) + \Delta n_{or}(t) = C_d \sigma_d(t) + C_{or} \sigma_{or}(t) \quad (2-18)$$

where $C_d$ and $C_{or}$ are distortional and orientational stress-optical coefficients, respectively. Later, Read [135] suggested that the distortional and orientational elements should be in a parallel orientation rather than a serial combination. Therefore, according to modification from Read, the total stress becomes
\[ \sigma(t) = \sigma_d(t) + \sigma_{oe}(t) \]  

(2-19)

and Eq. (2-18) still hold true.

Inoue and coworkers [136-138] carried out dynamics and stress relaxation experiments of PS. The obtained dynamic modulus and strain-optical coefficients do not superpose rigorously by the time-temperature superposition. After applying Read’s model [135] to their analysis, the orientational and distortional parts of \( E^* \) and \( E \) can be shifted quite well. Shyu et al. [140] performed tensile stress relaxation measurements on PS and PC to obtain the master curves of the strain-optical coefficient function. The experimental temperature was varied from 66\(^{\circ}\)C to 123\(^{\circ}\)C for PS and from 123\(^{\circ}\)C to 153\(^{\circ}\)C for PC. Read’s model [135] was also applied to analyze their data. Lin and Isayev [141] applied the concept to design a new tensile device with high data acquisition rate to investigate two optical grade of PCs. Both PCs indicate similar level of the stress-optical coefficient in the glassy state and lower stress-optical coefficient in the melt state compared to that of general purposed PC observed in ref. [140].

2.4.3 Flow- and Thermally-induced Birefringence

Similar to the development of the flow- and thermally-induced stresses, the development of the flow- and thermally-induced birefringence of amorphous polymers arise from the optical anisotropy of material caused by strong flow field and rapid cooling,
respectively. This optical anisotropy in polymeric materials termed birefringence has long been recognized in the field of stress analysis [81]. In particular, flow birefringence develop when the polymer is in the fluid and rubbery state, i.e., above the glass transition temperature. Therefore, the theoretical modeling of flow-induced birefringence is directly associated with the stress-optical rule [1], since the stress-optical coefficient is a constant at the temperatures above $T_g$. The corresponding details have been mentioned in Section 2.2.

The thermally-induced birefringence is caused by the nonequilibrium density or contraction and the viscoelastic behavior of polymers during an inhomogeneous rapid cooling through the $T_g$. Such flow- and thermally-induced birefringences are essentially coupled during injection molding process. The earlier studies regarding thermally-induced birefringence are mostly carried out in freely quenched polymeric strips or slabs (without melt contacting solid wall) experiments on PS [81, 142], PMMA [81, 144, 146] and PC [140, 141, 143-145]. Such quenching gives rise to thermal birefringence in planes parallel to the thickness direction. On the other hand, birefringence does not exist in planes perpendicular to the thickness direction. In fact, these experiments have indicated that no birefringence appears when a polarized light is passed perpendicular to the thickness of the strip, thus indicating that the values of

35
birefringence in the other two planes are equal. A typical residual thermally-induced birefringence curve through the thickness of a quenched strip exhibits a parabolic shape with either a concave or convex type which depends on the behavior of the stress-optical coefficient of material. The measured thermally-induced birefringence curves of PC and PMMA indicate negative and positive values of birefringence in the surface and core region, respectively. However, PS shows negative and positive values of birefringence in the core region and surface, respectively. Since the thermal stresses in a freely quenched sample are compressive in the surface and tensile in the core region, one would expect the sign change of the stress-optical coefficient for PS as compared with the PMMA and PC. In fact, the stress-optical coefficient of PC is always positive [140, 141] due to fewer obstacles from its side group. For PMMA, the value of the stress-optical coefficient is positive for the melt and negative at room temperature [146]. The value of the stress-optical coefficient for PS is negative above $T_g$ and positive below $T_g$ [140].

Theoretical modeling of such a freely quenched strip or slab was given in Section 2.4.2. Several photoviscoelastic constitutive equations were introduced for this purpose. However, the gapwise distribution of thermally-induced birefringence introduced by constrained and free quenching is totally different [81]. Constrained quenching is performed with the sample located between two solid plates, like in injection molding.
whereas free quenching is performed without any restriction at the surface of the sample. Thus, constrained quenching is actually closer representing the cooling process in the injection molding process. However, free quenching assumption has been used to describe the thermally-induced birefringence in injection molded PS disc. A good agreement with experimental results was obtained since the thermal birefringence is significantly lower than that of the flow birefringence [147].

To precisely describe the contribution of the thermal stress and birefringence, several attempts were made concerning different boundary conditions during cooling. Over several decades, the mechanism of development of the residual thermal stress and birefringence has drawn much attention in research of injection molding process. Recently, in numerical simulation of residual thermal stress and birefringence, a combination of the constrained and free quenching conditions was mostly employed. However, the proper treatment of switching between these conditions seems to be deficient. Therefore, the following review is an attempt to summarize various assumptions and define a clear physical mechanism to the present approach.

Douven [93] considered a two-dimensional simulation of four different cases during polymer cooling: (1) constrained quenching with fluid core; (2) constrained quenching with solid core; (3) free quenching in the mold; (4) free quenching after demolding. The
existence of melt pressure was used to differentiate between the constrained and free quenching. In cases (1) and (2), the material sticks to the mold wall and the global planar displacements are zero. Accordingly, the overall through thickness strain component, $\varepsilon_z$, was preserved as

$$\int_{-c}^{c} \varepsilon_z(z)dz = 0$$  \hspace{1cm} (2-20)

When the gap between part and mold surface is created, the pressure becomes zero and the free quenching condition was applied.

Jansen [148] used an elastic solid model to analyze the differences between the free quenching and constrained quenching mechanisms. He found that in constrained quenching case, the stresses are tensile near the surfaces and proportional to the maximum melt pressure. Ghoneim and Hieber [149] attempted to predict the residual thermal stress during a constrained quenching with inclusion of density relaxation phenomena when the shift factor $a_T$ increases to a critical value $a_{Tc}$ before ejection. After ejection, the free quenching was used. When the part is partially solidified with fluid core the lateral strain, $\varepsilon_y$, for each of outer solid layers was fixed and equal to the strain at vitrification and the lateral stress, $\sigma_y$, and the volumetric strain, $\varepsilon_v$, were calculated. The through thickness strain, $\varepsilon_z$, was obtained directly from $\varepsilon_v$ at this stage. When the polymer vitrifies the $\varepsilon_z$ as well as the $\varepsilon_v$ become constrained with their values at time of
solidification. Their research indicates that the ejection time is the most significant factor to affect the thermal stress profile. As the ejection time increases, the polymer is allowed more time for the cooling in the cavity. Accordingly, the shift factor increases, causing a reducing in thickness of the hot interior region. Consequently, this inhibits further development of the residual thermal stresses in the core region after ejection. Therefore, it was concluded that the duration of constrained quenching in the cavity is the most dominant factor in development of the residual thermally-induced stress. They also indicates that the density relaxation plays an important role in the evolution of the residual thermal stress. However, no birefringence data was presented in their study.

Lee et al. [88, 150] considered the temperature of $T_g + 30^\circ C$ as a no-flow temperature [101] to switch over between the constitutive equations for liquid and solid state. When melt temperature reaches no flow temperature, the constrained quenching was employed till the pressure is non-zero at those positions in the cavity. The free quenching was applied after the pressure drops to zero. Below the no-flow temperature, the lateral strain, $\varepsilon_y$, was determined by the melt pressure $p$ and the bulk modulus $K$ as follows.

$$\varepsilon_y(z) = \frac{-p}{3K}$$

(2-21)
The through thickness stress, $\sigma_z$, was defined by the melt pressure such that

$$\sigma_z = -p$$  \hspace{1cm} (2-22)

The lateral strain remained a constant throughout the constrained quenching period (no lateral strain increment allowed), the lateral stress $\sigma_y$ and through thickness strain, $\varepsilon_z$, were then calculated. After the melt pressure drops to zero, the free quenching was employed and the lateral strain increment was allowed until the end of calculation.

From these studies, one can conclude that the key feature to describe the development of the residual thermal stress and birefringence is the temperature condition at which to switch between different constitutive equations suitable for liquid and solid state. In solid state, the constrained quenching was employed as long as the molding sticks to the mold wall as determined by the presence of melt pressure. The global volumetric strain was restricted due to the injection of an additional melt to the cavity to compensate the contraction. The free quenching was applied after the pressure drops to zero or after ejection. The approach used in the present study was based on this described mechanism. Details of algorithm will be explained later in Chapter V.

Accordingly, two distinct calculations were performed to simulate the flow and thermal stress and birefringence. The total birefringence was obtained by the summation of both contributions as indicated by refs. [86, 88, 147, 151]. The calculation for the
residual stress and birefringence was developed based on a combination of CV/FEM/FDM along with a non-linear Leonov model to the entire molding process including filling, packing and cooling stages to calculate the pressure, temperature, and stress fields. The calculated pressure and temperature fields were then imposed to simulate the thermal stress and birefringence. Similar to the refs. [147, 151], the linear viscoelastic and photoviscoelastic constitutive equation along with volume relaxation were solved simultaneously over time steps, where only free quenching was considered. The constrained quenching was employed as long as the melt pressure is non zero. The free quenching was used when the melt pressure was zero or after ejection.

2.5 Anisotropic Shrinkage

Shrinkage happened due to the densification of material. However, unlike an isotropic shrinkage occurring in the elastic materials, an anisotropic shrinkage was observed in viscoelastic materials. Therefore, the anisotropic shrinkage is one of the most important characteristics of polymeric materials in various polymer processing operations. The origin of this anisotropy is related to the orientation of molecular chains. Mechanical, optical and many other properties of polymeric products can be anisotropic due to molecular orientation. Therefore, the prediction of the anisotropic shrinkage is essential.
in producing moldings with desirable mechanical, optical properties and dimensional specification. Shrinkage predictions are influenced by the underlying calculations of density variation, orientation and heat transfer [90] for amorphous polymers. The kinetic of crystallization has to be involved in shrinkage calculations of semi-crystalline polymers [91].

The thermal expansion coefficient, compressibility and elastic modulus of oriented polymers show anisotropy related to orientation. Hellwege et al. [152] studied the relationship between the thermal expansion coefficients and draw ratio for amorphous polymers. They found that the linear thermal expansion coefficient along the draw direction, $\alpha_a$, decreases with draw ratio while the linear thermal expansion coefficient perpendicular to the draw direction, $\alpha_p$, increases. They also indicated that the anisotropy ratio $A = \alpha_a / \alpha_p$ was strongly dependent on material. The value of $A$ was found to be 1.1 and 2.5 for PS and PMMA, respectively. Henning [153] also studied the orientation effect on anisotropy of the linear thermal expansion coefficient, compressibility and Young’s modulus of stretched amorphous polymers. His results indicate that the linear thermal expansion coefficient, compressibility and Young’s modulus along the stretching direction decrease as draw ratio increases. Choy et al. [154] investigated the draw ratio and the temperature dependence on the anisotropic thermal expansion of oriented
semi-crystalline polymers. The results showed that as the draw ratio or the orientation factor increases, the thermal expansion along the stretching direction, $\alpha_a$, decreases while the thermal expansion perpendicular to the stretching direction, $\alpha_p$, increases for PP and HDPE. Besides, anisotropic thermal expansion coefficients, $\alpha_a$ and $\alpha_p$, and isotropic expansion coefficient, $\alpha_0$, increase while temperature increases. According to these studies, the orientation introduced during processing can be the main reason for occurrence of the anisotropic shrinkage in different directions.

The relationship between anisotropic shrinkage and processing conditions was observed in many researches. Generally, shrinkage is affected by processing parameters such as holding time, holding pressure, melt temperature, mold temperature and injection speed. Jansen and his coworkers [155, 156] observed that the most significant processing conditions affecting shrinkage are holding pressure and time. In addition, the effect of the melt temperature is slightly less significant than that of injection speed, while the mold temperature does not show a general trend for all investigated polymers. It was also shown that the holding time only affected shrinkage at the time before gate freeze-off [92, 156]. Van Sweden [157] investigated the anisotropic shrinkage for molding made from PP of three different molecular weights. The results indicated that shrinkage was reduced at longer holding time. In addition, higher thickness shrinkage was observed for lower
molecular weight PP and the percentage of the thickness shrinkage was always higher than percentages of the length and width shrinkage.

A rapid inhomogeneous cooling of polymeric melt through the glass transition temperature or melting temperature introduces nonequilibrium volumetric changes, and frozen-in orientation in final molded parts. To model the anisotropic shrinkage of molded parts, a thermodynamic consideration together with a flow analysis should be incorporated. Hellmeyer and Menges [158] developed a multilayer model to predict volumetric shrinkage by the equation of state. Their results indicate a qualitative agreement with experimental data. Isayev and Hariharan [159] applied the equation of state along with a one-dimensional cavity filling simulation to predict volumetric shrinkage. In addition, they performed the first order rate theory for volumetric changes in conjunction with solving a convective heat transfer boundary condition to simulate the density variation in which the rate of volumetric relaxation was assumed to be dependent on temperature using WLF equation.

Calculation of shrinkage from the PVT data is limited, since the PVT data only indicate the material behavior in the equilibrium state. Shrinkage during polymer processing is influenced by the flow and thermal history. Therefore, material shows different shrinkage along the flow and cross flow directions, as well as in the thickness
direction. Typically, the thickness shrinkage can be a factor 2 to 10 larger than the length and width shrinkages. Various approaches were developed to predict the anisotropic shrinkage. Bushko and Stokes [160, 161] used simple thermorheological constitutive equation to predict the part shrinkage, warpage and the built-up of residual stresses in injection molding process. However, the flow effects were neglected and the in-plane shrinkage was assumed to be identical. Jansen [148] was the one who recognized that the pressure effect has to be included in the analysis of shrinkage because solidification during injection molding process happened mostly under high pressure. Later, Jansen and coworkers [155, 162, 163] proposed a simple thermoelastic model with inclusion of pressure effects and Poisson ratio on the thickness shrinkage. It was assumed that no relaxation or creep can happen at temperatures below the solidification temperature and the viscoelastic effects were not considered in their model. Later, this algorithm was extended to model semi-crystalline polymers [164] by using the Halpin-Tsai [165] and Schapery [166] equation. Furthermore, Kennedy and Zheng [167] used the residual strain and stress model to calculate shrinkage coefficients from the measured linear shrinkage data. Hieber [168] used a unified formulation to model shrinkage of injection molded isotactic PP. The time-dependent thickness shrinkage was calculated prior to ejection by solving a one-dimensional governing equation for the pressure field based on modified
material constants. Kwon and Isayev [90] applied Spencer-Gilmore PVT equation of state along with a one-dimensional non-linear viscoelastic simulation of injection molding to calculate the frozen-in molecular orientation, birefringence and elastic recovery. In addition, the anisotropy of the thermal expansion and compressibility affected by the frozen-in molecular orientation were introduced to determine the anisotropy of the length and width shrinkage of molded strips of PS. Simulated anisotropic shrinkage were compared with experimental measurements obtained at different injection speeds, packing pressures, packing times, melt temperatures and mold temperatures. The results indicate that percentage of the thickness shrinkage was highest compared to the lowest in the width direction and intermediate in the flow direction. This algorithm was then extended to various semi-crystalline polymers with inclusion of kinetic of crystallization [91]. Isayev and Lin [92] implemented algorithm [90] along with Tait PVT equation of state to two-dimensional LGP moldings of two optical grade PCs and compared the simulated anisotropic shrinkage with experimental measurements obtained at various processing conditions.
2.6 Light Guide Plate (LGP)

Edge-lit backlight systems have been widely used as light sources in many portable electronic devices due to several advantages over traditional light sources. They consume less energy, are light weight, and have highly uniform intensity. The backlight industry requires low power consumption, large area with a minimal thickness, high brightness, uniform luminance, and desirable viewing angles. Typical materials used for manufacturing LGPs are optical grade polycarbonates (PC) and polymethyl methacrylates (PMMA).

A typical schematic setup of backlight module as shown in Figure 2.1 is comprised of light sources, a light-guide plate (LGP) and layers of optical sheets, such as reflection sheets, diffusion sheets and optical prism sheets. The light rays from the source are directed into the side of the LGP, sometimes both sides, and are guided inside the plate based on the total internal reflection. The rays are reflected and refracted by micro-patterns at the bottom of the LGP. The micro-patterns could be an array of ink printed white spots [169] or V-groove microstructures [170, 171]. The emanated light from the top surface of the LGP disperses by the diffusion sheet but this may weaken the brightness or produce dark fringes made by spots. Usually, two cross prism sheets are
used to collimate and enhance the light transmitted by the diffusion sheet. At the bottom
and along sides of LGP, reflection sheets are usually used to reduce the optical loss from
exposed surfaces. In order to do that, white color sheet is preferred to reflect all rays
without any absorption of visible light. To improve the reflection performance, some
inorganic filler is used to make the polyester reflection sheet as white as possible. The
major concern in the manufacturing of LGP is the ability of light transmission, termed
luminance, because the LGP needs to deliver the light from its edges to the front surface
with the highest possible luminance. Typically, a backlight consumes more than 60% of
the total energy consumption in a liquid crystal display (LCD) modules.

Figure 2.1 A typical layout of a backlight module. CCFL: Cold cathode fluorescent lamp,
LED: Light emitting diodes.
To obtain the highest possible luminance, Togaya et al. [172] developed a backlight system using a highly scattering optical transmission (HSOT) polymer with high optical quality. More recently, Okumura et al. [170] created a highly efficient HSOT backlight system not requiring optical sheets. This is not only improved optical performance, but also reduced the size of the entire backlight module. By changing the material of light-guide plate, Visser [173] applied the organic light-emitting diodes (OLEDs) instead of conventional LED, in which the brightness can be increased significantly. Feng et al. [174, 175] developed an integrated micro-compressor element on the top surface of LGP and a micro-prism element at the bottom surface. By adjusting micro-prisms’ shape, the LGP is able to control the illumination angle, and by adjusting micro-prisms’ distribution and size, the LGP can achieve a uniform intensity.

Injection molding is one of the most widely used polymer processing operations in the manufacturing of complex-shaped and thin-walled polymeric optical products due to its low cost and fast production features. During injection molding, the polymer experiences rapid deformation and extreme thermal history that affects the final mechanical and optical properties as well as the dimensional specification of the products. Accordingly, the final dimension of parts can deviate from the original mold design. A
series of experiments was performed by Han et al. [176] to investigate the effects of cavity conditions on transcription molding of microscale prisms made of PMMA. It was found that melt filling of V-grooves can be affected by the pitch, direction of groove layout, and direction of melt flow and cavity pressure during the melt filling stage. It was concluded that the transcription during the melt filling stage dominates the entire transcription process. Typically, an ideal layout of V-grooves can be optimized by an optical simulation [174, 175]. However, a relation between molding conditions and resulting luminance performance has never been reported. In this study, measurements of the depth of melt filling of V-groove structures in LGPs made of two different grades of PC as a function of molding conditions were carried out. The influence of molding conditions on degree of filling of V-grooves and luminance performance of LGPs was elucidated [177].

The goal of the present study is to understand the effects of processing conditions on the residual stresses and birefringence and resulting luminance in the injection molded LGPs. To achieve this goal, a flow simulation of the injection molding process of LGP based on a hybrid finite element/finite difference/control volume (FEM/FDM/CV) solution of a Hele-Shaw flow along with a nonlinear constitutive equation is carried out.
to predict the flow-induced residual stresses and birefringence. In addition, a combination of constrained- and free-quenching was implemented to calculate the thermally-induced birefringence of LGP moldings. The total residual birefringence was obtained by summation of the flow- and thermally-induced birefringences. Finally, a relation between molding conditions and resulting luminance performance is reported.
CHAPTER III

INJECTION MOLDING EXPERIMENTS AND PROCEDURES

3.1 Materials

Two optical grade PCs, PC OQ1030 (MFI of 12.8 g/10 min at 250°C) and PC OQ3820 (MFI of 7.4 g/10 min at 300°C), from General Electric were used in this study. The glass transition temperatures of PCs were measured by DSC (TA Instrument) at heating rate of 15°C/min. The results indicate the $T_g$ are 143.7°C, 147.6°C for PC OQ1030 and PC OQ3820, respectively, as shown in Fig. 3.1. To measure the viscosity curves of these optical grade PCs, the PC pellets were dried under vacuum at 105°C for 4 hours to remove moisture and compression molded at 250°C and 260°C for PC OQ1030 and PC OQ3820, respectively, into a disc-shaped geometry of 2 mm in thickness and 2 cm in diameter. An ARES rheometer (TA Instrument) with parallel plates was used to measure the complex viscosity curves of PCs in a frequency range from 0.04 to 100 s$^{-1}$ and strain amplitude of 4% at various temperatures as shown in Figs. 3.2 and 3.3.
Figure 3.1 Measured glass transition temperatures of PC OQ1030 and PC OQ3820.

To determine the shift factors, the obtained complex viscosity curves of each PC were shifted to a reference temperature, $T_r$, of 210°C for both PCs. The WLF equation, Eq. (2-8), with natural logarithm of shift factors was used to obtain constants of $C_1$ and $C_2$ as shown in Fig. 3.4:

$$\ln a_T = \frac{-C_1(T - T_r)}{C_2 + T - T_r}$$  \hspace{1cm} (3-1)

The obtained WLF constants were then used to fit the viscosity curves by using two modes and four modes of Leonov model for PC OQ1030 and PC OQ3820, respectively. The multimode Leonov model under steady shear flow is given by [83]
\[ \eta(\dot{\gamma}) = \eta_s + \sum_{k=1}^{N} \frac{\eta_k}{1 + X_k} \]  \hspace{1cm} (3-2)

\[ X_k = \sqrt{1 + 4\dot{\gamma}^2 \theta_k^2} \]  \hspace{1cm} (3-3)

where \( \eta_k \) and \( \theta_k \) are the \( k \)th mode shear viscosity and relaxation time, respectively. \( N \), numbers of relaxation mode, \( s \), the factor ranged from zero to 1. Eq. (3-2) was fitted simultaneously by using the nonlinear least square method [178]. Figs 3.2 and 3.3 show measured (symbols) and fitted (curves) complex viscosity of PC OQ1030 and PC OQ3820, respectively, as a function of frequency obtained by the ARES rheometer.

Typical shear thinning behavior was observed for both PCs. However, nearly one order magnitude higher viscosity of PC OQ3820 than that of PC OQ1030 at all temperatures was observed. The two modes fitting used to describe the viscosity curves of PC OQ1030 exhibits a minor deviation from experimental measurement at temperature of 170°C. This is due to insufficient numbers of relaxation mode used. However, to increase the efficiency of injection molding calculation, one would like to use as less as possible number of relaxation modes to properly describe the experimental curves. Fig. 3.4 illustrates the fitting of empirical shift factors over experimental temperature ranges.

A polystyrene, PS (Styron 615-APR/DOW), was also used in this study. Fig. 3.5 shows the complex viscosity vs. frequency given by ref. [86]. The Leonov model with
two relaxation modes was used to fit these viscosity data. All rheological parameters and physical properties used in the injection molding simulation are shown in Table 3.1. Due to the lack of experimental data on PVT behavior of the optical grade PCs, the PVT data for PC given in the MOLDFLOW database [179] by the Tait equation as shown in Figure 3.6. In addition, the PVT data for PS based on the Tait equation given by ref. [180] were used as shown in Figure 3.7. The Tait equation of state is represented as [181]

\[
v(T, P) = v_0(T) \left[ 1 - 0.0894 \ln \left( 1 + \frac{P}{B(T)} \right) \right]
\]

(3-4)

where

\[
v_0(T) = b_{l1} + b_{l2}(T - b_s) \quad \text{if} \quad T > T_l
\]

(3-5)

\[
= b_{s1} + b_{s2}(T - b_s) \quad \text{if} \quad T > T_l
\]

(3-6)

\[
B(T) = b_{3l} \exp \left[ -b_{4l} \bar{T} \right] \quad \text{if} \quad T > T_l
\]

(3-7)

\[
= b_{3s} \exp \left[ -b_{4s} \bar{T} \right] \quad \text{if} \quad T > T_l
\]

(3-8)

\[
\bar{T} = T - b_s
\]

(3-9)

\[
T_l = b_s + b_6 P
\]

(3-10)

where \(v\) is the specific volume, the superscript 0 representing the properties measured at pressure of 1 atm, and the superscript l and s representing material parameters in either liquid or solid state.
Figure 3.2 Measured (symbols) and fitted (curves) viscosity of PC OQ-1030.

Figure 3.3 Measured (symbols) and fitted (curves) viscosity of PC OQ-3820.
Figure 3.4 Measured (symbols) and fitted (curves) temperature dependency of PC OQ1030 and PC OQ3820, respectively.

Figure 3.5 Measured (symbols) and fitted (curves) viscosity of PS Styron 615 [86].
Figure 3.6 The PVT data of optical grade PC OQ1030 at various pressures curves from ref. [179].

Figure 3.7 The PVT data of PS Styron 615 at various pressures curves from [180].
Table 3.1 Material specification and parameters for PCs and PS

<table>
<thead>
<tr>
<th></th>
<th>PC-Q1030</th>
<th>PC-OQ3820</th>
<th>PS Styron 615</th>
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<td>503.0</td>
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<td><strong>Tait Equation for PC [179] and PS [86]</strong></td>
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<td>9.0E-11[141]</td>
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3.2 Data Acquisition System

The data acquisition (DAQ) systems and plug-in devices are used in a wide range of applications in laboratory and manufacturing. Typically, the DAQ plug-in devices are general purpose instruments that are suitable for measuring the variation of voltage generated by machines. In this study, an integrated system including sensors, electric charge transformer, signal conditioning device were used to generate AC voltages. A data acquisition board was used to acquire these voltages and transfer into desired physical quantities by using the National Instrument LabVIEW software [183].

3.2.1 Data Acquisition System Hardware Installation

A schematic representation of the DAQ system is shown in Figure 3.8. The arrows indicate the direction of the electric signal flow. In particular, the electric signal generated by the pressure sensor must be optimized for the input range of the DAQ board. In this system, a pressure sensor, Kistler 6171BA, mounted in the nozzle of the injection molding machine requires converting electric charge to voltage in order to generate a voltage output. A charge monitor, Kistler 5085B, was used for this purpose. The measuring range of the charge monitor is adjustable and depends on the sensitivity (in unit of pico-Columb, pC) of the applied pressure sensor. That means the measuring range has to be defined for certain types of pressure sensor. For the charge monitor, Kistler
5085B, two values “a” and “n” were used to define the measuring range according to the following formula:

\[ [pC] = \text{Measuring range [bar]} \times \text{Sensitivity [pC/bar]} = a \times 10^n \quad (3-11) \]

For the pressure sensor, Kistler 6171BA, the sensitivity is 5 pC/bar and the measuring range is 10 Volts corresponding to 2000 bar according to the manufacturing calibration sheet. Thus, this sensor generates 10,000 pC with \( a = 100 \) and \( n = 2 \). These two parameters were specified by turning a tumbler switch located on the control panel of the charge monitor.

Figures 3.8 Schematic representation of the DAQ system used in the injection molding experiments.
3.2.2 Data Acquisition System Software Installation

To communicate with the DAQ devices, the NI (National Instrument) LabVIEW 6.0 was installed along with the NI-DAQ 6.9 driver software to a Windows 98 SE platform personal computer which has an IBM compatible Pentium III 32 bits processor equipped with 256MB of physical memory. The PCI-6024E data acquisition board was inserted to an available PCI slot of the PC. The hardware setting was configured by lunching the Measurement & Automation (MAX) software. By adding the SCXI -1000 signal conditioning to the “Devices and Interfaces”, the MAX is able to detect all attached SCXI modules automatically. After that, one has to clearly define all wiring channels (physical channels) of the SCXI modules to the MAX. After all wiring channels are specified, the virtual channels can be created for real measurements according to available physical channels. In this research, two physical channels and two virtual channels were created for measuring the voltage changes of pressure sensor, Kistler 6171BA, and the screw position of injection molding machine, as seen in Fig. 3.8. Once all hardware and MAX setting were tested correctly, the changes of voltage should be detected by their corresponding virtual channels.
3.2.3 Relationship between Voltage and Physical Quantities

To obtain the relationship between the screw position and voltage, a dry run of screw motion was carried out. First, the screw was moved from zero to a full stroke and the voltage change in the full range was observed. During this observation, the voltage from 0.68 to 8.08 Volt associated with zero to full stroke, respectively, was obtained. Therefore, a minimum to maximum voltage was set to be 0 to 10 Volts in this virtual channel. Once the range was defined, the screw was moved again to arbitrary positions within zero to full stroke to record the changes of voltage corresponding to its real positions as shown in Figure 3.9. By using the linear regression, a linear relationship between the screw position and the voltage can be obtained as \( y = ax + b \), where \( y \) is the physical quantity (screw position), \( x \), the analog input signal (voltage), \( a \), the slope and \( b \) is the intercept. The obtained parameters, \( a \) and \( b \), were imposed as scaling factors to its assigned virtual channel. By using the LabVIEW, the screw position can be measured.
Figure 3.9 The relationship between screw position and corresponding voltage.

In addition, such a calibration on the virtual channel for pressure sensor is provided by the original manufacturer. The full range of voltage for pressure sensor was 0 to 10 Volts corresponding to the pressure range of 0 to 2000 bar (29007.6 psi). Therefore, to obtain a pressure reading in psi, $a = 29007.6$ and $b = 0$ are assigned to the virtual channel. Therefore, a virtual instrument (VI) can be created [183] by the LabVIEW object oriented programming to record the pressure and screw position simultaneously during the injection molding experiments.
3.3 Design of Experiments in Injection Molding of LGP

The injection molded light guide plates (LGPs) were obtained on a Van Dorn 55F screw injection molding machine at various processing conditions. The PC pellets were dried under vacuum at 105°C for 4 hours to remove moisture and placed into hopper.

3.3.1 Mold geometry and Processing Conditions

A LGP mold with two cavities was used in this study. A schematic representation of the LGP cavity is shown in Fig. 3.10. A pressure transducer, KISTLER 6171BA, was installed at the nozzle of the injection molding machine. The thickness of LGP cavity was varied along the width direction as shown in Fig. 3.11. The thickness variation was made in order to provide a concentration of light. The V-groove patterns were made on the concave side of the LGP mold. The injection molding experiments were performed under different processing conditions by varying injection speed, packing pressure, packing time, mold temperature and melt temperature. The processing conditions used are shown in Tables 3.2 and 3.3 for two PCs and PS Styron 615, respectively. A constant cooling time of 20 s was applied at all conditions.
Figure 3.10 Planar views of the cavity and sprue used in LGP molding experiments. Dimensions are given in mm.

Figure 3.11 Thickness variations along the width direction (direction y).
Table 3.2 Processing conditions for injection molding of PC OQ1030 and PC OQ3820

<table>
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<tr>
<th>Run #</th>
<th>Injection Speed cm/s</th>
<th>Packing Pressure MPa</th>
<th>Packing Time s</th>
<th>Mold Temperature °C</th>
<th>PC1030 Melt Temperature °C</th>
<th>PC3820 Melt Temperature °C</th>
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Table 3.3 Processing conditions for injection molding of PS Styron 615

<table>
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<tr>
<th>Run #</th>
<th>Injection Speed cm/s</th>
<th>Packing Pressure, MPa</th>
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<td>2.54</td>
<td>34.47</td>
<td>5</td>
<td>50</td>
<td>235</td>
</tr>
<tr>
<td>2</td>
<td>2.54</td>
<td>34.47</td>
<td>2</td>
<td>50</td>
<td>235</td>
</tr>
<tr>
<td>3</td>
<td>2.54</td>
<td>34.47</td>
<td>5</td>
<td>50</td>
<td>255</td>
</tr>
</tbody>
</table>
Figure 3.12 exhibits the pressure time traces (symbols) in the nozzle and corresponding screw positions time traces (curves) acquired by the DAQ system at different injection speeds (Runs# 1 to 3) during filling and the onset of packing stage during injection molding PC OQ1030 in LGP cavity. Three pressure curves indicate similar distinct regions during filling stage, but show different filling time resulting from the change of injection speed.

In the filling stage, the pressure starts increasing from zero to the maximum pressure at which time the cavity is filled. The shot size or volume of melt injected is determined by the difference between maximum and minimum points on screw position curve. The pressure development during the filling of runner system is completed at time corresponding to the end of plateau of pressure. The pressure increases again due to the melt passing through the gate into the cavity. The pressure increases further until the end of the filling stage due to the significant increase of resistance of flow such that more pressure is required to maintain a constant screw speed. After completion of the filling stage, the pressure quickly drops to the applied packing pressure. This pressure is maintained for duration of packing time needed to compensate the shrinkage due to cooling. In addition, it is important to note that the inertial effect of screw movement becomes more considerable as the injection speed increased. This is indicated by screw
position curves of Fig. 3.12. It means that more material is forced into the cavity with increasing injection speed, even though the shot size is set up to be a constant.

Figure 3.12 Acquired pressure traces in the nozzle (symbols) and corresponding screw positions (curves) at various injection speeds (Runs #1 to 3) during the filling and onset of packing stage during injection molding of PC OQ1030 in LGP cavity.

Figures 3.13 and 3.14 shows the pressure traces obtained by the DAQ system at various packing pressures (Runs #1, 4 and 5) and packing time (Runs #1, 6 and 7), respectively, during injection molding of PC OQ1030 in LGP cavity. Figure 3.13 indicates a similar pressure development at three different packing pressures in the filling
stage but different packing pressures in the packing stage. Figure 3.14 shows that the packing pressures quickly drop to zero at the end of the packing stage and cooling stage starts. Also, as indicated in Fig. 3.14, the packing pressure is gradually drifting over the duration of the packing time. It should be noted that pressure traces obtained at other processing conditions and materials will be compared with simulation later in Chapter V.

Figure 3.13 Acquired pressure traces in the nozzle (symbols) at various packing pressures (Runs# 1, 4 and 5) during the filling and onset of packing stage during injection molding of PC OQ1030 in LGP cavity.
Figure 3.14 Acquired pressure traces in the nozzle (symbols) at various packing times (Runs# 1, 6 and 7) during the filling and packing stage of injection molding of PC OQ1030 in LGP cavity.

3.3.2 Measurements of the Depth of V-groove Patterns

The V-groove patterns were made along the length direction, x, of the LGP mold, as shown in Fig. 3.15. The depth of the V-grooves, h(y) (y is the width direction) was a constant along the length direction. In contrast, the depth of the V-grooves in the width direction was varied. The groove pitch was 250 µm throughout the LGP, as indicated in Fig. 3.15.
Figure 3.15 Schematic representation of V-grooves in a LGP mold.

The actual depth of V-grooves along the width direction was measured by a MicroProf optical profiler (FRT of America). Figure 3.16 shows the measured curvature as described in Fig. 3.11 with zigzag shapes of V-groove pattern along the width direction. Figure 3.17 indicates the measured depth of V-groove variation in the width direction on the concave side indicated by Fig. 3.16. A linear relationship was used to describe the depths of V-groove \( h(y) \) in the width direction. The results indicate lower depth at the position where the light comes in and gradually increased in the width direction. It is seen that the depth of V-grooves increases linearly in the width direction. This implies that the angle of each V-groove becomes sharper with distance in the width direction. A sharper
angle and a deeper V-groove are required to deliver the light at positions further away from the light source.

Figure 3.16 A curvature of the LGP mold and V-groove pattern along the width direction measured by the FRT optical profiler.
3.4 Measurements of Melt Front Propagation

The measurements of melt front propagation provide useful information of injection molding process, such as determination of the switch over or cutoff position in the filling stage to avoid overfilling of material. In particular, for complicated cavity geometry, the measurements of melt front propagation can help an engineer to understand the formation of welding line, jet flow, air trap and so on. This information can be further utilized to improve the mold design especially for determining the location of gate.
Experimentally, the measurements of melt front propagation can be made by conducting a series of short shots. However, it is usually difficult to carry out such measurements for a huge or multiple cavities. Therefore, a numerical simulation of the melt front propagation appears to be a reasonable way to avoid problems in injection molding and generation of waste.

To compare the simulated trace of melt front propagation throughout the cavity of the LGP mold, a series of short shot experiments were carried out in this study. An injection speed of 2.54 cm/s and a mold temperature of 100°C were used for short shot experiments of PC OQ3820 at a melt temperature of 280°C. The corresponding melt filling time was determined from the screw position that was measured from the data obtained by the real time data acquisition system, as described in Section 3.2. The resulting filling time are listed in Table 3.4.

Table 3.4 Corresponding filling time for short shot experiments of PC OQ3820

<table>
<thead>
<tr>
<th>Run</th>
<th>Materials</th>
<th>PC-OQ3820 Filling time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.2629</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.2997</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.3321</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.3768</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.4182</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.4677</td>
</tr>
</tbody>
</table>
The prepared short shot samples were mounted on an optical rail along with a digital camera Sony Cybershot T10 to ensure obtaining of undistorted pictures. The obtained pictures of short shot experiment were converted into negative films to make the edge of moldings to be highly visible by commercial graphic software Photoshop 6.0, as shown in Figure 3.18. Fig. 3.18 shows the picture of melt front propagation in negative film related to the processing condition Run #6 of PC OQ3820. The planar coordinates of the trace of melt front can be read from the Photoshop 6.0 software. The resulting measurements of melt front propagation at various short shots are shown in Figure 3.19.

Figure 3.18 Negative form of a picture of melt front propagation prepared at a condition of Run #6 of PC OQ3820.
Figure 3.19 Measured traces of melt front propagation in the cavity of the LGP mold at conditions from Run#1 to Run#6. The distance between two filled circles represents the position of a fan gate.

Figure 3.19 indicate the measured traces of melt front propagation during the filling of the LGP cavity. The PC melt starts propagating from the gate which is represented by filled circles in the Fig. 3.19. The melt front was then propagated until the entire cavity was filled. This is due to the LGP cavity is nearly a rectangular shape without significant
changes in thickness. These results will be used later in order to compare them with the simulated melt front propagation.

3.5 Measurements of Residual Birefringence

To measure the birefringence distribution of LGP moldings, a polarized optical microscope of Leitz Laborlux 12POL S was used. It was equipped with a 4\textsuperscript{th} and 30\textsuperscript{th} order compensator (Leitz Laborlux) to measure the optical retardation. The specimens were prepared by cutting a slice about 500\textmu m of thickness from the LGP moldings at the positions under investigation by using a diamond saw (Buehler Isomet). A constant cutting speed of 60 rpm and an oil bath were applied during cutting to avoid additional heat which may cause accelerating relaxation of birefringence. Two transverse optical retardations were obtained from these slices. Also, the normal retardation was measured directly by the polarized optical microscope without cutting the moldings. A schematic representation of three measured birefringence components is shown in Fig. 3.20.

Once the optical retardations were obtained the thickness of sample was measured by a micrometer (Mitutoyo). The birefringence was determined as

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

(3-12)

where \( \Gamma \) is the measured optical retardation and the \( c \) is thickness of sample.
Figure 3.20 Schematic representations of three birefringence components measured in this study. The solid arrows indicate the direction of polarized light.

3.6 Measurements of Anisotropic Shrinkage

The dimensions of LGP moldings in the length and width direction were measured by a Digimatic caliper (Mitutoyo) and in the thickness direction by a Digimatic micrometer (Mitutoyo). To calculate the percent shrinkages, the difference between part and mold dimensions were divided by the mold dimensions. The thickness profile of the mold was determined by the MicroProf optical profiler (FRT of America) as indicated in Fig. 3.11. The thickness shrinkage was measured at the portion of the highest thickness.
3.7 Finite Element Mesh

The numerical simulations of injection molding process of LGP were carried out by the CV/FEM/FDM scheme using a Compaq Visual FORTRAN version 6.2 of scientific language compiler. A personal computer equipped with a single core Pentium IV 2.8GHz CPU and 1GB of physical memory was used to perform all calculations in a Windows XP platform. The two-dimensional triangular finite element mesh was created over the mold cavity and a fan gate entrance. The one-dimensional tube element was used for the entire delivery system (nozzle, sprue and runners). The total number of elements including one- and two-dimensional elements was 676 and the total number of nodes was 381, as shown in the Figure 3.21. The thickness direction was discretized by 40 nodes equally spaced throughout the cavity and delivery system for the finite difference calculation. The thickness variation of mold cavity is shown in Figure 3.11. In particular, the density of mesh was determined through trial tests until simulations indicating minor variations.
Figure 3.21 Finite element mesh: two-dimensional triangular elements in the mold cavity including a fan gate, and one-dimensional tubular elements in the delivery system used in simulations. unit: (mm). The letters A, B and C indicate the locations of measuring transverse birefringence. The letter D indicates the location of measuring thickness shrinkage.
PCs have been widely used in a variety of optical components by various molding processes. Three components of birefringence introduced by frozen in molecular orientation leads to optical anisotropy which may induce a polarization shift and polarization dependent loss lowering the optical performance [184]. Therefore, a minimization of residual birefringence of optical components is required. Some modifications of the chemical structure of PCs by substitution of different side chain groups have been made. Such modifications change their stress-optical coefficients in solid and melt states allowing one to reduce the residual birefringence [185-189]. However, optical behavior in the glass transition region, which may have significant effect on birefringence development, was not considered in these studies. The phenomenological theory of linear viscoelasticity was applied to optical behavior of amorphous polymers by Osaki and Inoue [136]. They provided relations between the
time-dependent stress- and strain-optical coefficients and the birefringence during the stress relaxation at constant strain, creep, oscillatory deformation, constant strain rate and recoil. Also, Hwang et al. [190] measured the birefringence at small-amplitude oscillatory tensile strains and obtained the complex Young’s modulus and the complex strain-optical coefficient for one specific grade of bisphenol-A PC in the transition region from the rubbery to the glassy state. They also reported values of the stress-optical coefficient in the glassy and rubbery states.

The effect of processing conditions on frozen-in birefringence of plastic components has been investigated by many researchers [3, 86, 191]. The birefringence in molded parts appears to be from two main sources. The first is the flow-induced birefringence introduced by melt flow during the mold filling process. The second source is the thermal birefringence due to a non-equilibrium volume contraction during the rapid cooling of the melt. As cooling progresses, the thermal stresses and birefringence develop and become residual when the polymer vitrifies. Thermal equilibrium is not able to reach during processing because of the high temperature gradients and cooling rates. The additional non-equilibrium volume that is generated provides more room for molecular motion leading to volume relaxation. Therefore, the non-equilibrium free volume should be
included in the WLF equation based on the free volume approach in calculation of the thermal birefringence. In addition, the time-dependent volume relaxation should also be taken into account.

Due to the complexity of photoviscoelastic behavior of polymers during transformation from the glassy to the melt state over a wide range of temperatures, there is no constitutive equation which is able to describe the overall material responses in the fluid, rubbery and glassy states and in the glass transition region. However, it is feasible to separately consider material behavior in the fluid and rubbery states and in the transition region from the rubbery to the solid state using available constitutive equations. In our previous research [86, 140], a methodology was developed to calculate the transient frozen-in thermal stress and birefringence from both mechanical and optical functions of polymers.

In the present study, simultaneous stress and birefringence relaxation experiments over a wide range of temperatures were performed to determine the relaxation modulus and strain-optical coefficient functions for two optical grades PCs in the glass transition region. Our new data will be compared with the results of earlier studies on a commercial grade of polycarbonate (PC) [86, 140]. It should be noted that such data is required for
modeling of the performance of optical components, but are not readily available in literature for optical grades PCs. These functions are then used to predict the residual birefringence in freely quenched plates by using a model based on viscoelasticity and photoviscoelasticity [86, 119] including volume relaxation. In particular, the volume relaxation was based on the first-order rate equation [118].

4.1 Linear Viscoelasticity and Photoviscoelasticity

For the case of linear photoviscoelastic materials, Dill [132] in 1964 considered the refraction index tensor $n_{ij}$ to be a functional of the strain (or stress) tensor. For the case of small strains, an expansion of the functional in power series and an application of time-temperature superposition lead to the following constitutive equation for linear photoviscoelastic materials:

$$n_{ij} - \frac{n_{kk}}{3} \delta_{ij} = \int_0^\xi C_\sigma(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \sigma_{ij} - \frac{\sigma_{kk}}{3} \delta_{ij} \right] d\tau = \int_0^\xi C_\varepsilon(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{ij} - \frac{\varepsilon_{kk}}{3} \delta_{ij} \right] d\tau \quad (4-1)$$

where $C_\sigma$ is the stress-optical coefficient, $C_\varepsilon$ is the strain-optical coefficient, $\delta_{ij}$ is the unit tensor, $\sigma_{ij}$ is the stress tensor, $\varepsilon_{ij}$ is the strain tensor and $\xi$ is the reduced time which is defined as:

$$\xi = \int_0^\tau \frac{1}{C_\sigma} \left( \sigma_{kk} - \frac{\sigma_{kk}}{3} \right) d\tau$$
\[
\xi = \int_{0}^{t} \frac{d\tau}{a_{T}^{*} T(\tau)}
\]  \hspace{1cm} (4-2)

where \(a_{T}^{*}\) is the shift factor.

In the case of one-dimensional stress relaxation and creep experiments, Eq. (4-1) becomes

\[
\Delta n = n_{11} - n_{33} = \int_{0}^{t} \xi C_{\sigma}(\xi - \tau) \frac{d}{d\tau} \left[ \sigma_{11} - \sigma_{33} \right] d\tau = \int_{0}^{t} \xi C_{\varepsilon}(\xi - \tau) \frac{d}{d\tau} \left[ \varepsilon_{11} - \varepsilon_{33} \right] d\tau
\]  \hspace{1cm} (4-3)

\(C_{\varepsilon}(t)\) can be determined through stress relaxation experiments at a constant step strain, \(\Delta \varepsilon_{11}\). Assuming a constant Poisson’s ratio, \(\nu\), for PC in Eq. (4-3), the time-dependent birefringence function \(\Delta n(t)\) at a constant temperature can be used to determine the value of \(C_{\varepsilon}(t)\)

\[
C_{\varepsilon}(t) = \frac{\Delta n(t)}{(1 + \nu) \Delta \varepsilon_{11}}
\]  \hspace{1cm} (4-4)

By applying a linear viscoelastic constitutive equation, the stress-optical coefficient function, \(C_{\sigma}(t)\), can be obtained from the measured strain-optical coefficient function, \(C_{\varepsilon}(t)\), and the shear relaxation modulus function, \(G(t)\), by an inverse of the convolution integral [86, 119]:

\[
C_{\varepsilon}(t) = 2 \int_{0}^{t} G(t - \tau) \frac{dC_{\sigma}(\tau)}{d\tau} d\tau + 2C_{\sigma}(0)G(t)
\]  \hspace{1cm} (4-5)

86
The shear relaxation modulus function $G(t)$ is related to the Young’s relaxation modulus function, $E(t)$, obtained in a stress relaxation experiment in tension.

$$G(t) = \frac{E(t)}{2(1+v)} \quad (4-6)$$

It should be noted that one needs to apply Eq. (4-5) in order to obtain $C_\sigma(t)$ from creep experiment which is not easy to perform. Therefore, a more convenient form of Eq. (4-5) has been derived to obtain the stress-optical coefficient function from both the strain-optical coefficient function and the shear relaxation modulus function, as follows:

$$C_\sigma(t) = \frac{1}{2} \left[ \int_0^t C_\epsilon(t-\tau) \frac{\partial J(\tau)}{\partial \tau} d\tau + C_\epsilon(t)J(0) \right] \quad (4-7)$$

To apply Eq. (4-7), the creep compliance function, $J(t)$, is required. However, to obtain this function, a constant stress imposed is needed which is not easy to perform experimentally. Accordingly, an interrelation connecting the stress relaxation modulus, $G(t)$, and the creep compliance, $J(t)$, is desired to find the creep compliance function from the available stress relaxation modulus function. However, these functions are not simply reciprocal of each other. In fact, it was shown that [192]

$$G(t)J(t) \leq 1 \quad (4-8)$$

Therefore, to obtain the creep compliance, the theoretical interrelations between the step responses are [192]
\[
P(t) = t = \int_0^t G(t - \tau)J(\tau) \, d\tau = \int_0^t G(t)J(t - \tau) \, d\tau \tag{4-9}
\]

The convolution integrals of Eq. (4-9) can be solved numerically by the method proposed by Hopkins and Hamming [193, 194]. In this method, the interval of integration is divided into subintervals which are small enough so that the target function over the subinterval can be taken out of the integral. If \( G(t) \) is given by a set of experimental data \( G(t_i) \), then the Eq. (4-9) can be divided into \( n \) equally spaced subintervals and leads to

\[
P(t_n) = t_n = \sum_{i=1}^{n} \int_{t_{i-1}}^{t_i} G(t_n - \tau)J(\tau) \, d\tau \tag{4-10}
\]

where \( t_0 = 0 \). If the interval \( t_i-t_{i-1} \) is chosen so that \( J(\tau) \) does not vary significantly over its range, then \( J(\tau) \) can be taken out from under the integral sign with a mean value \( J(t_{i-1/2}) \) at

\[
t_{i-1/2} = (t_i + t_{i-1}) / 2 \tag{4-11}
\]

Therefore, the Eq. (4-10) becomes

\[
t_n = \sum_{i=1}^{n} J(t_{i-1/2}) \int_{t_{i-1}}^{t_i} G(t_n - \tau) \, d\tau \tag{4-12}
\]

The original version proposed by Hopkins and Hamming was using the trapezoidal rule to discretize Eq. (4-12). For that reason, that algorithm can be only apply when the \( G(t_i) \) are equally spaced on the time axis, which is realistically difficult to perform. Instead, if one sets \( \xi = t_n - \tau \), then it leads to

\[
t_n = -\sum_{i=1}^{n} J(t_{i-1/2}) \int_{t_{i-1/2}}^{t_i} G(\xi) \, d\xi
\]

\[
= J(t_{n-1/2}) \int_0^{t_{n-1/2}} G(\xi) \, d\xi - \sum_{i=1}^{n} J(t_{i-1/2}) \int_{t_{i-1/2}}^{t_{i-1}} G(\xi) \, d\xi \tag{4-13}
\]
Separating the $n^{th}$ term from Eq. (4-13) will result in

$$J(t_{n-1/2}) = t_n + \sum_{i=1}^{n-1} J(t_{i-1/2}) \int_{t_{i-1/2}}^{t_{i-1/2}} G(\zeta) d\zeta$$

(4-14)

Therefore, the integrations from Eq. (4-14) can be evaluated by performing the numerical integration of the $G(t)$ versus time curve and obtain a list of integration values corresponding to each time point. By using interpolation between any two time points, these integrations can be obtained without requiring equally spaced.

By performing this calculation, the stress-optical coefficient function $C_\sigma(t)$ can be obtained from known functions $G(t)$ and $C_\varepsilon(t)$ that can be measured by carrying out a simultaneous stress and birefringence relaxation experiments. In order to use Eq. (4-7), the master curve of the shear relaxation modulus and the strain-optical coefficient functions need to be obtained. Then, Eq. (4-6) can be used to convert the Young’s relaxation modulus to the shear relaxation modulus. The function $C_\varepsilon(t)$ can be determined by Eq. (4-4). By applying the Prony’s series, one can fit both curves into analytical functions, $G(t)$ and $C_\varepsilon(t)$, with a certain number of relaxation modes by using Levenberg-Marquardt chi-square scheme [178]. However, a conventional chi-square scheme can result in a negative modulus which has no physical meaning. Accordingly, a
sign control method [195] was incorporated into this chi-square scheme to guarantee that all modulus values are positive. Then, to obtain the stress-optical coefficient function, $C_\sigma(t)$, over a wide range of time, the convolution integral of Eq. (4-7) can be evaluated by the Gauss quadrature [178, 196].

4.2 Free Quenching of Slabs

To predict the thermally-induced birefringence in freely quenched slabs, a one-dimensional transient heat transfer equation and volume relaxation are used.

4.2.1 Governing Equations

To solve a one-dimensional transient heat transfer problem, the following initial (IC) and boundary (BC) conditions are considered:

\[
\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2}
\]

**IC:** \( t = 0 \); \( T = T_i \)

**BC:** \( z = \pm c \), \( -k \frac{\partial T}{\partial z} = h(T - T_q) \)  
\( z = 0 \), \( \frac{\partial T}{\partial t} = 0 \)  

(4-15)
where \( \rho, C_p, k \) and \( h \) are the density, the heat capacity, the thermal conductivity and heat transfer coefficient, respectively, and \( T_i \) and \( T_q \) are the initial and quenching temperature.

The linear viscoelastic constitutive equation in a non-isothermal process is given as follows:

\[
\sigma_{ij} = \int_0^z \left[ 2G(\xi - \tau) \frac{\partial}{\partial \tau} \left( \varepsilon_{ij} - \frac{1}{3} \varepsilon_{kk} \delta_{ij} \right) + \delta_{ij} K(\xi - \tau) \frac{\partial}{\partial \tau} \left( \varepsilon_{kk} - 3\varepsilon_{T} \right) \right] d\tau
\]

(4-16)

Here, \( \varepsilon_T \) is the thermal strain and \( K \) is the time dependent bulk modulus function.

### 4.2.2 Free Volume and Modified WLF Equation

The thermal strain \( \varepsilon_T \) including volume relaxation in a nonisothermal process can be described as follows [118]:

\[
\frac{d\varepsilon_T}{dt} = \alpha_g \frac{dT}{dt} - \frac{\varepsilon_T - \varepsilon_{Te}}{\tau_a \tau_r}
\]

(4-17)

where \( \varepsilon_T \) and \( \varepsilon_{Te} \) are the actual and equilibrium thermal strain, respectively, at temperature \( T \). The value of \( \tau_r \) is the volume relaxation time at reference temperature \( T_r \), with \( \alpha_g \) being the modified shift factor for the volume relaxation and \( \alpha_g \) is the linear expansion coefficient in the glassy state.

The modified form of the WLF equation is:
\[ \log a_r = \frac{-C_1(T_{\text{eff}} - T_r)}{C_2 + T_{\text{eff}} - T_r} \quad (4-18) \]

where \( T_{\text{eff}} \) is the effective temperature, corresponding to the temperature when an equilibrium state has the same amount of free volume as the non-equilibrium state. This temperature is related to the actual temperature through

\[ T_{\text{eff}} = T + \frac{\varepsilon_T - \varepsilon_{T_2}}{\alpha_1 - \alpha_g} \quad \text{if} \quad T \geq T_2 \quad (4-19) \]

\[ T_{\text{eff}} = T_2 + \frac{\varepsilon_T - \varepsilon_{T_2}}{\alpha_1 - \alpha_g} \quad \text{if} \quad T < T_2 \quad (4-20) \]

The equilibrium thermal strain is given as:

\[ \varepsilon_{Te} = \alpha _1 (T - T_1) \quad \text{if} \quad T \geq T_2 \quad (4-21) \]

\[ \varepsilon_{Te} = \alpha _1 (T_2 - T_1) + \alpha _g (T - T_2) \quad \text{if} \quad T < T_2 \quad (4-22) \]

where \( \alpha_1 \) and \( \alpha_g \) are the thermal expansion coefficients in the liquid and glassy states, respectively. \( T_2 \) is the glass transition temperature observed at infinitely slow cooling rate. This temperature can be determined by the WLF equation as follows. The free volume, \( V_f \), is defined as the difference of total macroscopic volume, \( V \), and the actual volume, \( V_0 \).

\[ V_f = V - V_0 \quad (4-23) \]
The relationship between the viscosity and the free volume using Doolittle’s semi-empirical equation is [197]:

\[ \log \eta = \log A + B \left( \frac{1}{f} - 1 \right) \]  \hspace{1cm} (4-24)

where \( A \) and \( B \) are constants and \( f \) is the fractional free volume defined as \( V_f/V \). By using linear viscoelasticity, the shift factor is defined as:

\[ \log a_T = \log \left[ \frac{\eta(T)}{\eta(T_r)} \right] = \log \left[ \frac{\tau(T)}{\tau(T_r)} \right] \]  \hspace{1cm} (4-25)

where \( \eta \) and \( \tau \) are viscosity and relaxation time, respectively. Then, Eq. (4-24) can be substituted into Eq. (4-25) to obtain

\[ \log a_T = B \left[ \frac{1}{f(T)} - \frac{1}{f(T_r)} \right] \]  \hspace{1cm} (4-26)

From the PVT behavior of amorphous polymers, it is reasonable to assume that the equilibrium fractional free volume increases linearly with temperature at temperatures larger than \( T_2 \). Then the fractional free volume becomes

\[ f = \alpha_1 (T - T_2) \]  \hspace{1cm} (4-27)
where $\alpha_f$ is the thermal expansion coefficient of the fractional free volume above $T_2$.

Substituting Eq. (4-27) into Eq. (4-26) results in

$$
\log a_f = \frac{-B(T - T_f)}{\alpha_f (T_r - T_2)[(T_r - T_2) + T - T_r]} = \frac{-C_1(T - T_r)}{C_2 + T - T_r}
$$

(4-28)

Accordingly, once the WLF equation is obtained, $T_2$ can be calculated as $C_2 - T_r$.

Then, Eq. (4-3) and Eq. (4-16) can be used to evaluate the thermal birefringence. However, according to Eq. (4-18), the shift factor will become infinity when $C_2$ is equal to $T_r - T_{\text{eff}}$. For this reason, an additional assumption has to be made concerning the effective temperature if the current temperature is less than $T_2$. Although in Eq. (4-18) the reference temperature can be chosen arbitrary, the effective temperature introduced is below $T_g$ since the additional non-equilibrium free volume appears in temperature range between $T_g$ to $T_{\text{eff}}$. For that reason, the reference temperature $T_r$ in Eq. (4-18) was chosen as $T_g$.

4.3 Measurement of Stress-Optical Coefficient Function

In this study, two optical grade PCs, Lexan PC OQ1030 (MFI of 12.8 g/10 min at 250°C) and PC OQ3820 (MFI of 7.4 g/10 min at 300°C) from General Electric Company,
have been used to obtain master curves for both the relaxation modulus and strain optical coefficient functions.

4.3.1 Experimental Setup

The glass transition temperatures of these two polycarbonates, measured by DSC at 15°C/min, are 143.7°C and 147.6°C for PC OQ1030 and PC OQ3830, respectively. PC pellets were dried at 105°C for 4 hours, then compression molded into a plate with dimensions of 220×220×2 mm³ at a temperature of 230°C. The plate was extremely slow cooled down to the room temperature. Dumbbell specimens of a size of 2×7.0×62.5 mm³ with a gauge length of 35 mm were cut from these compression molded plates using a Tensilkut machine (model 10-23/Sieberg Industries). The specimens were annealed in an oven at 140°C for the duration sufficient enough to remove the residual stresses from molding and cutting in order to obtain residual birefringence-free or stress-free samples. To ensure that the residual birefringence was removed completely, the annealed sample was placed between a polarizer and an analyzer of a polarized optical microscope (Laborlux POL/Leitz Wetzlar). A birefringence free sample shows a completely dark field over a full rotation of the sample.
Figure 4.1 and 4.2 show a schematic representation and a photo of the mechanical optical system used to conduct the relaxation experiments, respectively. The Minimat (Miniature Materials Tester/Polymer Laboratories) tensile test machine has been used to impose a constant strain in the range of 0.5 to 3.5% at a crosshead speed of 60 mm/min. A heating chamber is used to maintain the desired temperature which varied from room temperature to a temperature close to the glass transition temperature. Two load cells (beams) of 20N and 200N capacities with a LVDT (Sangoma) are used to measure the force as a function of time. A polarized He-Ne laser light source (wavelength $\lambda = 632.8$ nm, OEM2P/Aerotech) passes through a filter and a pin hole in order to reduce the beam size and obtain a better resolution of intensity. The plane polarized light is then passed through the transparent heating chamber of the Minimat tensile test machine to the sample and an analyzer (Glan Thompson polarizer, 03PTH101/Melles Griot) subjected to rotation under a constant speed of 60 rpm. The resulting intensity was detected by a photomultiplier (71823/Oriel). All signals were collected by a data acquisition system (DI-720/Dataq) and digitally recorded by a computer. A data sampling rate of 25 points per second was used to record both light intensity and force at the same time.
Figure 4.1 Setup for carrying out relaxation experiments for simultaneous measurements of both relaxation modulus and strain optical coefficients. PL: polarized He-Ne laser; F: filter and pin hole; M: Minimat testing frame; S: sample; MD: machine direction; RP: motor-driven constant speed rotating polarizer; PM: photo-multiplier

Figure 4.2 A photograph of the real measuring device setup.
4.3.2 Calibration Procedures

The data acquisition system (DI-720/Dataq) is used to convert the input voltages to physical quantities similar to the NI-DAQ system as mentioned in Section 3.2. Therefore, to obtain a desired physical quantity output, the following calibration procedures are required prior to experiments.

4.3.2.1 Light Intensity Calibration

The calibration of light intensity is straightforward, because the absolute light intensity measured by the photomultiplier is directly proportional to the output voltage. Therefore, at first all environmental light sources were turned off and the laser was turned on to allow the laser beam passing through optical setup. Then, rotating the analyzer to the position perpendicular to the polarizer, a zero absolute light intensity was obtained. Then, by starting the DI-WinDaq software, input the value of zero at “Low Calibration” menu of the assigned light intensity channel (channel 20 by default).

Then, rotating the analyzer to the position parallel to the polarizer, a certain maximum value of light intensity was obtained. By adjusting the gain knob on the front panel of the photomultiplier, the measured light intensity value was changed by the defining of gain value. It is recommended to adjust the resulting value of light intensity to around 9 to 11 units from the photomultiplier to reach a certain level of resolution. Then,
the value of light intensity measured from photomultiplier was input to “High Calibration” menu of the light intensity channel. By rotating the analyzer to any arbitrary position, one can observe the light intensity values between the readings on the digital panel of the photomultiplier and the output of DI-WinDaq to verify the consistency of calibration.

4.3.2.2 Force Calibration

Before calibration of force, a blank test for the consistency of time response between data acquisition system and the Minimat are compared, as shown in Figs. 4.3 and 4.4. Fig. 4.3 displays the real time response acquired by the DI-720/Dataq compared to that imposed by the stepper motor controlling by the Minimat. Such test was carried out at a displacement of 3 mm by setting up cross head speed of 5, 10, 20, 30, 45, 60, 75 and 90 mm/min, respectively. Fig. 4.4 exhibits the real time response acquired by the DI-720/Dataq compared to the time imposed by the stepper motor at a cross head speed of 60 mm/min to set up displacements of 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 mm, respectively. Both results indicate that the real time response measured by the DI-720/Dataq system is accurate and independent on the Minimat setup.
Figure 4.3 Real time response acquired by the DI-720/Dataq compared to the time imposed by the stepper motor at a displacement of 3 mm at various speeds.

Figure 4.4 Real time response acquired by the DI-720/Dataq compared to the time imposed by the stepper motor at a speed of 60 mm/min at various displacements.
Since the force measured by the Minimat device is determined by the deflection of load beam, its calibration is required. To do such a calibration, a spring was used. The spring constant was determined by loading known weights on this spring and comparing the resulting force to the force measured by the Instron tester.

First, the Instron tester was used to clamp one end of the spring. By placing different known weights on the free end of the spring, the elongations were measured by the Instron tester equipped with a strain gauge. Then, a spring constant was obtained by means of the linear regression of dependence of the imposed force versus measured elongation as shown in Fig. 4.5. The slope indicates the spring constant and the intercept exhibits the yield force of the pre-stressed spring.

This spring with determined rigidity constant can now be used as a reference to calibrate the force output from the Minimat tester. First, the spring was placed and clamped in the perpendicular orientation to the load beam of the Minimat tester. By setting various displacements from 1.0 to 5.0 mm with increments of 0.5 mm, the measured force from the digital panel of Minimat was read. The results are shown in Fig. 4.6 exhibiting the measured force of Minimat tester versus displacement before scaling. Clearly, Minimat indicates lower force values compared to line obtained by calibration of spring.
Figure 4.5 Line shows the linear regression of dependence of the imposed forces versus measured elongations for spring.

Figure 4.6 Comparison of forces imposed by the pre-calibrated spring and measured by the Minimat tester.
Therefore, the measured force from Minimat was multiplied by an empirical constant of 1.150 determined from calibration. The measured data points were shifted to match the spring calibration line, as shown in Fig. 4.7. Accordingly, this constant was used as a calibration factor for the Minimat control box. For the detail of how to specify such a calibration factor into the control box one should refer to the Minimat operation manual. Now, the force reading from the digital panel of the Minimat coincides with the spring calibration line.

![Diagram](image)

Figure 4.7 Determination of the calibration factor for the Minimat was obtained by empirical shifting the measured forces to match the spring calibrated line.
A similar calibration procedure for the light intensity has to be carried out in order to input calibration factor into the DI-720/Dataq.

To calibrate the channel of the DI-720/Dataq for force measurement, the measured force of the Minimat was used as a reference. First, the elongation of spring at 5 mm was imposed and the measured force from Minimat was input at “High Calibration” menu of the force channel (channel 17 by default). Then the elongation was changed to 1.5 mm and the measured force from Minimat was specified at “Low Calibration” menu of the force channel. An elongation of 1.5 mm was chosen to avoid the measured force being close to the yield force indicated by the pre-stressed spring. At this stage, the calibration of force and light intensity channels were completed. It has to be noted that the above procedure was performed on the load beam with a capacity of 20 N. In order to calibrate the load beam of higher capacity, a stronger spring should be used and the above procedures should be repeated. Due to the lack of higher rigidity spring, the same spring was used to calibrate a load beam of 200 N capacity used in this study.

In addition, the displacement of Minimat was calibrated by setting different displacements from the Minimat control box. A Digimatic caliper (Mitutoyo) was used to measure displacements and no differences were observed between the Minimat reading and reading from the caliper.
4.3.3 Transmission Method

To measure the birefringence, the transmission method [198] is applied. For a non-scattering, non-absorbing birefringent sample, the monochromatic light intensity detected after crossed polarizers with their polarization axes at 45° to the optic axis or the machine direction of the samples is given by

\[
T_{\perp}(t) = \frac{I_\perp}{I_\perp + I_\parallel} = \sin^2 \left( \frac{\pi R(t)}{\lambda} \right)
\]

\[
T_{\parallel}(t) = \frac{I_\parallel}{I_\perp + I_\parallel} = \cos^2 \left( \frac{\pi R(t)}{\lambda} \right)
\]

(4-29)

where

\[
I_\perp + I_\parallel = I_0
\]

\[
T_{\perp} + T_{\parallel} = 1
\]

(4-30)

where \( R(t) \) is the retardation function of the sample given by

\[
R(t) = c\Delta n(t)
\]

(4-31)

where \( c \) is the thickness of the sample and \( \Delta n \) is the birefringence at the wavelength of monochromatic light \( \lambda \). In addition, \( I_\perp \) and \( I_\parallel \) represent the absolute intensity values measured at the cross and parallel orientation of polarizer. However, values of \( I_\perp \) and \( I_\parallel \) depend on the gain factor of the photomultiplier. Thus, values of \( T_{\perp} \) and \( T_{\parallel} \) representing
the relative values of intensity, ranging from 0 to 1, were used in calculating the retardation function, \( R(t) \), according to Eq. (4-29).

To determine values of \( T_\perp \) and \( T_\parallel \), the polarizer and analyzer is positioned at 45° and -45° before starting the experiment, as shown in Figure 4.1. Then, a strain is imposed on the birefringence-free sample causing the development of retardation. Number of waves included in the retardation response is determined from the light intensity during stretching. After the stretching reaches the required strain value, rotation of the analyzer was initiated to measure the value of \( I_\perp \) and \( I_\parallel \). A transmission-time plot was obtained by means of Eq. (4-29). By using Eqs. (4-29) to (4-31), the birefringence \( \Delta n(t) \) was determined.

Figure 4.8 shows typical curves of measured force and intensity versus time during the stretching and relaxation stages. As seen from Fig. 4.8, at the cessation of stretching a retardation of about \( \frac{5}{8} \) wavelengths was developed in the sample. In less than 1 s after the cessation of stretching, the rotation of the analyzer was imposed and the light intensity was measured. The maxima and minima of the light intensities in Fig. 4.8 corresponds to values of \( I_\perp \) and \( I_\parallel \) from which the variation of \( I_o = I_\perp + I_\parallel \) was determined. Then, the measured intensity curves, \( I_\perp \), \( I_\parallel \) and \( I_o \), were used to calculate
the relative intensities, $T_\perp$ and $T_\parallel$ according to Eq. (4-29). Accordingly, a typical transmission-time plot shown in Figure 4.4 was obtained by selecting peak values of intensity and used to calculate the optical retardation, $R(t)$, and birefringence $\Delta n(t)$.

![Figure 4.8 Typical curves of force and light intensity versus time during stretching and relaxation.](image-url)
Figure 4.9 Evolution of relative light intensity at the cross and parallel orientation of polarizers.

4.4 Residual Birefringence in Free Quenching Plates

Free quenching experiments in water have been performed on both PCs. Initial temperatures were 150, 160 and 175°C and quenching temperature was 25°C.

4.4.1 Free Quenching Experiments

PC plates of dimensions 220×220×2 mm³ were made by compression molding at 230°C. The drying conditions were the same as mentioned in Section 4.3.1. These plates
were then cut into slabs of dimensions $40 \times 40 \times 2 \text{ mm}^3$ for the quenching experiments. To attain a thermodynamic equilibrium, the samples were put in a large beaker filled with silicon oil at a specified temperature for a certain period of time (5, 20, 120 minutes for 175, 160 and 150$^\circ$C, respectively). Then, the samples were immediately dumped into a large volume of water to quench. The quenched plates were then cut to a thickness of 0.5 mm using a low speed diamond saw (ISOMET low speed saw/BUECHLER). The residual birefringence distribution along the thickness direction was measured by using a polarizing optical microscope (Laborlux POL/LEITZ WETZLAR) equipped with a tilted 4$^{\text{th}}$ order compensator (1592K/LEITZ WETZLAR) within two or three days after quenching to avoid the contribution of fast relaxation of birefringence during this period.

4.4.2 Results and Discussions

Figures 4.10 and 4.11 present the Young’s relaxation modulus and the strain-optical coefficient functions of PC OQ3820 at various strains at a temperature of 25$^\circ$C, respectively. Both functions are seen to decrease with strain indicating a nonlinear behavior even at strains in the range of 0.4 to 1.3 %. It should be noted that similar nonlinear behavior of the Young’s relaxation modulus at room temperature has been observed earlier on different grades of PCs [199] but in the range of strains of 1 to 4.5%.
However, the nonlinear behavior of the strain-optical coefficient has not been reported in literature to date. Due to the observed nonlinear behavior, the low temperature measurements reported below were performed at a strain of 0.4%.

Figure 4.12 exhibits the experimental curves of the Young’s relaxation modulus (a) and the strain-optical coefficient functions (b) with respect to time. It is seen that the relaxation of $G(t)$ and $C_\varepsilon(t)$ is not observed in time span of experiment until a temperature of 115$^\circ$C. At higher temperatures the relaxation process speeds up. A further increase of temperature slows down relaxation process due to approach to the rubbery state.

Figure 4.10 The Young’s relaxation modulus function for PC OQ 3820 measured at various strains at a temperature of 25$^\circ$C.
Figure 4.11 The strain-optical coefficient function for PC OQ 3820 measured at various strains at a temperature of 25°C.

Figure 4.13 shows the master curves of $E(t/a_T)$, the calculated compliance function, $J(t/a_T)$ (a), and $C_\varepsilon(t/a_T)$ (b) at a reference temperature of 143.7°C for PC OQ1030 obtained by use of time-temperature superposition. Fig. 4.13 also indicates the curve fitting of the relaxation modulus and creep compliance function (a) and strain-optical coefficient (b) functions by using the following Prony’s series:

$$G(t) = \sum_{i=1}^{n} G_i \exp \left( \frac{-t}{\tau_i} \right)$$  
(4-32)

$$J(t) = J_0 + \sum_{i=1}^{n} \left[ 1 - J_i \exp \left( \frac{-t}{\tau_i} \right) \right]$$  
(4-33)
\[ C(t) = \sum_{i=1}^{n} C_i \exp\left(\frac{-t}{\tau_i}\right) \]  \hspace{1cm} (4-34)

Similar data was obtained for PC OQ3820. Figure 4.14 shows the experimental curves of the Young’s relaxation modulus (a) and the strain-optical coefficient (b) functions for PC OQ3820. Again, these curves were shifted to generate master curves of \( G(t/a_T) \) and \( C_v(t/a_T) \) at a reference temperature of 147.5°C. The creep compliance function, \( J(t/a_T) \), was again calculated from relaxation modulus function. These curves were fitted to Prony’s series according to Eqs. (4-32) and (4-34). The experimental and fitted master curves are shown in Figure 4-15. The corresponding coefficients of Prony’s series for both PCs are listed in Table 4.1 and 4.2.
Figure 4.12 The Young’s relaxation modulus function (a) and the strain-optical coefficient function (b) for PC OQ1030 measured at various temperatures.
Figure 4.13 The experimental (various symbols) and fitted (solid curve) Young’s relaxation modulus as well as calculated (circles) and fitted (solid curve) creep compliance J(t) function (a) and strain-optical coefficient function (b) for PC OQ1030 at a reference temperature of 143.7°C.
Figure 4.14 The Young’s relaxation modulus function (a) and the strain-optical coefficient function (b) for PC OQ3820 measured at various temperatures.
Figure 4.15 The experimental (various symbols) and fitted (solid curve) Young’s relaxation modulus as well as calculated (circles) and fitted (solid curve) creep compliance $J(t)$ function (a) and strain-optical coefficient function (b) for PC OQ3820 at a reference temperature of 147.6°C.
Table 4.1 The relaxation time and corresponding Prony’s series coefficients for fitting the relaxation modulus function of PC OQ1030 and PC OQ3820 at a reference temperature of 143.7°C and 147.6°C, respectively.

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Table 4.2 The relaxation time and corresponding Prony’s series coefficients for fitting the creep compliance function of PC OQ1030 and PC OQ3820 at a reference temperature of 143.7°C and 147.6°C, respectively.

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The shift factor functions and their fitting by WLF equation are shown on Figure 4.16 and 4.17 for PC OQ1030 and OQ3820, respectively. Clearly, below 130°C the shift factors do not follow the WLF equation. This is due to the fact that the WLF equation does not include the nonequilibrium free volume that remained during cooling to temperature below $T_g$. Thus the experimental shift factor should be smaller than that calculated from the WLF equation at a temperature significantly lower than $T_g$ as shown in Figs. 4.16 and 4.17.

Figure 4.16 Temperature dependence of the shift factor of PC OQ1030, $T_g$ used as a reference temperature.
Figure 4.17 Temperature dependence of the shift factor of PC OQ3820, $T_g$ used as a reference temperature.

From the master curves of both PCs, typical modulus-time curves of amorphous polymers are observed. Interestingly, the viscoelastic relaxation (modulus relaxation) is seen to start earlier than that of photoviscoelastic relaxation (strain-optical coefficient relaxation). Apparently, the optical retardation relaxation below $T_g$ occurs on segmental level of macromolecular chains, while the mechanical relaxation in addition occurs at the level lower than segmental one. Also, it is observed that the strain-optical coefficient
function of optical grade PCs shows the presence of a slow relaxation region at times close to the rubbery state. Such a behavior of optical grade PCs is quite different than that observed for a general purpose PC, Lexan-141, in our earlier studies [86, 119], where the function $C_\varepsilon(t)$ continuously drops with time. This is possibly due to the some differences in the chemical structure of the optical grade PCs in comparison with that of Lexan 141. The substitution of side groups in PC may cause changes in its stress-optical coefficient in both the solid and melt states as shown in other studies [185-189]. However, the optical behavior of PC in the glass transition region has not been reported in these studies. Also, to verify this point, one has to determine the chemical structure of different polycarbonates, but this is not the purpose of the present study.

The master curves of the stress-optical coefficient function of three different polycarbonates, Lexan 141, PC OQ1030 and PC OQ3820 were calculated from the master curves of the strain-optical coefficient function and creep compliance function according to Eq. (4-7) and are presented in Figure 4.18. In order to compare three different polycarbonates, these curves were shifted to the same reference temperature ($T_r = 130^\circ C$), based on the WLF equation. $C_\sigma(t)$ is an increasing function of time and reaches a constant value at large time corresponding to the rubbery state. It is seen that the optical
grade polycarbonates show significantly lower stress-optical coefficients in the rubbery and fluid states than the general purpose polycarbonate studied earlier [86, 119]. At the same time the stress optical coefficient of three PCs are almost similar at small times corresponding to the solid state.

Figure 4.18 Comparison of the stress-optical coefficients as a function of reduced time for three different PCs at a reference temperature of 130°C.

The master curves of $G(t)$ and $C_e(t)$ along with a heat transfer calculation were used to predict thermal birefringence by Eqs. (4-3) and (4-16). The predicted (curves) and
measured (symbols) of residual birefringence profiles in both polycarbonate plates quenched in water at 25°C are shown in Figs. 4.19 and 4.20. The details of numerical algorithm will be given later in Chapter V. These data were obtained using the heat transfer coefficient of $h = 490 \text{ J/s m}^2 \text{ °K}$. The physical properties of PCs used in the numerical simulation are listed in Table 4.3.

Figure 4.19 Measured (symbols) and predicted (curves) residual thermal birefringence distribution along the thickness direction of PC-OQ1030 plates quenched in 25°C water from different initial temperatures.
Figure 4.20 Measured (symbols) and predicted (curves) residual thermal birefringence distribution along the thickness direction of PC-OQ3820 plates quenched in 25°C water from different initial temperatures.

The birefringence is positive in the extended core region and negative near the surface. The position of zero birefringence moves toward the core as the initial temperature decreases. It also shows that an increase in the initial temperature leads to an increase in the residual birefringence in both the core and surface regions. These results
qualitatively coincide with our previous study on Lexan 141 [86, 119], but higher residual birefringence is observed on both optical grade polycarbonates at any initial temperature of the present study. This is due to the fact that the glass transition temperatures of optical grade PCs are lower than that of the Lexan 141. Therefore, at the same initial temperature the difference between the initial temperatures and $T_g$ becomes smaller for Lexan 141. Accordingly, the thermal birefringence of optical grade PCs starts to develop at lower initial temperatures and it is expected to be higher at the same initial temperature.

Table 4.3 Physical properties of PC used in simulation

<table>
<thead>
<tr>
<th>Properties</th>
<th>PC OQ1030</th>
<th>PC OQ3820</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$ (K$^{-1}$) [179]</td>
<td>0.0002265</td>
<td>0.0002265</td>
</tr>
<tr>
<td>$\alpha_g$ (K$^{-1}$) [179]</td>
<td>0.0000853</td>
<td>0.0000853</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>143.7</td>
<td>147.6</td>
</tr>
<tr>
<td>$T_2$ (°C)</td>
<td>83.17</td>
<td>97.28</td>
</tr>
<tr>
<td>$\tau_r$ (s)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Thermal diffusivity (m$^2$/s) [200]</td>
<td>$7.31 \times 10^{-8}$</td>
<td>$7.31 \times 10^{-8}$</td>
</tr>
<tr>
<td>Heat conductivity (J/s.m.K) [180]</td>
<td>0.234</td>
<td>0.234</td>
</tr>
<tr>
<td>Poisson ratio [201]</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>Bulk modulus (GPa) [201]</td>
<td>1.67 (&gt;T_g)</td>
<td>1.67 (&gt;T_g)</td>
</tr>
<tr>
<td></td>
<td>3.33 (&lt;T_g)</td>
<td>3.33 (&lt;T_g)</td>
</tr>
<tr>
<td>WLF equation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_1$</td>
<td>15.33</td>
<td>13.56</td>
</tr>
<tr>
<td>$C_2$ (°C)</td>
<td>60.53</td>
<td>50.32</td>
</tr>
<tr>
<td>$T_r$ (°C)</td>
<td>143.7</td>
<td>147.6</td>
</tr>
</tbody>
</table>
Based on Eq. (4-3) and Eq. (4-16), the calculated thermal birefringence was obtained by integration of the stress-optical coefficient function, reduced time, and the time derivative of stress difference. Since the PC samples were quenched from the molten state, one would expect that the Lexan141 should exhibit a higher thermal birefringence than that of optical grades PCs at the same initial temperature, because of a higher value of \( C_\sigma \) in the melt state. However, it was noted earlier that the quenched slabs of the optical grade PCs exhibit thermal birefringence higher than that of Lexan141. This is due to the fact that the optical grade PCs, having a lower \( T_g \), exhibit the rise of \( C_\sigma \) at an earlier time as shown in Figure 4.18. In fact, the DSC results show that the \( T_g \) values of PC OQ1030, PC OQ3820 and Lexan141 are 143.7°C, 147.6°C and 149.8°C, respectively. Another reason may be that the volume relaxation time of different polycarbonates is different. The thermal strain is calculated by the first order rate equation, Eq. (4-17), with a volume relaxation time of \( \tau_v = 0.05 \) s, providing the contribution to the level of the thermal strain. In fact the thermal strain increases at lower volume relaxation times increasing contribution of bulk modulus into thermal stresses and birefringence. Due to the lack of experimental information concerning the volume relaxation behavior of these three polycarbonates, one relaxation time was used to predict the experimental results. A further investigation on the volume relaxation behavior of PCs is required. Evidently, the
one relaxation time does not represent the overall volume relaxation behavior. Multiple relaxation times are required to obtain a better prediction of the thermal birefringence.

4.5 Conclusions

An optical instrument has been built to simultaneously measure the strain-optical coefficient function and the Young’s relaxation modulus function. Behaviors of two optical grade PCs have been investigated and compared with that of the general purpose PC studied earlier [86, 119]. The relaxation modulus and the strain-optical coefficient were found to be sensitive to the level of the imposed elongational strain such that these functions exhibit a nonlinear behavior even at low strains at room temperature. The linear viscoelastic and photoviscoelastic constitutive equations were used to convert these functions in the linear region to the stress-optical coefficient function. It was found that the stress-optical coefficients in rubbery state of optical grade PCs are lower than that of a general purpose PC, while in the glassy state the values are almost the same. The Young’s moduli of all PCs have been found to be close to each other in the glassy state but differ in the transition region from the glassy to rubbery state. The observed
differences in the behavior of PCs are probably caused by the presence of different side
groups in these polymers.

The linear viscoelastic and photoviscoelastic constitutive equations along with the
first order rate equation for volume relaxation have been applied to predict the residual
birefringence in quenched slabs from the measured mechanical and optical relaxation
functions on two optical grade PCs. The model predictions are in qualitative agreement
with the measured thermal birefringence in quenched plates. However, to obtain a
quantitative agreement with the measured residual birefringence, further investigation of
the volume relaxation behavior of PCs is required.
CHAPTER V

VISCOELASTIC SIMULATION OF INJECTION MOLDING OF LGP

5.1 Governing Equations

Mold filling during the injection molding process is comprised of three stages: filling, packing and cooling. The governing equations for a generalized Newtonian inelastic fluid under non-isothermal conditions for a CV/FEM/FDM scheme are given in various books and papers [3, 52, 72, 86]. The governing equations given below are for a viscoelastic flow under non-isothermal conditions for a numerical CV/FEM/FDM scheme that was proposed by Isayev and his coworkers [49, 86].

5.1.1 Flow-induced Stresses and Birefringence

Since the thickness of the LGP cavity is much smaller than planar dimensions, the velocity component in the gapwise direction is assumed to be zero. Moreover, the velocity gradient in the flow direction neglected, compared to the velocity gradient in the gapwise direction. In addition, the pressure is assumed to be a constant in the gapwise
direction. Therefore, the momentum equations, in the absence of inertia and body forces, and the continuity equation for two-dimensional planar flow are \([3, 49, 86]\):

\[
\begin{align*}
\mathbf{v} &= v_x \mathbf{e}_x + v_y \mathbf{e}_y + 0 \mathbf{e}_z \\
v_x &= v_x(z) \quad \text{and} \quad v_y &= v_y(z)
\end{align*}
\]

(5-1a)

\[
\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} = 0
\]

(5-2a)

\[
\frac{\partial \sigma_{yy}}{\partial y} + \frac{\partial \sigma_{yz}}{\partial z} = 0
\]

(5-2b)

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

(5-3)

where \(x\) and \(y\) are planar directions and \(z\) is the gapwise direction, \(\sigma_{ij}\) represents the total stress, \(\rho\) is the density, \(v_x\) and \(v_y\) are velocity components in the \(x\) and \(y\) directions, respectively.

By employing the Leonov constitutive equation, the stress field can be related to the velocity gradient field as follows:

\[
\sigma = -p \mathbf{I} + \eta_0 s (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) + \sum_k \frac{\eta_k}{\theta_k} \mathbf{C}_{\alpha_k}
\]

(5-4)

where \(p\) is the pressure, \(\mathbf{I}\) is the identity tensor, the \(s\) is a rheological parameter lying between zero to one, and \(\eta_k\) and \(\theta_k\) are the \(k^{th}\) mode shear viscosity and relaxation time, respectively, and \(\mathbf{C}_{\alpha_k}\) is the elastic strain tensor for the \(k^{th}\) relaxation mode. The \(\eta_0\) is the zero shear rate viscosity defined as:

\[
\eta_0 = \frac{\sum \eta_k}{1-s}
\]

(5-5)
The Leonov multi-mode viscoelastic constitutive equation was used to describe the evolution of $C_k$ during flow of polymer melts as:

$$\frac{\nabla V}{C_k} + \frac{1}{2\theta_k} \left[ C_k^2 + \frac{1}{3} \left( I_C^k - I_C^k \right) C_k - I_k \right] = 0$$  \hspace{1cm} (5-6a)$$

where $\nabla V_k$ is the Jaumann derivative of the elastic strain tensor defined as

$$\nabla V_k = \frac{D}{Dt} C_k - \omega \cdot C_k$$  \hspace{1cm} (5-6b)$$

and $\omega$ is defined by $\omega = [(\nabla v) - (\nabla v)^T]/2$ known as the vorticity tensor. The $I_C^k$ and $I_C^k$ are the first and second invariant of the elastic strain tensor. In the case of a two-dimensional flow, the elastic tensor, $C_k$, can be expressed as:

$$C_k = \begin{bmatrix} C_{xx,k} & 0 & C_{xz,k} \\ 0 & C_{yy,k} & C_{yz,k} \\ C_{xz,k} & C_{yz,k} & C_{zz,k} \end{bmatrix}$$  \hspace{1cm} (5-7)$$

Therefore, the Eq. (5-6a) can be expanded as follows:

$$\frac{DC_{xx,k}}{Dt} - 2C_{xz,k} \frac{\partial v_x}{\partial z} + \frac{1}{2\theta_k} \left( C_{xx,k}^2 + C_{xz,k}^2 - 1 \right) = 0$$  \hspace{1cm} (5-8)$$

$$\frac{DC_{yy,k}}{Dt} - 2C_{yz,k} \frac{\partial v_y}{\partial z} + \frac{1}{2\theta_k} \left( C_{yy,k}^2 + C_{yz,k}^2 - 1 \right) = 0$$  \hspace{1cm} (5-9)$$

$$\frac{DC_{zz,k}}{Dt} + \frac{1}{2\theta_k} \left( C_{xx,k}^2 + C_{yy,k}^2 + C_{zz,k}^2 - 1 \right) = 0$$  \hspace{1cm} (5-10)$$

$$\frac{DC_{xz,k}}{Dt} - C_{zz,k} \frac{\partial v_x}{\partial z} + \frac{1}{2\theta_k} \left( C_{xx,k} C_{xz,k} + C_{zz,k} C_{xz,k} \right) = 0$$  \hspace{1cm} (5-11)$$

$$\frac{DC_{yz,k}}{Dt} - C_{zz,k} \frac{\partial v_y}{\partial z} + \frac{1}{2\theta_k} \left( C_{yy,k} C_{yz,k} + C_{zz,k} C_{yz,k} \right) = 0$$  \hspace{1cm} (5-12)$$
\[ \begin{aligned}
\det[C_k] &= C_{xx,k}C_{yy,k}C_{zz,k} - C_{xz,k}^2C_{yy,k} - C_{yz,k}^2C_{xx,k} = 1 \\
\text{where } \frac{DC_{ij,k}}{Dt} \text{ is the substantial derivative of } C_{ij,k} \text{ with respect to time.}
\end{aligned} \] (5-13)

\[ \begin{aligned}
\frac{DC_k}{Dt} &= \frac{\partial C_k}{\partial t} + v_x \frac{\partial C_k}{\partial x} + v_y \frac{\partial C_k}{\partial y} \\
(5-14)
\end{aligned} \]

In a non-isothermal flow, the energy equation is used to solve the temperature field as follows:

\[ \begin{aligned}
\rho C_p \left( \frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} \right) &= \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + \Phi \\
(5-15)
\end{aligned} \]

where \( C_p, \kappa \) and \( \Phi \) are the specific heat, thermal conductivity and the dissipation function, respectively. The dissipation function is given as [49]

\[ \begin{aligned}
\Phi &= 2\eta_s \cdot \text{tr} \varepsilon^2 + \sum_k \frac{\eta_k}{2\nu_k^2} \left[ \frac{I_1(I_2 - I_1)}{3} + \text{tr} \varepsilon_k \varepsilon_k^T - 3 \right] \\
(5-16)
\end{aligned} \]

where

\[ \varepsilon = \frac{1}{2} \left( \nabla v + \nabla v^T \right) \] (5-17)

To calculate the pressure, velocity and temperature field, a set of appropriate boundary conditions is required. Assuming symmetry along centerline and no slip velocity at the solid wall of the cavity, the boundary conditions may be summarized as:

\[ \begin{aligned}
v_x &= v_y = 0 \text{ at } z = b \\
\frac{\partial v_x}{\partial z} &= \frac{\partial v_y}{\partial z} = 0 \text{ at } z = 0 \\
(5-18, 5-19)
\end{aligned} \]

In the filling stage, pressure at the melt front is assumed to be zero and the flow rate is specified at the nozzle or entrance.
p = 0 \text{ at the melt front} \quad (5-20)

Q = Q_0 \text{ at the nozzle or entrance} \quad (5-21)

In the packing stage, the pressure at the nozzle or entrance is assigned according to the applied packing pressure and the flow rate is solved.

p = p_{\text{packing}} \text{ at the nozzle or entrance} \quad (5-22)

To calculate the temperature field, symmetry along centerline and a constant wall temperature was assumed.

T = T_w \text{ at } z = b \quad (5-23)

\frac{\partial T}{\partial z} = 0 \text{ at } z = 0 \quad (5-24)

where T_w is the mold temperature, b is the half thickness of the cavity at a certain position and Q is the volumetric flow rate. In addition, the temperature-dependence of viscosity and relaxation time were determined by the shift factor, a_T, such as

\eta_k(T) = \eta_k(T_r) \frac{a_T}{a_{Tr}} \quad (5-25)

\theta_k(T) = \theta_k(T_r) \frac{a_T}{a_{Tr}} \quad (5-26)

where a_T is the shift factor at the temperature T and is determined by the WLF equation.

\ln a_T = \frac{-C_1(T - T_r)}{C_2 + T - T_r} \quad (5-27)

The T_r is the reference temperature, and C_1 and C_2 are constants that obtained by curve fitting of temperature shift factor from viscosity curves measured at different
temperatures. By substituting Eq. (5-18) into Eqs. (5-1), (5-2), and integrating the results with respect to \( z \) and using the symmetric boundary conditions, Eq. (5-19), the velocity gradients are:

\[
\frac{\partial v_x}{\partial z} = \frac{\partial P}{\partial x} \eta_x \tag{5-28}
\]

\[
\frac{\partial v_y}{\partial z} = \frac{\partial P}{\partial y} \eta_y \tag{5-29}
\]

where:

\[
\eta_x = \eta_0 s + \frac{1}{\frac{\partial v_x}{\partial z}} \sum_k \eta_k C_{xz,k} \tag{5-30}
\]

\[
\eta_y = \eta_0 s + \frac{1}{\frac{\partial v_y}{\partial z}} \sum_k \eta_k C_{yz,k} \tag{5-31}
\]

Integration of Eqs. (5-28) and (5-29), using Eq. (5-19), leads to:

\[
v_x = -\frac{\partial P}{\partial x} \int_x^b \frac{z'}{\eta_x} \, dz' \tag{5-32}
\]

\[
v_y = -\frac{\partial P}{\partial y} \int_y^b \frac{z'}{\eta_y} \, dz' \tag{5-33}
\]

Substitution of Eqs. (5-32) and (5-33) into the Eq. (5-3) leads to the governing equation for pressure:

\[
G \frac{\partial P}{\partial t} + H - \frac{\partial}{\partial x} \left( S_x \frac{\partial P}{\partial x} \right) - \frac{\partial}{\partial y} \left( S_y \frac{\partial P}{\partial y} \right) = 0 \tag{5-34}
\]

where

\[
G = \int_0^b \frac{\partial P}{\partial x} \, dz \tag{5-35}
\]

\[
H = \int_0^b \frac{\partial P}{\partial T} \left( \frac{\partial T}{\partial t} \right) \, dz \tag{5-36}
\]
\( S_x = \int_0^b (z \int_0^z \rho dz') \frac{dz}{\eta_x} \) \quad (5-37)

\( S_y = \int_0^b (z \int_0^z \rho dz') \frac{dz}{\eta_y} \) \quad (5-38)

For one-dimensional flow, Eq. (5-34) reduces to

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

(5-39)

Eqs. (5-34) and (5-39) are the classical Hele-Shaw equations that needs to be solved by numerical methods \([3, 86]\). To obtain the FEM forms, the linear shape functions are applied to the Eqs. (5-34) and (5-39) \([72]\). In case of two dimensional elements, the pressure field can be expressed through the linear triangular shape function

\[
P^i(x, y, t) = \sum_{i=1}^{3} L^i_1(x, y) P_i^l(t)
\]

(5-40)

\[
L^i_1(x, y) = \frac{1}{2A^l} \left[ b^i_{11} + b^i_{21}x + b^i_{31}y \right]
\]

(5-41)

where subscript \( i \) presents local node number, \( i = 1 \) to \( 3 \), and \( l \) represents global element number. The \( A^l \) denotes the element area and \( b^i_j \) indicates weighting factors for \( i = 1, 2, 3 \), with its matrix form being

\[
\begin{bmatrix}
b^1_{1i} \\
b^2_{2i} \\
b^3_{3i}
\end{bmatrix} =
\begin{bmatrix}
x_2^i y_3^i - x_3^i y_2^i & x_1^i y_3^i - x_3^i y_1^i & x_1^i y_2^i - x_2^i y_1^i \\
y_2^i - y_3^i & y_1^i - y_3^i & y_1^i - y_2^i \\
x_3^i - y_2^i & x_1^i - y_3^i & x_2^i - y_1^i
\end{bmatrix}
\]

(5-42)
where \( x \) and \( y \) are components of the rectangular coordinate of each local triangular finite
element. Therefore, in case of two-dimensional flow, the FEM form of equation (5-35)
becomes [202]

\[
G^l A^l \sum_{n=1}^{1} E_{1N}^l \frac{P_{w}^l - P_{w+1}^l}{\Delta t} + S^l \sum_{n=1}^{1} D_{1N}^l P_{w+1}^l = -\frac{A^l H^l}{3}
\]

(5-43)

where \( w \) and \( w+1 \) is a current and new time step, respectively, and

\[
E_{1N}^l = \begin{cases} 
1/6 & \text{if } i = N \\
1/12 & \text{if } i \neq N 
\end{cases}
\]

(5-44)

\[
D_{1N}^l = \frac{1}{4A^l} \left[ b_{11}^l b_{22}^{lN} + b_{11}^l b_{33}^{lN} \right]
\]

(5-45)

Eq. (5-43) is the FEM form of the governing equation suitable for introducing the
concept of control volume. If one assumes \( G^l \) is evaluated at each node \( M \), as \( G_M \),
separation of diagonal and off-diagonal components, leads to

\[
\sum_{j=1}^{CV} \left( \frac{A^l G^l}{\Delta t} E_{qj}^l + S^l D_{qj}^l \right) P_{M}^{w+1} = \sum_{j=1}^{CV} \left( \frac{A^l G^l}{\Delta t} \sum_{k \neq q}^{3} E_{qk}^l (P_N^w - P_N^{w+1}) \right)
\]

\[
- \sum_{j=1}^{CV} S^l \sum_{k \neq q}^{3} (D_{qk}^l P_N^{w+1}) + \sum_{j=1}^{CV} \frac{A^l G^l}{\Delta t} E_{qq}^l P_M^w - \sum_{j=1}^{CV} \frac{A^l H^l}{3} + \frac{Q_M}{2}
\]

(5-46)

where \( M = NELNOD(l, q) \) and \( N = NELNOD(l, k) \). The function \( M = NELNOD(l, q) \)
indicates the global node number \( M \) of the local \( q^{th} \) node of element \( l \). In Eq. (5-46)
\[
Q_M = 0 \quad \text{Fully \textendash filled nodes}
\]
\[
Q_M = Q_{Em} \quad \text{for Entrance nodes}
\]
\[
Q_M = Q_{MF} \quad \text{Melt front nodes}
\]

Now, the governing equation (5-46) can be used to solve for pressure field in a two-dimensional flow by under relaxation iteration [49, 86]. To obtain the FEM form of governing equation in a one-dimensional flow, the pressure field can be expressed through the linear shape function

\[
P_i(x,t) = \sum_{i=1}^{2} L_i(x)P_i(t)
\]  
\[
L_i(x) = \frac{1}{L_i} \left[ b_{i1} + b_{i2}x \right]
\]

where \(L_i\) is the length of the one-dimensional element, and \(b_{ij}\) indicates the weighting factors for \(i = 1, 2\), with its matrix form being, as

\[
\begin{bmatrix}
b_{i1} \\
b_{i2}
\end{bmatrix} =
\begin{bmatrix}
x_2^i \\
-x_1^i \\
-1 \\
1
\end{bmatrix}
\]

Substitution of Eqs. (5-48) and (5-49) into Eq. (5-39) and applying Green theorem results in [202]:

\[
\frac{G^iL_i}{2} \sum_{n=1}^{2} E_{in} \frac{P_{w}^n - P_{w+1}^n}{\Delta t} + S^i \sum_{n=1}^{2} D_{in} P_{w+1}^n = -\frac{\Delta P_l}{2}
\]  

where
\[ E_{IN} = \begin{cases} 2/3 & \text{if } i = N \\ 1/3 & \text{if } i \neq N \end{cases} \quad (5-52) \]

\[ D_{IN}^l = \frac{1}{L} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \quad (5-53) \]

Similarly, Eq. (5-51) can be discretized by separation of the diagonal and off-diagonal components to obtain

\[
\sum_{i=1}^{CV} \left( \frac{L G_M}{2\Delta t} E_{qq} + S^l D_{qq}^l \right) P_M^{w+1} = \sum_{i=1}^{CV} \left( \frac{L G_M}{2\Delta t} \sum_{k=q}^{2} E_{qq}^l (P_N^w - P_N^{w+1}) \right)
- \sum_{i=l}^{CV} S^l \sum_{k=q}^{2} (D_{qq}^l P_N^{w+1}) + \sum_{i=1}^{CV} \frac{L G_M}{2\Delta t} E_{qq}^l P_M^w - \sum_{i=1}^{CV} \frac{L H^l}{2} + Q_M \quad (5-54)
\]

The conditions on \( Q_M \) are the same as in Eq. (5-47). Accordingly, the control-volume finite element method [52, 72] with triangular and linear shape functions is used to solve for the pressure field by using Eq. (5-46) and (5-54), respectively. It should be noted that G and H are constant in each control volume; \( S_x \) and \( S_y \) are constant in each element. In addition, it has to be noted that Eq. (5-46) and (5-54) are used in the filling and packing stages. The only difference is that flow rate is assigned at entrance nodes to solve for pressure in the filling stage while flow rate is calculated by specified entrance pressure in the packing stage. Once the pressures and elastic strain tensor components at calculated nodes were converged, the stress components were calculated.
according to Eq. (5-4) at each time step. Then the flow-induced birefringence components were evaluated by applying the stress-optical rule [1, 2]

$$\Delta n_{xx}^{\text{flow}} = C_\sigma \sqrt{\left(\sigma_{xx} - \sigma_{zz}\right)^2 + 4\sigma_{xx}^2}$$

$$\Delta n_{yx}^{\text{flow}} = C_\sigma \sqrt{\left(\sigma_{yy} - \sigma_{zz}\right)^2 + 4\sigma_{yz}^2}$$

$$\Delta n_{xy}^{\text{flow}} = C_\sigma \left(\sigma_{xx} - \sigma_{yy}\right)$$

(5-55)

where the $C_\sigma$ is the stress-optical coefficient in the melt state of polymer.

5.1.2 Thermally-induced Stresses and Birefringence

The thermally-induced stresses and birefringence are caused by the nonequilibrium density or contraction and the viscoelastic behavior of polymers during an inhomogeneous rapid cooling till the polymer solidifies. The flow- and thermally-induced birefringence is essentially coupled during injection molding process. The constitutive equation used to describe flow behavior is no longer valid to describe the formation of stresses in solid state. Since polymeric materials exhibit a linear viscoelastic behavior at the temperature below glass transition temperature, a linear viscoelastic and photoviscoelastic constitutive equations were used to evaluate the evolution of stresses and birefringence. Accordingly, the linear viscoelastic and photoviscoelastic constitutive equations given in Chapter IV are used to calculate the thermally-induced stresses and birefringence. However, in this case a combination of constrained and free quenching
conditions was employed, instead of only free quenching consideration, described in Chapter IV.

For convenience, the Eqs. (4-1), (4-2) and (4-16) are repeated as follows

\[ n_{ij} - \frac{n_{kk}}{3} \delta_{ij} = \int_0^\xi C_\sigma(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \sigma_{ij} - \frac{\sigma_{kk}}{3} \delta_{ij} \right] d\tau \]

\[ = \int_0^\xi C_\sigma(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{ij} - \frac{\varepsilon_{kk}}{3} \delta_{ij} \right] d\tau \]

\[ \sigma_{ij} = -P + \int_0^\xi \left\{ 2G(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{ij} - \frac{1}{3} \varepsilon_{kk} \delta_{ij} \right] + \delta_{ij} K(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_{kk} - 3 \varepsilon_{kk} \right] \right\} d\tau \]

\[ \xi = \int_0^\tau \frac{d\tau}{A_t[T(\tau)]} \]

5.1.2.1 Constrained quenching

Constrained quenching is employed when the melt pressure in the cavity is non-zero. In addition, when the temperature is lower than the glass transition temperature \( T \leq T_g(P) \) \([93]\), the linear viscoelastic and photoviscoelastic constitutive equations, Eqs. (5-56) and (5-57), are applicable. This implies that the stresses and strains in the polymer are sufficiently small. The pressure dependence of the glass transition temperature, \( T_g(P) \), is given as \( T_g = T_g^0 + b_3 P \) as described by the Tait equation, Eq. (3-8), with the \( T_g^0 \) being \( T_g \) at 1 atm and \( b_3 \) being a constant in the Tait equation. In case of the constrained quenching, the through thickness thermal stress and lateral strain was determined [88]:

\[ \sigma_z = -p \]
\[ \varepsilon_y(z) = \frac{-p}{3K} \quad (5-60) \]

The lateral strain, \( \varepsilon_y \), was calculated at the time of the occurrence of vitrification and maintained until the pressure released or till ejection. At gapwise location where solidification takes place, the lateral stress, \( \sigma_y \), and the through thickness strain, \( \varepsilon_z \), can be calculated as follows. First, if shear stresses are negligible, one considers the linear viscoelastic constitutive equation, Eq. (5-57), with \( x \) and \( z \) presenting the lateral and thickness direction, respectively. Then Eq. (5-57) leads to

\[
\sigma_y = -P + \int_0^z \left\{ \frac{2}{3} G(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_y - \varepsilon_z \right] + K(\xi - \tau) \frac{\partial}{\partial \tau} \left[ 2 \varepsilon_y + \varepsilon_z - 3 \varepsilon_z \right] \right\} d\tau 
\quad (5-61)
\]

\[
\sigma_z = -P + \int_0^z \left\{ -\frac{4}{3} G(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_y - \varepsilon_z \right] + K(\xi - \tau) \frac{\partial}{\partial \tau} \left[ 2 \varepsilon_y + \varepsilon_z - 3 \varepsilon_z \right] \right\} d\tau 
\quad (5-62)
\]

From Eqs. (5-59) and (5-62), one can obtain that

\[
\int_0^z K(\xi - \tau) \frac{\partial}{\partial \tau} \left[ 2 \varepsilon_y + \varepsilon_z - 3 \varepsilon_z \right] d\tau = \int_0^z \frac{4}{3} G(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_y - \varepsilon_z \right] d\tau \quad (5-63)
\]

Then substitution of Eq. (5-63) into Eq. (5-61) leads

\[
\sigma_y = \int_0^z 2G(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_y - \varepsilon_z \right] d\tau 
\quad (5-64)
\]

To solve the convolution integral of Eq. (5-63), the piecewise continuous approximation [114] was used to obtain the through thickness strain. This approximation can be used only when the change of strain is small enough such that

\[
\int_0^t f(\xi - \tau) \frac{\partial q(\tau)}{\partial \tau} d\tau = \sum_{i=1}^k \left( \Delta q^{r^{k,i}} \right) 
\quad (5-65)
\]

in which
\[
\Delta q^i = q(t^i) - q(t^{i-1}) \tag{5-66}
\]

\[
f^{k,i} = \frac{1}{\Delta t^i} \int_{t^{i-1}}^{t^i} f(\xi - \tau) d\tau \tag{5-67}
\]

Therefore, the convolution integral in Eq. (5-63) can be discretized as

\[
\int_0^\xi G(\xi - \tau) \frac{\partial \varepsilon^{\tau}}{\partial \tau} d\tau = \sum_{i=1}^{k} (\Delta \varepsilon_{\gamma}^i G^{k,i}) \tag{5-68}
\]

in which

\[
\Delta \varepsilon_{\gamma}^i = \varepsilon_{\gamma}^i (\xi^i) - \varepsilon_{\gamma}^i (\xi^{i-1}) \tag{5-69}
\]

\[
G^{k,i} = \frac{1}{\Delta \xi^i} \int_{\xi^{i-1}}^{\xi^i} G(\xi - \tau) d\tau \tag{5-70}
\]

Accordingly, Eq. (5-63) becomes

\[
\frac{4}{3} \sum_{i=1}^{k} \left[ G^{k,i} (\Delta \varepsilon_{\gamma}^i - \Delta \varepsilon_{\tau}^i) \right] + \sum_{i=1}^{k} \left[ K^{k,i} (2 \Delta \varepsilon_{\gamma}^i + \Delta \varepsilon_{\tau}^i - 3 \Delta \varepsilon_{\tau}^i) \right] = 0 \tag{5-71}
\]

Separation of the \(k\)th term corresponding to the current time step generates

\[
\varepsilon_{\gamma}^k \left( \frac{4}{3} G^{k,k} + K^{k,k} \right) + \varepsilon_{\tau}^k \left( -\frac{4}{3} G^{k,k} + 2 K^{k,k} \right) - \frac{4}{3} \mu^{k,i} + \lambda^{k,i} = 0 \tag{5-72}
\]

or

\[
\varepsilon_{\gamma}^k = -\left( \frac{4 G^{k,k} - 6 K^{k,k}}{4 G^{k,k} + 3 K^{k,k}} \right) \varepsilon_{\tau}^k + \left( \frac{4 \mu^{k,i} - 3 \lambda^{k,i}}{4 G^{k,k} + 3 K^{k,k}} \right) = A^{k,k} \varepsilon_{\gamma}^k + B^{k,k} \tag{5-73}
\]

in which

\[
\mu^{k,i} = -G^{k,k} (\varepsilon_{\gamma}^{k-1} - \varepsilon_{\gamma}^{k-1}) + \sum_{i=1}^{k-1} \left[ G^{k,i} (\Delta \varepsilon_{\gamma}^i - \Delta \varepsilon_{\tau}^i) \right] \tag{5-74}
\]

\[
\lambda^{k,i} = -K^{k,k} (I_{\gamma}^{k-1} + 3 \Delta \varepsilon_{\gamma}^i) + \sum_{i=1}^{k-1} \left[ K^{k,i} (\Delta I_{\gamma}^i - \Delta \varepsilon_{\tau}^i) \right] \tag{5-75}
\]
Therefore, the strain components are fully determined. By applying the same treatment to Eq. (5-64), one obtains
\[
\sigma_y = \sum_{i=1}^{k} 2G^{k,i} \left( \Delta e^i_y - \Delta e^i_z \right) = 2 \left[ \mu^{k,j} + G^{k,k} \left( e^k_y - e^k_z \right) \right] \quad (5-76)
\]

Once the strain components were obtained, Eq. (5-56) can be used to calculate the residual thermal birefringence as
\[
\Delta n^b = n_y - n_z = \int_{0}^{\xi} C_{\epsilon} (\xi - \tau) \frac{\partial}{\partial \tau} \left[ \epsilon_y - \epsilon_z \right] d\tau \quad (5-77)
\]

Applying the piecewise continuous approximation to Eq. (5-77) leads to
\[
\Delta n^b = \sum_{i=1}^{k} C^{k,j} \left( \Delta e^i_y - \Delta e^i_z \right) = \sum_{i=1}^{k} \frac{\Delta e^i_y - \Delta e^i_z}{\xi^i - \xi^{i-1}} \int_{\xi^{i-1}}^{\xi^i} C_{\epsilon} (\xi - \tau) d\tau \quad (5-78)
\]

Eq. (5-78) was used to calculate the thermally-induced birefringence as long as strain components were obtained. In addition, it is important to mention that the through thickness strain of each fluid layer satisfies a zero volumetric contraction due to the fact that the melt was added to the fluid core
\[
\int_{-b}^{b} \epsilon_z (z) dz = 0 \quad (5-79)
\]

The above equations were used to solve thermally-induced stresses and birefringence when the part is partially solidified with the core layers in the molten state and the outer layers in the solidified state. The melt pressure acts only when the molten resin is connected to the barrel through the continuous molten core [149]. When the core vitrifies and all layers are in the solid state, the total through-thickness strain should also
become constrained assuming a fixed value. Consequently, the pressure can no longer be prescribed but rather solved for till it vanishes. Otherwise, a higher prescribed pressure can cause over-constraint leading to incorrect prediction of the thermal stresses [149]. In the present study, to predict the thermally-induced birefringence the pressure and temperature fields were taken from the flow simulation.

5.1.2.2 Free quenching

The free quenching condition is employed when melt pressure drops to zero. Then the through thickness stress $\sigma_z$ equals to zero. The integration of the transverse stress $\sigma_y$ along the thickness direction leads to [87, 119]

$$\sigma_z = 0$$

$$\int_{-b}^{b} \sigma_y dz = 0$$

where $b$ is the half of thickness of cavity. The pressure term in Eq. (5-57) drops and the viscoelastic constitutive equation becomes

$$\sigma_{ij} = \int_{0}^{\xi} \left\{ 2G(\xi - \tau) \frac{\partial}{\partial\tau} \left[ \epsilon_{ij} - \frac{1}{3} \epsilon_{kk} \delta_{ij} \right] + \delta_{ij} K(\xi - \tau) \frac{\partial}{\partial\tau} \left[ \epsilon_{kk} - 3\epsilon_{rr} \right] \right\} d\tau$$

To solve the through thickness strain, the similar treatment that was used in deriving Eq. (5-73) was employed. However, the lateral strain, $\epsilon_y$, is no longer a fixed value. It can be solved by combining Eqs. (5-64) and (5-81). It should be noted that the Eq. (5-64) is
still valid in case of free quenching. Therefore, by substituting Eq. (5-64) into Eq. (5-81), one obtains

\[ \int_0^b \left\{ \int_0^s 2G(\xi - \tau) \frac{\partial}{\partial \tau} \left[ \varepsilon_y - \varepsilon_z \right] d\tau \right\} dz = 0 \quad (5-83) \]

By using the piecewise continuous approximation, Eq. (5-83) becomes

\[ \int_0^b \left\{ \sum_{i=1}^k 2G^{k,i} \left( \Delta \varepsilon^i_y - \Delta \varepsilon^i_z \right) \right\} dz = 0 \quad (5-84) \]

Separation of the \( k \)th term leads to

\[ \varepsilon^k_z = \frac{\int_0^b \left[ G^{k,k} A^{k,k} - \mu^{k,i} \right] dz}{\int_0^b \left[ G^{k,k} \left( 1 - A^{k,k} \right) \right] dz} \quad (5-85) \]

Therefore, once the strain components \( \varepsilon^k_z \) and \( \varepsilon^k_y \) at the current time, \( k \), were obtained from Eqs. (5-73) and Eq. (5-85), the lateral stress and birefringence can be calculated according to Eqs. (5-76) and (5-78). This algorithm was originally proposed by Isayev and his coworkers for calculation of residual thermal stress and birefringence in free quenching of amorphous [119] and semi-crystalline [87] polymers. However, use of free quenching assumption is too simplistic to describe the residual thermal stress and birefringence in the injection molding process, especially when the thermal stress and birefringence are comparable to that of the flow-induced stress and birefringence. In fact, for the molded parts of a complicated geometry or when a non-zero pressure exists in a cavity, the molded parts do not detach from the wall until the pressure releases to zero.
Therefore, the constrained quenching was added to remedy this deficiency. Once the flow
and thermally induced birefringence was calculated, the total birefringence is assumed to
be the summation of both as follows:

\[ \Delta n = \Delta n_{\text{flow}} + \Delta n_{\text{th}} \]  \hspace{1cm} (5-86)

5.1.3 Anisotropic Shrinkage in LGP

The shrinkage in moldings is mainly contributed from the thermal and pressure
history effects on specific volume of polymers. However, the frozen-in stresses introduce
anisotropy of molecular orientation leading to the anisotropic shrinkage in moldings. In
this study, a methodology that relates the molecular anisotropy with history of specific
volume, proposed by Kwon et al. [90], to obtain anisotropic shrinkage in LGP moldings
was used. In particular, the volumetric shrinkage was calculated according to the history
of the specific volume, \( V \), of the polymer melt during the injection molding process. The
volumetric shrinkage was calculated as [159].

\[ S_V = \frac{\nabla_i - V_f}{V_i} \]  \hspace{1cm} (5-87)

where \( \nabla_i \) is the initial specific volume of melt and \( V_f \) is the final specific volume at
room temperature. Since the polymer melt undergoes severe pressure and temperature
changes in a short time, the initial specific volume can not be assumed the same as that at
constant pressure and temperature conditions. In the present simulation, the initial specific volume is calculated as [159]

\[
\bar{V}_i = \frac{1}{(t_p - t_f)} \int_{t_f}^{t_p} \bar{V}(t)dt
\]

(5-88)

where \( t_f \) is the time at the end of the filling stage, \( t_p \) is the packing time and \( \bar{V}(t) \) is the time-dependent specific volume averaged through the gapwise direction for a particular cross section such that

\[
\bar{V}(t) = \frac{1}{b} \int_0^b V(z,t)dz
\]

(5-89)

The specific volume, \( V(z, t) \), is described by Tait equation of state, Eqs. (3-4) to (3-10). The amount of shrinkage in the injection molded products is affected by cooling, and pressure effects. However, polymer solidifies under different packing pressures. After completion of the packing stage, the molding tends to expand proportional to pressure value imposed at the end of packing stage [91]. Also, at the end of packing stage, a recovery of the elastic strain introduced during flow occurs at the position where \( T > T_g \) due to abrupt pressure decay caused by release of the packing pressure. By combining three effects, linear expansion, compressibility and the elastic strain, the anisotropic shrinkage was calculated as

\[
S_i = \alpha_i (T_g - T) - \beta_i \bar{P} + S_{\gamma_i}, \quad i = x, y
\]

(5-90)
where $T_\infty$ is the ambient temperature, $\beta_i$ is the compressibility, $\bar{P}$ is the average solidification pressure at each cross section and $\alpha_i$ is the linear thermal expansion coefficient evaluated based on biaxial orientation functions:

$$\alpha_i = \alpha_0 \left(1 - f_{or,i}\right) \quad (5-91)$$

in which $f_{or,i}$ is the orientation function in $i$ direction, obtained as

$$f_{or,i} = \frac{\Delta n_i}{\Delta n^0} \quad (5-92)$$

where $\Delta n_i$ is the calculated birefringence along $i$ direction, and $\Delta n^0$ is the intrinsic birefringence of polymer. The value of $S_{\gamma_e}$ is the elastic strain which is calculated based on the total elastic recovery accumulated until the end of the packing stage.

$$S_{\gamma_e} = \int_0^{t_e} \gamma_e(t) dt \quad (5-93)$$

It was found that contribution of compressibility to anisotropic shrinkage is negligible due to small difference in the anisotropic compressibility introduced by the low value of orientation function developed during molding [90]. Also, the simulation showed that the temperature of melt at the end of packing stage drops below $T_g$ at any point in the LGP cavity. Therefore, in this study terms corresponding to compressibility and elastic recovery in Eq. (5-90) were negligible and dropped in further calculation of shrinkage. Accordingly, the Eq. (5-90) for width and length shrinkage reduces to

$$S_i = \alpha_i (T_g - T_\infty) \quad i = x, y \quad (5-94)$$
Then, the shrinkage in the thickness direction is calculated based on the volumetric shrinkage and planar shrinkage as

$$S_z = S_v - S_x - S_y$$

(5-95)

The flow charts for calculation of the flow birefringence as well as anisotropic shrinkage and thermal birefringence are shown in Figures 5.1 and 5.2, respectively.
Figure 5.1 Flow chart for calculation of the flow-induced birefringence and anisotropic shrinkage.
Figure 5.2 Flow chart for calculation of the thermally-induced birefringence.

- Input T and P
- $t = t + dt$
- Calculate reduced time of $\xi_G$ and $\xi_C$
- $p > 0$ or $t < t_{ejection}$
  - True: Constrained quenching, calculate $\Delta n^\text{th}(t)$
  - False: Free quenching, calculate $\Delta n^\text{th}(t)$
    - $(\Delta n^\text{th}(t+dt) - \Delta n^\text{th}(t)) / \Delta n^\text{th}(t+dt) < \text{tolerance}$
      - True: Stop, End of calculation
      - False: Continue
5.2 Numerical Algorithm

The numerical algorithm of CV/FEM/FDM scheme in injection molding process is based on variable time step.

5.2.1 CV/FEM/FDM

A new set of velocity, pressure, temperature and elastic strain tensor were calculated and updated at a newer time step, w+1. Therefore, the first question is how to determine the duration of each time step in the filling stage. In a one-dimensional problem, as occurs in delivery system, this is done by calculating the time required for the current melt front to fill the next control volume, which is defined as the volume constructed by connecting the center point of two consecutive nodes except for entrance and end nodes as shown in Figure 5.3. In Fig. 5.3, the larger circles present the physical nodes and the small circles are the center points of two consecutive nodes defining a control volume. In a two-dimensional flow, as occurs in LGP cavity, the situation becomes more complex but follows the same philosophy. The control volume of a physical node is defined by the volume constructed by connecting the geometric center of neighboring elements as indicated in Figure 5.4. Therefore, in such a two-dimensional problem, time step is determined by the shortest time required for melt front to fill one of the neighboring control volumes. Fully filled, partially filled or empty nodes are defined, as shown in
Figure 5.4. Figure 5.4 shows the determination of time step in two-dimensional CV/FEM scheme, in which the arrows indicate the direction of melt front propagation, solid, shaded and empty circle being the fully filled, partially filled and empty node, respectively.

Figure 5.3 Time step in one-dimensional flow is determined by the time required to fully fill a control volume. (Large circle: physical nodes, Small circle: boundary of control volumes, Dashed line: control volume)

Once the time step is calculated, the melt front nodes are determined to be fully filled, partially filled or empty and then the pressure is iteratively solved according to Eq. (5-46) and Eq. (5-54). To apply Eqs. (5-46) and Eq. (5-54) to calculate the pressure field, the Tait equation of state, Eqs. (3-4) to (3-10) along with calculated time step were used to evaluate the $G_M$ and $H^L$ by using Eqs. (5.35) and (5.36). However, since the $S^L$ is
coupled with the shear rate as indicated by Eqs. (5-37) and (5-38), and the shear rate is related to velocity and elastic strain tensor, as shown in Eqs. (5-30) to (5-33) and (5-8) to (5-13). Therefore, an iterative process is required to solve these equations simultaneously to determine $S_L$. To initiate this process, an initial guess of elastic strain tensor components is required.

Figure 5.4 Time step in two-dimensional flow is determined by the shortest time required to fully fill one of the neighboring control volumes. (solid circle: fully filled node, shaded circle: partially filled node, empty circle: empty node)
Accordingly, the steady state solution of elastic tensor components is used as the initial guess of each calculated node except for the entrance node. For the entrance node, since the temperature is fixed until the end of packing stage, it is reasonable to assume that a steady state solution of elastic strain tensor components can be directly applied. Therefore, Eqs. (5-30) to (5-33) and (5-8) to (5-13) can be solved simultaneously until the shear rate converged. The calculated shear rate was then used to evaluate $S^L$. Then the pressure can be obtained by Eqs. (5-46) and Eq. (5-54). Once the new pressure of node $m$, $p_{m}^{w+1,new}$, obtained, the under relaxation method [49, 86] is used to calculate the updated pressure according to

$$p_{m}^{w+1,update} = (1 - \omega_p) p_{m}^{w+1,old} + \omega_p p_{m}^{w+1,new}$$  \hspace{1cm} (5-96)$$

where $\omega_p$ is the weighting factor varying from 0 to 1. Typically, this value in the present study was 0.7 to 0.8. If the $p_{m}^{w+1,new}$ is not equal to $p_{m}^{w+1,update}$, the entire process repeated until a convergence is reached.

In addition, the calculation of temperature field should be also incorporated into the iteration process for pressure calculation since the relaxation time, $\theta_k$, and viscosity, $\eta_k$, are temperature dependent, as indicated in Eqs. (5-25) and (5-26). However, to simplify the calculation, the temperature obtained in the $w^{th}$ time step is used for the entire pressure iteration. After velocity field, the pressure field and elastic strain tensor
components obtained, the energy equation, Eq. (5-15), is solved for the temperature field at time step $w+1$ by using under relaxation method as

$$T_{m}^{w+1, \text{update}} = (1 - \omega_T)T_{m}^{w+1, \text{old}} + \omega_T T_{m}^{w+1, \text{new}}$$  \hspace{1cm} (5-97)

where $\omega_T$ is the weighting factor varying from 0 to 1. This algorithm is continued until the end of the filling stage which means that the cavity is filled.

In the packing stage, the algorithm is similar to the filling stage, but the time steps are assigned rather than solved for since no melt front propagation is involved in this stage. Eqs. (5-46) and Eq. (5-54) are still valid, but the pressure at the entrance is assigned by the applied packing pressure and the flow rate of entrance, $Q_c1$ is calculated. The obtained velocity, pressure and elastic strain tensor fields are used to calculate a flow rate by summation of flow rate in each node at the melt front, $Q_c2$. The convergence reaches when $Q_c1$ is equal to $Q_c2$.

In the cooling stage, shear rate and velocity vanished, and the energy equation, Eq. (5-15), reduces to one-dimensional transient heat conduction equation:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right)$$  \hspace{1cm} (5-98)

The Leonov equation, Eq. (5-6a), reduces to

$$\frac{\partial C_k}{\partial t} + \frac{1}{2\theta_k} \left[ \frac{2}{3} C_k + \frac{1}{3} \left( \Pi_k - I_c \right) \right] = 0$$ \hspace{1cm} (5-99)
Therefore, a relaxation process dominates the cooling stage since no more pressure is applied, and the initial conditions for $C_{k}$ and $T$ are the values of $C_{k}$ and $T$ at the end of the packing stage. The Eq. (5-98) is solved by implicit method to obtain the temperature field and the Euler method [203] is used to integrate Eq. (5-99) to obtain the elastic strain tensor components.

In addition, in order to avoid a cumbersome numerical calculation in two-dimensional formulation of elastic strain tensor, Eqs. (5-8) to (5-13), for general planar geometries, the elastic strain tensor, $C_{k}$, can be determined in the streamwise coordinate system $(s, \theta, z)$ [49, 86], where $s$ is the streamwise flow direction, $\theta$ is perpendicular to the $s$ in the counterclockwise direction, and $z$ is the gapwise direction.

Therefore, the Leonov model reduces to

$$\frac{DC_{s,k}}{Dt} - 2C_{sz,k} \frac{\partial v_s}{\partial z} + \frac{1}{2\theta_k} \left( C_{ss,k}^2 + C_{sz,k}^2 - 1 \right) = 0 \quad (5-100)$$

$$\frac{DC_{sz,k}}{Dt} - C_{zz,k} \frac{\partial v_s}{\partial z} + \frac{1}{2\theta_k} \left( C_{ss,k}C_{sz,k} + C_{zz,k}C_{sz,k} \right) = 0 \quad (5-101)$$

$$\frac{DC_{zz,k}}{Dt} + \frac{1}{2\theta_k} \left( C_{sz,k}^2 + C_{zz,k}^2 - 1 \right) = 0 \quad (5-102)$$

$$\det|C_k| = C_{ss,k}C_{zz,k} - C_{sz,k}^2 = 1 \quad (5-103)$$

in which only three elastic strain tensor components left to be solved instead of five. The components of elastic strain tensor in a global coordinate system can be recovered as
\[ C_{xx,k} = C_{ss,k} \cos^2 \phi + \sin^2 \phi \] (5-104)

\[ C_{yy,k} = C_{ss,k} \sin^2 \phi + \cos^2 \phi \] (5-105)

\[ C_{sz,k} = \cos \phi \] (5-106)

\[ C_{yz,k} = -C_{sz,k} \sin \phi \] (5-107)

where \( \phi \) is the angle between vector \( x \) and \( s \).

Eqs. (5-100) to (5-103) indicate a set of elliptic partial differential equations. To solve such PDEs, the upwinding finite difference scheme can be applied [86, 206] in which the forward difference is used to discretize time variable, and the backward difference for space variable. However, such an algorithm can be only stable at the following condition:

\[ \frac{v}{ds} \frac{dt}{ds} < 1 \] (5-108)

Therefore, a very small time step is required especially when the velocity value is high. If the current time step is large, then a subdivision of time step is required. This introduces significant calculation effort and limits the ability of handling various processing conditions. Accordingly, an unconditionally stable upwinding scheme [62] is used in this study to remedy this limitation and reduce the calculation time. With the new proposed unconditionally stable upwinding scheme, the forward difference is still used to discretize time variable, but the backward difference is used to discretize space variable at \( t + 1 \). If \( t \)
+ 1 presents the current time and \( t \) is the previous time, the Eqs. (5-100) to (5-102) result in a nonlinear system of equations:

\[
F_1 = C_{ss,i}^{t+1} - C_{ss,i}^t + \frac{\Delta t}{\Delta s} v_s (C_{ss,i}^{t+1} - C_{ss,i-1}^{t+1}) - 2\Delta t\dot{C}_{sz,i}^{t+1} = 0
\]

\[
F_2 = C_{sz,i}^{t+1} - C_{sz,i}^t + \frac{\Delta t}{\Delta s} v_s (C_{sz,i}^{t+1} - C_{sz,i-1}^{t+1}) - \Delta t\dot{C}_{zz,i}^{t+1} = 0
\]

\[
F_3 = C_{zz,i}^{t+1} - C_{zz,i}^t + \frac{\Delta t}{\Delta s} v_s (C_{zz,i}^{t+1} - C_{zz,i-1}^{t+1}) + \frac{\Delta t}{2\theta} \left[ (C_{zz,i}^{t+1})^2 + (C_{zz,i}^{t+1})^2 - 1 \right] = 0
\]

To solve this nonlinear system of equations, the Newton-Raphson method [63, 178] is used as follows

\[
-F(X_n) = J(X_n)(X_{n+1} - X_n)
\]

where

\[
F = \begin{bmatrix} F_1 & F_2 & F_3 \end{bmatrix}^T
\]

\[
X_n = \begin{bmatrix} C_{ss,i}^{t+1} & C_{sz,i}^{t+1} & C_{zz,i}^{t+1} \end{bmatrix}^T
\]

and \( J \) is the Jacobian matrix defined as

\[
J = \begin{bmatrix}
\frac{\partial F_1}{\partial C_{ss,i}^{t+1}} & \frac{\partial F_1}{\partial C_{sz,i}^{t+1}} & \frac{\partial F_1}{\partial C_{zz,i}^{t+1}} \\
\frac{\partial F_2}{\partial C_{ss,i}^{t+1}} & \frac{\partial F_2}{\partial C_{sz,i}^{t+1}} & \frac{\partial F_2}{\partial C_{zz,i}^{t+1}} \\
\frac{\partial F_3}{\partial C_{ss,i}^{t+1}} & \frac{\partial F_3}{\partial C_{sz,i}^{t+1}} & \frac{\partial F_3}{\partial C_{zz,i}^{t+1}}
\end{bmatrix}
\]
Therefore, the set of discretized equations were solved by means of Newton-Raphson method at each time step. The resulting $C_{ij}$ tensors were used to calculate new shear rates until a convergence was met and the initial guess of $C_{ij}$ tensors was taken as an average value from upwind nodes [204, 205]. However, to determine the upwinding nodes correctly, the sequence of calculation is essential to ensure that the calculated sequence of $C_{ij}$ is always from downstream nodes. In case of one-dimensional flow, the solution is straightforward since the sequence of calculation is the same as the sequence of nodes numbering. However, it becomes complicated in case of two-dimensional flow since the numbering of node is arbitrary. To resolve this issue, the calculated nodal pressures were used as an indicator to determine the sequence of calculation, since the flow always takes place from high to low pressure location.

Therefore, the calculated pressure from previous time step was compared at the beginning of current time step and the sequence of calculation is determined.

5.2.2 Numerical Test

To verify the new proposed numerical scheme, a numerical test for an injection molding of PS disc was carried out to compare the simulated results with those of Shyu et al. [206]. Table 5.1 shows the processing condition used in this test. The material parameters used in this test are given in Table 3.1.
Table 5.1 Processing condition for the injection molding of PS disc.

<table>
<thead>
<tr>
<th>Flow Rate (cm³/s)</th>
<th>Mold Temperature (°C)</th>
<th>Melt Temperature (°C)</th>
<th>Packing Pressure (MPa)</th>
<th>Packing Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.8</td>
<td>225</td>
<td>40</td>
<td>15</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 5.5 exhibits the finite element mesh of a quarter disc in which 315 linear triangular elements and 184 nodes are used in the planar direction with 40 evenly spaced finite difference grids in the gapwise direction. The radius and thickness of the disk are 5.08 cm and 0.2 cm, respectively. Also, in the Fig. 5.5, the global nodal numbers of 26, 44, 66, 92 and 139 correspond to the radius of 1.79, 2.43, 3.07, 3.72 and 4.68 cm, respectively. These positions indicated in ref. [206] and are used for comparison with the present simulated results.
Figure 5.5 Finite element meshes for simulation of an injection molding of disc. The crosshatched circles represent the entrance nodes and the solid circles along with the global node numbers indicate where the simulated results were compared.

Figure 5.6 shows a comparison of pressure traces during the filling stage and at the onset of packing stage at the gate and at radii of 1.79 and 3.72 cm calculated by
conventional (symbols), used in [206], and unconditionally stable upwinding scheme (curves), used in the present study. Figure 5.7 indicates the calculated pressure traces during the filling and the entire packing stage at the same locations. Nearly identical predictions are observed in the filling stage but some deviation starts to happen at locations of 1.79 and 3.72 cm at the midway of the packing stage. In particular, the results calculated by unconditionally stable upwinding scheme exhibit a slightly faster pressure relaxation than the conventional scheme.

Figure 5.6 Comparison of calculated pressure traces during the filling stage and at the onset of packing stage at various locations by conventional (symbols), used in [206], and unconditionally stable upwinding scheme (curves), used in the present study.
Figure 5.7 Comparison of calculated pressure traces during the filling and packing stages at various locations by conventional (symbols) , used in [206], and unconditionally stable upwinding scheme (curves) , used in the present study.

Figure 5.8 demonstrates the calculated gapwise birefringence at the end of filling stage at various locations by conventional (symbols) , used in [206], and unconditionally stable upwinding scheme (curves) , used in the present study. The $\Delta n$ calculated by unconditionally stable upwinding scheme shows slightly higher values of birefringence than that calculated by conventional scheme. Figure 5.9 shows the calculated gapwise birefringence at the end of packing stage at various locations by conventional (symbols),
used in [206], and unconditionally stable upwinding scheme (curves), used in the present study. Again, the $\Delta n$ calculated by unconditionally stable upwinding scheme shows higher values of birefringence. The most significant deviation happens at the maximum birefringence of radius 1.79 cm indicated 9.2% higher value than that of the same position calculated by conventional scheme.

![Graph](image)

Figure 5.8 Calculated gapwise birefringence at the end of filling stage at various locations by conventional (symbols), used in [206], and unconditionally stable upwinding scheme (curves), used in the present study.
Figure 5.9 Calculated gapwise birefringence at the end of packing stage at various locations by conventional (symbols), used in [206], and unconditionally stable upwinding scheme (curves), used in the present study.

Although a slight deviation between numerical results obtained by two algorithms is observed, the calculation time is reduced from 2 hours to 30 minutes by using unconditionally stable upwinding scheme. This is due to a subdivision of the time step is required for the conventional upwinding scheme, if Eq. (5-108) is not satisfied. That means the current time step has to be divided by 2 and the entire calculations repeated. If the convergence is still not met, the same procedure has to be carried out again. In fact,
when the number of elements and local velocity are increased, the time saving is substantially increased due to complete elimination of the subdivision of time step.

From this numerical test, it is concluded that the unconditionally stable upwinding scheme is more efficient and resulted in similar results. Therefore, this new proposed numerical scheme is able to provide a faster solution for a viscoelastic simulation of injection molding. Accordingly, it is more feasible for use in commercial applications.

5.3 Prediction of Melt Front Propagation

To observe the melt front propagation, a series of short shot experiments were carried out. These observed melt front propagations as mentioned in Section 3.4 were compared with those predicted by simulation. The processing conditions described in Section 3.4 were used in the numerical simulation of the filling stage of the LGP cavity. Figure 5.10 shows the measured (symbols) and calculated (curves) melt front propagation during the filling of the LGP cavity. The results show that these measured and calculated values are in fair agreement. A waviness of the calculated melt front is due to the fact that lines were directly obtained at the melt front nodes. These nodes were determined by filling percentage of control volume, as described in Section 5.2.1. To obtain a smoother melt front, a finer finite element mesh is required. However, this leads to increase of the calculation time and also may cause the convergence problem in the viscoelastic
simulation [207]. Alternative way to smooth the melt front is to use curve fitting of the melt front nodes like it is done in most commercial software.

Figure 5.10 Measured (symbols) and simulated (curves) melt front propagation in the cavity of the LGP mold at conditions listed in Table 3.4.

5.4 Prediction of Pressure Evolution

The following results are shown for comparisons between measured and predicted pressure traces at the nozzle in the filling stage and initial portion of the packing stage.

5.4.1 Polycarbonates

Figure 5.11 shows the measured and calculated pressure traces at the nozzle of the LGP mold in Run #1 for two different PCs. Change of pressure versus time shows a
complex behavior due to the shape of the delivery system that includes nozzle, sprue, runners and gates. Various stages in the pressure variation are clearly seen including the filling stage, where variation of pressure shows several distinct regions depending on the location of the melt front during the filling stage, as mentioned earlier in Section 3.3.1. Clearly, the predicted data is in good agreement with experimental results of PC OQ1030, but shows some deviation in PC OQ3820. In molding PC OQ3820, constant injection speed was not possible to maintain, as indicated by curved screw position line in Fig. 5.11. However, this variation of screw movement forward was less significant for low viscosity PC.

![Figure 5.11](image_url)

Figure 5.11 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold and screw positions versus time of Run # 1 for two PCs.
In addition, it should be noted that in the filling stage a maximum injection pressure was imposed till the cavity was completely filled. Accordingly, the transfer of the pressure from the injection stage to the packing stage cannot be accomplished instantaneously. Therefore, the peak of the measured pressure does not coincide with the calculated pressure.

Figures 5.12 and 5.13 show the predicted pressure traces at locations of nozzle, A, B and C of the LGP mold of Run # 1 for PC OQ1030 and PC OQ3820, respectively. Both PCs show distinct behaviors in relaxation of cavity pressure. In the filling stage, the three cavity pressures show a different onset due to their locations. In the packing stage, Fig. 5.12 indicates that the pressure imposed by hydraulic unit is easier to transfer into the cavity in case of lower viscosity PC OQ1030. It means that polymer melt of lower viscosity provides better ability to flow during the packing stage, therefore resulting in a slower relaxation of cavity pressure in this stage. In other words, the effect of the packing stage is much stronger in case of PC OQ1030 than that of PC OQ3820.
Figures 5.12 The predicted pressure traces at locations of nozzle, A, B and C of the LGP mold for PC OQ1030 in Run # 1.

Figures 5.13 The predicted pressure traces at locations of nozzle, A, B and C of the LGP mold for PC OQ3820 in Run # 1.
The following figures show the measured and calculated pressure traces at the nozzle of the LGP mold at different injection speeds, packing pressures, packing times, mold temperatures and melt temperatures for PC OQ1030 and PC OQ3820.

Figs. 5.14 and 5.15 show the measured and simulated pressure traces and screw position at different injection speeds for PC OQ1030 and PC OQ3820, respectively. From Fig. 5.14, the simulated results show a good prediction from zero time to the end of pressure plateau corresponding to the completion of filling of runner system. At a low injection speed (Run #1), there is a good agreement between the measured and simulated pressure traces.

Figure 5.14 Measured (symbols) and predicted (curves) pressure traces and screw positions (symbols) at different injection speeds for PC OQ1030.
Figure 5.15 Measured (symbols) and predicted (curves) pressure traces and screw positions (symbols) at different injection speeds for PC OQ3820.

However, with increasing injection speed, deviation is observed especially when the pressure increases due to the melt passing through the gate and into the cavity. It is seen from Fig. 5.15, that in case of PC OQ3820, more deviation is observed in the filling stage. This is due to the fact that constant injection speed is no longer can be maintained. The variation of injection speed was less significant for low viscosity PC OQ1030.

In addition, the maximum of the simulated pressures does not indicate a significant variation with injection speed but measurements do. This is due to the fact that the inertial effect of screw movement becomes considerable with an increase of the injection
speed, as indicated by screw position curves in Fig. 5.16. Fig. 5.16 shows a comparison of ideal and real screw movement at different injection speeds for two PCs. The ideal screw movement is defined as a screw movement corresponding to a constant injection speed during the filling stage. It means that more material is forced into the cavity with increasing injection speed, even though the shot size is set up to be a constant. It is seen from Fig. 5.16, that at high speed the inertial effect is more considerable in lower viscosity PC OQ1030 than that in higher viscosity PC OQ3820. That explains why the measured maximum pressure of PC OQ1030 increases significantly with increasing injection speed.

![Figure 5.16 Comparison of ideal and real screw movement at different injection speeds for two PCs in Runs 1, 2 and 3.](image_url)
Figs. 5.17 and 5.18 exhibit a comparison of the measured and simulated pressure at different packing pressures in the filling stage for PC OQ1030 and PC OQ3820, respectively. Pressures in the packing stage were assigned based on pressure setup on the injection molding machine. It indicates a pressure development is similar in the filling stage but different in the packing stage. Again, a good agreement between the measured and predicted pressures is observed for PC OQ 1030 but more deviation was observed for PC OQ 3820 in the filling stage.

Figure 5.17 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different packing pressures for PC OQ1030.
Figure 5.18 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different packing pressures for PC OQ3820.

Figs. 5.19 and 5.20 show a comparison of the measured and simulated pressures at different packing times for PC OQ1030 and PC OQ3820, respectively. The applied packing pressure is reached at a short time after filling stage and after that it is maintained a constant. A consistency of the predicted and measured time is observed. However, Fig. 5.19 shows that the measured packing pressure relaxed during packing time, but this behavior is not significant in higher viscosity PC OQ3820, as indicated in Fig. 5.20. In addition, the measured pressure traces show a wavy shape of signal at time around 2 s after the packing pressure was released. This is caused by the screw recovery stage during which the screw moves backward due to transporting the melt forward for the next shot.
Figure 5.19 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different packing times for PC OQ1030.

Figure 5.20 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different packing times for PC OQ3820.
Figs. 5.21 and 5.22 exhibit a comparison of the measured and simulated pressures at different mold temperatures for PC OQ1030 and PC OQ3820, respectively. Both experimental and simulated pressures show a minor variation with mold temperatures. Clearly, the mold temperature does not play an important role in the evolution of pressure in the nozzle at mold temperature range used in this study. However, it should be noted that the variation of temperature due to cooling at different mold temperatures at locations A and C is significant in the filling stage and at onset of the packing stage, as shown in Fig. 5.23. This figure shows the temperature profiles at locations A and C at the end of the filling stage of PC OQ1030. At location A, closer to the gate, viscous heating contribution is high due to viscous heating at the gate that was transferred to the core region and due to high shear rates in the cavity at location A being in proximity from the gate. A higher melt temperature in the core region was observed at lower mold temperature. This is due to a higher thickness of the solidified layer at lower mold temperature, as shown in Fig. 5.23. However, away from the gate at location C, less viscous heating was observed because the shear rate at this location is not as high as at location A. Even though the mold temperature has shown some effect on melt temperature profile, such an effect is found to be insignificant to affect the pressure development in the nozzle. The contribution of temperature at location C to the overall
pressure in the nozzle is low. This is the reason why the pressure in the nozzle is not affected by changing the mold temperatures.

Figs. 5.24 and 5.25 exhibit a comparison of the measured and simulated pressures at different melt temperatures for PC OQ1030 and PC OQ3820, respectively. In the filling stage, the pressure decreases with an increase of the melt temperature. This is due to less resistance to flow. Fig. 5.24 indicates a good agreement between the measured and predicted pressures for PC OQ 1030 at three different melt temperatures. However, for PC OQ 3820 deviations are observed as indicated in Fig. 5.25. This is due to the inability to maintain the linear screw movement in case of higher viscosity PC OQ3820.

Figure 5.21 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different mold temperatures for PC OQ1030.
Figure 5.22 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different mold temperatures for PC OQ3820.

Figure 5.23 Calculated melt temperature profiles at different mold temperatures at locations A and C at the end of the filling stage of PC OQ1030.
Figure 5.24 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different melt temperatures for PC OQ1030.

Figure 5.25 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold at different melt temperatures for PC OQ3820.
5.4.2 Polystyrene

The following discussions demonstrate the influences of processing conditions on pressure traces for Run #1 and #2 corresponding to different packing times, for Run #1 and Run #3 corresponding to different melt temperatures for PS 615. The details of processing conditions are listed in Table 3.3. Fig. 5.26 displays a comparison of the measured and simulated pressure at different processing conditions for PS 615. At the highest melt temperature, Run #3, a slightly lower pressure in the filling stage was obtained than that in Run #1 and #2 due to lower viscosity. The Run #1 and #2 show similar traces in the filling stage but the pressure of Run #2 is released at the packing time of 2 s. The predicted pressures are lower than that simulated ones. This is again due to the effect of the variation of injection speed during the filling stage. This effect is significant in higher viscosity material, but less significant in lower viscosity material.

The numerical simulation of pressure evolution was carried out on two different PCs and a PS at various processing conditions. It was found that the measured pressures of lower viscosity PC was relatively accurately predicted than that of the higher viscosity PC or PS. For high viscosity PC, the injection speed is not constant during the filling stage. Also, the inertial effect during injection was observed in case of high injection
speed. This effect is more considerable in low viscosity PC and introduces more material into the cavity. The latter causes a stress overshoot leading to high pressure peak.

Figure 5.26 The measured (symbols) and predicted (curves) pressure traces at the nozzle of the LGP mold and screw positions versus time at different processing conditions for PS 615.

5.5 Prediction of Flow-induced Birefringence

The development of the flow- and thermally-induced birefringence in moldings of amorphous polymers arises from the optical anisotropy of material caused by strong flow field and rapid cooling, respectively. Therefore, the flow- and thermally-induced
birefringence are essentially coupled each other during injection molding process. However, since the temperature difference between two neighboring material points during injection molding in plane is not significant. Development of thermally-induced birefringence in normal direction is negligible. Therefore, it is reasonable that one can compare the predicted and measured normal birefringence without consideration of thermal birefringence.

5.5.1 Normal Residual Birefringence

The normal birefringence is defined as the averaged normal component of birefringence that measured in the 1-2 plane perpendicular to the gapwise direction as $\Delta n_{12}$ indicated in Fig. 3.20. The thermally-induced birefringence is negligible in this plane since cooling mainly takes place along the gapwise direction. Therefore, the Eq. (5-55) can be used to fully define the normal birefringence component, $\Delta n_{12}(z)$, at each grid point along the gapwise direction. Then the thickness averaged birefringence, $<\Delta n_{12}>$, was used to obtain the normal birefringence:

$$<\Delta n_{12}> = \frac{1}{b} \int_{0}^{b} \Delta n_{12}(z)dz$$

(5-116)

where b is the half thickness at the location under investigation. The calculated results obtained at various processing conditions are compared to the simulated data.
5.5.1.1 Polycarbonates

Figures 5.27 to 5.36 show the measured and predicted normal birefringence, \( \Delta n_{12} \), along the flow direction (in A to C direction indicated in Fig. 3.21) at different injection speeds, packing pressures, packing times, mold temperatures and melt temperatures for PC OQ1030 and PC OQ3820. Figs. 5.27 and 5.28 show such a comparison at different injection speeds for PC OQ1030 and PC OQ3820, respectively. Both PCs show not only different level of normal birefringence, but also different patterns. Higher values of the normal birefringence in moldings of PC OQ3820 are observed. It is caused by a higher stress-optical coefficient in the melt state, as depicted in Fig. 4.18, and also higher normal and shear stresses resulting from relatively higher viscosity, as indicated in Figs. 3.2 and 3.3.

The measured normal birefringence along the flow direction demonstrates the highest value near the gate due to a high level of molecular orientation and decreases along the flow direction. However, the measured normal birefringence of PC OQ1030 exhibits a sudden increase then decreases near the gate forming a maximum. This maximum is not observed in PC OQ3820 at this processing condition. However, such a maximum of the normal birefringence PC OQ3820 was observed at higher melt temperature corresponding to Run #10 and will be shown later. Therefore, it seems that a
lower viscosity melt may cause a maximum of the normal birefringence, since the development of birefringence close to the gate is a competition between the build up and relaxation processes during melt floe near the gate area. Such a build up and relaxation of birefringence occurs in contraction and expansion flow [3].

In addition, Fig. 5.27 shows some effect at different injection molding speeds on the measured normal birefringence from the gate to 6 mm away from the gate. This is due to a dominating effect of the relaxation process. In contrast, the measured normal birefringence of PC OQ1030 is not affected by injection speed at distances higher than 6 mm away from the gate. This is due to a freezing effect on formation on birefringence. A similar tendency is observed on PC OQ3820, except no formation of a maximum as indicated in Fig. 5.28. The measured normal birefringence of Run #1 corresponding to lower injection speed shows a slightly higher value of birefringence. However, the injection speed is not a significant processing condition affecting the development of the normal birefringence in LGP.

The simulated normal birefringence of PC OQ1030 does not show that it is affected by injection speed. The simulation is able to predict the level of residual normal birefringence but not able to describe the exact shape of curves especially the formation of the maximum. This may be due to the elongational flow that occurs around the gate
area. Such a behavior is not considered in the simulation since the elastic strain tensor was calculated based on a simple shear flow. In addition, the predicted normal birefringence of PC OQ3820 is lower at lower injection speeds than that in the measurements. This may be also due to the calculated pressure is being lower than the measured pressure during the cavity filling since injection speed was not constant, as shown in Fig. 5.15.

Figures 5.29 and 5.30 display a comparison of the measured and predicted normal birefringence, $\langle \Delta n_{12} \rangle$, along the flow direction at different packing pressures for PC OQ1030 and PC OQ3820, respectively. The normal birefringence increases with increasing packing pressure in moldings of two PC. However, the effect is less significant in PC OQ1030. This may be due to a lower molecular weight of PC OQ1030 exhibiting lower relaxation time accelerating the relaxation process. Again, the simulations are in a qualitative agreement with experimental data of the residual normal birefringence. However, they are not able to describe correctly the shape of curves near the gate.
Figure 5.27 The measured (symbols) and predicted (curves) normal birefringence $<\Delta n_{12}>$ along the flow direction at different injection speeds in LGP moldings for PC OQ1030.

Figure 5.28 The measured (symbols) and predicted (curves) normal birefringence $<\Delta n_{12}>$ along the flow direction at different injection speeds in LGP moldings for PC OQ3820.
Figure 5.29 The measured (symbols) and predicted (curves) normal birefringence $\langle \Delta n_{12} \rangle$ along the flow direction at different packing pressures in LGP moldings for PC OQ1030.

Figure 5.30 The measured (symbols) and predicted (curves) normal birefringence $\langle \Delta n_{12} \rangle$ along the flow direction at different packing pressures in LGP moldings for PC OQ3820.
Figures 5.31 and 5.32 exhibit a comparison of the measured and predicted normal birefringence, $<\Delta n_{12}>$, along the flow direction at different packing times for PC OQ1030 and PC OQ3820, respectively. The measured and predicted normal birefringence shows minor effect with regard to variation of the packing time. This is due to the fact that gate freezing occurs in about 2 s, which is the shortest packing time applied in this study. In the previous study of PC disk [147], it was shown that the normal retardation near the cavity entrance increased significantly due to the packing time. Also, the normal retardation was shown to reduce along the flow direction. Its value at the distances further away from the entrance was the same at the end of the packing and filling stages. However, in the packing stage, additional materials were added to compensate for shrinkage only before the gate freezing. When the gate freezes, the development of birefringence is dominated by relaxation process. In the present study, one-dimensional tubular elements were used to incorporate the delivery system and cavity to investigate the effect of gate freezing. It was found that at processing condition Run #1, the gate freezes off at 2.16 and 2.54 s for PC OQ1030 and PC OQ3820, respectively. Accordingly, the predicted normal birefringence is very little affected by the variation of the packing time.
Figure 5.31 The measured (symbols) and predicted (curves) normal birefringence $\Delta n_{12}$ along the flow direction at different packing times in LGP moldings for PC OQ1030.

Figure 5.32 The measured (symbols) and predicted (curves) normal birefringence $\Delta n_{12}$ along the flow direction at different packing times in LGP moldings for PC OQ3820.
Figures 5.33 and 5.34 depict a comparison of the measured and predicted normal birefringence, $\Delta n_{12}$, along the flow direction at different mold temperatures for PC OQ1030 and PC OQ3820, respectively. Experiments and simulations show that the normal birefringence increases with reducing mold temperature. The PC OQ1030 shows a dominating effect of relaxation process at locations further away from the gate where the normal birefringence is not affected by the mold temperature. But such phenomenon is not observed in PC OQ3820. Although the predictions show a qualitative agreement with experimental data, a noticeable deviation is observed in Run #8 of PC OQ3820. This may be due to the increase of elongation stress in the gate region caused from lower mold temperature resulting in increase of cooling rate and relaxation time preventing the stress relaxation.

Figures 5.35 and 5.36 demonstrate a comparison of the measured and predicted normal birefringence, $\Delta n_{12}$, along the flow direction at different melt temperatures for PC OQ1030 and PC OQ3820, respectively. The normal birefringence increases with reducing melt temperature, but the effect is not as much as the effects of the packing pressure increase and mold temperature decrease.

In addition, both PCs show minor changes in the normal birefringence due to a dominating effect of relaxation process at locations further away from the gate. In Fig.
5.35, the predictions are in a fair agreement with the measurements at locations after 4 mm away the gate. However, more deviations are found near the gate where the normal birefringence exhibits a maximum. In Fig. 5.36, the measured normal birefringence at processing condition of Run #10 corresponding to the highest melt temperature indicates a formation maximum which is not observed in other conditions of PC OQ3820 in the same Figure. It seems like that a lower viscosity at high melt temperature causes the appearance of the maximum of normal birefringence. Also, the predictions of higher melt temperatures (Run # 9 and 10) show a good agreement with experimental data at locations further away from the position of the maximum.

Figure 5.33 The measured (symbols) and predicted (curves) normal birefringence \(<\Delta n_{12}\>\) along the flow direction at different mold temperatures in LGP moldings for PC OQ1030.
Figure 5.34 The measured (symbols) and predicted (curves) normal birefringence $\langle \Delta n_{12} \rangle$ along the flow direction at different mold temperatures in LGP moldings for PC OQ3820.

Figure 5.35 The measured (symbols) and predicted (curves) normal birefringence $\langle \Delta n_{12} \rangle$ along the flow direction at different melt temperatures in LGP moldings for PC OQ1030.
Figure 5.36 The measured (symbols) and predicted (curves) normal birefringence $<\Delta n_{12}>$ along the flow direction at different melt temperatures in LGP moldings for PC OQ3820.

5.5.1.2 Polystyrene

The following discussions demonstrate the influences of processing conditions on the normal birefringence for Run #1 and #2 corresponding to different packing times, for Run #1 and Run #3 corresponding to different melt temperatures for PS 615. The details of processing conditions were listed in Table 3.3.

Figure 5.37 exhibit a comparison of the measured and predicted normal birefringence, $<\Delta n_{12}>$, along the flow direction at different processing condition for PS 615. The normal birefringence reduces with increasing melt temperature and reducing
packing time. Similar to PCs, the effect of melt temperature on the normal birefringence is not significant. However, in contrast to PCs, the packing time affects the development of the normal birefringence significantly in case of PS. This is due to the gate freezing time of PS is significantly higher than that found on both PCs. In fact, according to the simulation results, the gate freezing time for PS in Run #1 is 3.35 s in contrast to 2.16 s and 2.54 s at Run #1 for PC OQ1030 and PC OQ3820, respectively. This indicates the cooling rate of PS is considerably lower than that in both PCs.

Figure 5.37 The measured (symbols) and predicted (curves) normal birefringence $<\Delta n_{12}>$ along the flow direction at different processing conditions in LGP moldings for PS 615.
Also, even though the PS 615 has much higher value of the stress-optical coefficient in the melt state, compared to the PC OQ3820, their normal birefringence indicates a similar level. This is due to the slower cooling in case of PS 615 accelerating the relaxation process during moldings.

5.5.1.3 Conclusions

The numerical simulation of normal birefringence was carried out and the results were compared to the measurements. Since the temperature difference between any two neighboring material points on the 1-2 plane is not significant, the development of the thermally-induced birefringence in this plane is negligible. The effect of various processing conditions on the development of the normal birefringence of PCs can be ranked from most to least: packing pressure, mold temperature, melt temperature, injection speed and packing time. However, the packing time is a significant factor in case of LGP moldings made of PS 615 due to a longer gate freezing time. Both PCs show not only different level of the normal birefringence, but also dissimilar patterns. A higher value of the normal birefringence of PC OQ3820 in comparison with PC OQ1030 is observed due to a higher stress-optical coefficient of PC OQ3820 and also higher normal and shear stresses achieved during the cavity filling caused by its higher viscosity.
It is concluded that the simulation is able to predict the level of the residual normal birefringence but unable to describe the exact shape of curves especially the formation of a maximum of the normal birefringence. This may be due to the elongational flow behavior in the gate area [3]. Simulation of such elongational flow requires an inclusion of contraction and expansion flows which are not considered in the current simulation. In calculations of the elastic strain tensor, it is assumed that a simple shear flow occurs during flow through the gate. In addition, the predicted normal birefringence of PC OQ3820 is lower than the measured one. This may be also due to the lower calculated cavity pressure than the measured one since injection speed was not a constant during the cavity filling.

5.5.2 Transverse Birefringence

The transverse birefringences, $\Delta n_{13}$ and $\Delta n_{23}$, are defined as the gapwise distribution of birefringence measured at 1-3 and 2-3 planes, respectively, as indicated in Fig. 3.20. Since the temperature difference between any two neighboring material points along the gapwise direction is significant, the contribution of the thermally-induced birefringence to birefringence $\Delta n_{13}$ and $\Delta n_{23}$ is substantial. The nonlinear constitutive equation used to describe flow behavior is not valid to describe the development of the thermal stresses. Accordingly, the following discussions only focus on the flow-induced transverse
birefringences. The prediction of the thermally-induced birefringence will be discussed later in Section 5.7.

5.5.2.1 Polycarbonates

The calculation of the elastic strain tensor was carried out in the streamwise direction, which varies with directions of the velocity vector and pressure gradient vector as described in Eqs. (5-28) and (5-29). Therefore, the calculated transverse birefringences in the streamwise coordinates $\Delta n_{13s}$ and $\Delta n_{23s}$ have to be transferred into the Cartesian coordinate. The birefringence components of $\Delta n_{12}$ and $\Delta n_{23}$ along the Cartesian coordinate were calculated as

$$
\Delta n_{13} = \Delta n_{13s} \frac{\nabla p_y}{\nabla p_s} + \Delta n_{23s} \frac{\nabla p_s}{\nabla p_s}
$$

(5-117)

$$
\Delta n_{23} = \Delta n_{23s} \frac{\nabla p_y}{\nabla p_s} + \Delta n_{13s} \frac{\nabla p_s}{\nabla p_s}
$$

(5-118)

$$
\nabla p_s = \sqrt{(\nabla p_x)^2 + (\nabla p_y)^2}
$$

(5-119)

where subscript $s$ represents the streamwise direction and $\nabla p_x$, $\nabla p_y$ and $\nabla p_y$ are the pressure gradients along the streamline ($s$), length ($x$) and width ($y$) directions, respectively. The values were calculated at the time step when freezing occurs at the locations under consideration since pressure gradient are not available after this time step.
Figure 5.38 exhibits the calculated birefringence $\Delta n_{13}$ at processing condition of Run #1 at locations A, B, and C for PC OQ1030 at the end of filling stage and cooling stage. Birefringence distribution shows similar pattern as in PS disc in Figs. 5.8 and 5.9. At the end of the filling stage, a maximum value of $\Delta n_{13}$ happens near the wall due to the formation of solidified layer. Thickness of this layer increases from location A to C since A is closer to the gate. In the packing stage, more material is forced into the cavity to compensate the shrinkage. This introduces a second maximum that is located further away from the wall. At the same time, the maximum near the wall relaxes causing a concave area between two maxima. In addition, the development of second maximum is not significant at locations away from the gate due to a weaker flow during the packing stage at these positions.

Figure 5.39 exhibits the calculated birefringence $\Delta n_{23}$ at processing condition of Run #1 of locations A, B, and C for PC OQ1030 at the end of the filling stage and cooling stage. A very similar shape of birefringence distribution is observed, but the predicted value is almost one order magnitude smaller. Although the flow in the LGP cavity is two-dimensional, the locations under investigation have stronger flow in the direction of 1 than the direction of 2. Therefore, a higher pressure gradient acts along the direction of 1 resulting in higher value of $\Delta n_{13}$.
Figure 5.40 shows a comparison of the measured and calculated gapwise distribution of residual birefringence component $\Delta n_{13}$ in the LGP molding of PC OQ1030 obtained at processing condition of Run #1 at positions B and C. It indicates a much higher measured birefringence compared to simulations. This is due to the fact that the thermally-induced birefringence has a significant contribution to the overall birefringence which is not considered at this point. It is also seen that the measured birefringence $\Delta n_{13}$ at locations B and C is comparable indicating that the contribution from the thermally-induced birefringence plays more important role than that of the flow-induced birefringence in the LGP molding.

Figure 5.41 shows a comparison of the measured and calculated gapwise distribution of birefringence component $\Delta n_{23}$ in the LGP molding of PC OQ1030 obtained at processing condition of Run #1 at positions B and C. Again, a much higher measured transverse birefringence, $\Delta n_{23}$, is observed since the contribution from the thermally-induced birefringence is not considered in the current simulations.
Figure 5.38 Calculated birefringence $\Delta n_{13}$ at processing condition of Run #1 at locations A, B, and C in LGP moldings for PC OQ1030 at the end of filling and cooling stages.

Figure 5.39 Calculated birefringence $\Delta n_{23}$ at processing condition of Run #1 at locations A, B, and C in LGP moldings for PC OQ1030 at the end of filling and cooling stages.
Figure 5.40 The measured (symbols) and calculated gapwise birefringence $\Delta n_{13}$ (curves) at processing condition of Run #1 at locations B and C in LGP moldings for PC OQ1030.

Figure 5.41 The measured (symbols) and calculated gapwise birefringence $\Delta n_{23}$ (curves) at processing condition of Run #1 at locations B and C in LGP moldings for PC OQ1030.
To understand the flow-induced birefringence affected by processing conditions, Figures 5.42 to 5.51 display the predicted $\Delta n_{13}$ in LGPs obtained at different injection speeds, packing pressures, packing times, mold temperatures and melt temperatures for PC OQ1030 and PC OQ3820. Figs. 5.42 and 5.43 show the predicted $\Delta n_{13}$ at locations B and C in LGPs for different injection speeds for PC OQ1030 and PC OQ3820, respectively. Both PCs exhibit distinct pattern in development of $\Delta n_{13}$. In particular, the PC OQ1030 indicates a highly pronounced maximum of $\Delta n_{13}$ further away from the wall, introduced due to the flow-induced birefringence in the packing stage, than that found in PC OQ3820. However, the PC OQ3820 develops a significant maximum of the residual flow-induced birefringence near the wall which is observed to be lower in PC OQ1030. The presence of the maximum birefringence near the wall is due to a nearly one order magnitude higher viscosity of PC OQ3820 retarding the relaxation of the transverse birefringence during cooling. A lower level of the maximum birefringence near the wall in case of PC OQ1030 is due to a faster relaxation process in this polymer. In addition, the PC OQ3820 shows a higher flow-induced birefringence in both normal and transverse directions. This is due to the fact that PC OQ3820 has a higher stress-optical coefficient in the melt state. Also, in PC OQ3820, higher shear and normal stresses are developed during molding due to its high viscosity.
Besides, the increase of injection speed causes a lower maximum of $\Delta n_{13}$ further away from the wall and lower birefringence near the wall, as indicated in Fig. 5.42, but the effect is observed to be minor. This is due to shorter filling time and more viscous heating resulting in higher melt temperature in the cavity leading to a faster relaxation of birefringence.

Figure 5.42 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different injection speeds in LGP moldings of PC OQ1030.
Figure 5.43 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different injection speeds in LGP moldings of PC OQ3820.

Figs. 5.44 and 5.45 show the predicted gapwise distribution of birefringence $\Delta n_{13}$ at locations B and C in LGPs obtained at different packing pressures for PC OQ1030 and PC OQ3820, respectively. It clearly indicates that the magnitude of the maximum $\Delta n_{13}$ further away from the wall is significantly increased by the packing pressure. At the same time, the value of $\Delta n_{13}$ near the wall shows minor variation with varying packing pressure. This effect is due to the fact that stresses near the wall are frozen mainly during the cavity filling stage.
Figure 5.44 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different packing pressures in LGP moldings of PC OQ1030.

Figure 5.45 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different packing pressures in LGP moldings of PC OQ3820.
Figs. 5.46 and 5.47 show the predicted gapwise distribution of birefringence $\Delta n_{13}$ at locations B and C in LGPs obtained at different packing times for PC OQ1030 and PC OQ3820, respectively. The predictions show minor effect on birefringence with packing time. As mentioned earlier, this is due to the fact that gate freezes at 2.16 and 2.54 s for PC OQ1030 and PC OQ3820, respectively, at processing condition of Run #1. This gate freezing time is closed to the shortest packing time applied in this study. Therefore, the predicted transverse birefringence, $\Delta n_{13}$, shows a minor effect with respect to the packing time.

![Diagram showing predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different packing times in LGP moldings of PC OQ1030.](image)

Figure 5.46 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different packing times in LGP moldings of PC OQ1030.
Figure 5.47 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different packing times in LGP moldings of PC OQ3820.

Figures 5.48 and 5.49 show the predicted gapwise distribution of birefringence $\Delta n_{13}$ at locations B and C in LGPs obtained at different mold temperatures for PC OQ1030 and PC OQ3820, respectively. For PC OQ1030, as shown in Fig. 5.48, the higher mold temperature significantly affects the maximum of birefringence $\Delta n_{13}$ further away from the wall. This increase of maximum is due to the fact that higher mold temperature leads to less resistance in the melt core allowing more melt to be pushed into the cavity. However, in case of PC OQ3820, as shown in Fig. 5.49, the effect of mold temperature on the maximum of birefringence further away from the wall is less significant due to its
high viscosity. At the same time, the birefringence near the wall decreases with an increase of mold temperature. In addition, the maximum located further away from the wall on both PCs was observed to be shifted towards the wall with increasing mold temperature. This is due to a slower cooling rate caused by increase of mold temperature resulting in thinner solidified layer. This is also evident from the birefringence maximum located near the wall region that is shifted away from the wall with increase of mold temperature. In particular, a higher mold temperature allows a relatively faster relaxation near the wall region leading to decrease of birefringence at higher mold temperature in the wall region. However, this effect is more pronounced in case of PC OQ 3820 than that of PC OQ1030.

Figures 5.50 and 5.51 demonstrate the predicted gapwise distribution of birefringence $\Delta n_{13}$ at locations B and C in LGPs obtained at different melt temperatures for PC OQ1030 and PC OQ3820, respectively. At location B of PC OQ1030, the value of maximum $\Delta n_{13}$ further away from the wall increases with reducing melt temperature, but an opposite tendency was observed at location C. This is due to a competition between build up and relaxation of birefringence further away from the wall. Although higher melt temperature accelerates the relaxation process, it allows more materials to be pushed into the cavity at the same time due to lower viscosity. In fact, PC OQ3820 shows that a built
up process of maximum birefringence further away from the wall dominates the relaxation process at location B. Therefore, the value of maximum $\Delta n_{13}$ further away from the wall increases with increasing melt temperature. The same tendency was observed at location C but it is less significant.

As shown in Fig. 5.50, the maximum birefringence $\Delta n_{13}$ in the wall region increases with reducing melt temperature. This is due to the fact that solidification of polymer at lower melt temperature happened at earlier time than that of higher melt temperature. However, this effect is more pronounced at locations B and C of PC OQ1030 than in PC OQ3820. In fact, the maximum birefringence $\Delta n_{13}$ in the wall region of PC OQ3820 exhibits a similar level at various melt temperatures. This is due to the fact that in high viscosity material a slower relaxation of birefringence occurs.
Figure 5.48 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different mold temperatures in LGP moldings of PC OQ1030.

Figure 5.49 The predicted gapwise distribution of $\Delta n_{13}$ at locations B and C for different mold temperatures in LGP moldings of PC OQ3820.
Figure 5.50 The predicted gapwise distribution of birefringence $\Delta n_{13}$ at locations B and C for different melt temperatures in LGP moldings of PC OQ1030.

Figure 5.51 The predicted gapwise distribution of birefringence $\Delta n_{13}$ at locations B and C for different melt temperatures in LGP moldings of PC OQ3820.
5.5.2.2 Polystyrene

The following discussions demonstrate the influences of processing conditions on the calculated transverse birefringence of $\Delta n_{13}$ for Run #1 and #2 corresponding to different packing times, for Run #1 and Run #3 corresponding to different melt temperatures for PS 615. The details of processing conditions were listed in Table 3.3.

Figure 5.52 demonstrates the prediction of the gapwise birefringence distribution of $\Delta n_{13}$ at locations B and C in LGPs obtained at different processing conditions for PS 615. The value of the gapwise birefringence distribution $\Delta n_{13}$ is all negative due to the negative stress-optical coefficient of PS 615 in the melt state. The maximum birefringence further away from the wall at locations B and C increases with an increase of the packing time. This is due to the fact that more materials were added to compensate the shrinkage before the gate freezing. Unlike in case of two PCs, the packing time shows significant effect on development of the maximum of birefringence further away from the wall. As mentioned earlier, this is because the gate freezing time for PS in Run #1 is 3.35 s in contrast to 2.16 s and 2.54 s at Run #1 for PC OQ1030 and PC OQ3820, respectively. In addition, the maximum of birefringence in the wall region shows little effect with a change of packing time. This is due to the development of birefringence in this region was mainly completed in the melt filling stage.
Also, the maximum birefringence further away from the wall at locations B and C in LGPs indicates an increase with an increase of melt temperature. This is due to the fact that at higher melt temperature more melt can be pushed into the cavity due to its lower viscosity thus overriding the relaxation process. In particular, the maximum of birefringence in the wall region at locations B and C indicates a decrease with an increase of melt temperature. This is because a lower level of the flow stresses induced by a higher melt temperature.

![Figure 5.52 The predicted gapwise distribution of birefringence $\Delta n_{13}$ at locations B and C at different processing conditions in LGP moldings of PS 615.](image-url)
5.5.2.3 Conclusions

The numerical simulation of the transverse birefringence in LGPs was carried out and the results were compared to the experimental measurements. The measured birefringence is much higher than that of simulations without inclusion of the thermally-induced birefringence. This is due to the temperature difference between any two neighboring material points on the 1-3 and 2-3 planes are significant. This causes a tremendous contribution of the thermally-induced birefringence to the overall birefringence. However, the non-linear constitutive equation used to describe flow behavior is not applicable to describe the formation of the thermal stresses and birefringence in solid state. Therefore, another approach is required to describe the formation of thermal stresses and strains. This will be discussed later in Section 5.7.

To understand the effect processing conditions on the flow-induced birefringence, simulations of birefringence component of $\Delta n_{13}$ were carried out at various processing conditions. Both PCs and a PS exhibit distinct pattern in development of $\Delta n_{13}$. The PC OQ1030 indicates a highly pronounced maximum of $\Delta n_{13}$ further away from the wall than that found in PC OQ3820. However, the PC OQ3820 develops a significant residual flow-induced birefringence near the wall which is observed to be lower in PC OQ1030 due to low viscosity of PC OQ1030 leading to a faster relaxation process. It is concluded
that the viscosity plays an important role on how the processing conditions affect the development of the residual flow-induced transverse birefringence.

Comparison the transverse birefringence $\Delta n_{13}$ among two PCs and PS shows distinct tendencies in its development. Due to a slower cooling rate, the development of the transverse birefringence $\Delta n_{13}$ for PS at location C shows considerable value of $\Delta n_{13}$ compared to that of both PCs. Also, the PC OQ1030 shows an opposite tendency in development of the maximum birefringence further away from the wall with respect to variations of melt temperature than that found on PS and PC OQ3820 because of a dominating effect of relaxation of birefringence in PC OQ1030. In addition, the duration of the packing time provides a tremendous impact on the development of birefringence due to a slower cooling rate of PS. However, this is not observed in both PCs due to the shortest packing time on both PCs was set to be close to the gate freezing time.

5.6 Anisotropic Shrinkage

Anisotropic shrinkage including the length, width and thickness shrinkages of moldings results from the anisotropic molecular orientation. For amorphous polymers, such shrinkage development is influenced by volumetric shrinkage, flow-induced residual stresses and orientation and heat transfer during the molding process. To investigate the effects of processing conditions on the anisotropic shrinkage, a methodology proposed by
Kwon et al. [90] is introduced to the current simulation to compare with experimental measurements. To avoid measuring error, the thickness shrinkage was measured at the portion of the highest thickness indicated as D position in Fig. 3.21.

5.6.1 Polycarbonates

Figures 5.53 to 5.62 show the measured and predicted length, width and thickness shrinkage in LGPs at different injection speeds, packing pressures, packing times, mold temperatures and melt temperatures for PC OQ1030 and PC OQ3820. It should be noted that the error of measurement is less than 2%. In particular, Figs. 5.53 and 5.54 indicate a comparison of three shrinkages as a function of the injection speed for PC OQ1030 and PC OQ3820, respectively. Among three different directions, the thickness shrinkage of both PCs shows the highest value. It slightly decreases with increasing injection speed. The PC OQ3820 displays a higher value of shrinkage in every direction than that found in PC OQ1030. The length and width shrinkage (in plane shrinkage) does not show a significant difference, but the width shrinkage is slightly smaller than the length shrinkage. This result indicated by both measurements and simulations. This is due to a low level of molecular orientation introduced in moldings of amorphous polymers.

From these observations, it is clear that the injection speed has a slight influence on the anisotropic shrinkages of LGP molding. This is due to the fact that the shrinkage is
mainly determined by specific volume history during the packing stage. The injection speed plays only limited role in the packing stage.

The thickness shrinkage exhibits a gradual decrease with the injection speed in this study. A higher injection speed results in higher local pressure. In turn, it should lower the value of specific volume at the end of filling stage, according to Eq. (5-88). However, at a higher injection speed, more viscous heating is introduced. Therefore, the value of specific volume at the end of filling stage may be increased. Accordingly, the tendency of shrinkage variation caused by injection speed is due to a competition between an increase and decrease of the specific volume at the end of the filling stage due to variations of temperature and pressure.

Figures 5.55 and 5.56 indicate a variation of anisotropic shrinkages in LGPs with the packing pressure for PC OQ1030 and PC OQ3820, respectively. The thickness shrinkage is reduced by increasing packing pressure, as indicated by measurements and simulations. The predicted anisotropic shrinkage indicates a good agreement with measurements on LGP moldings of both PCs. However, the PC OQ3820 displays a higher value of shrinkage in every direction than that of PC OQ1030, although their PVT behavior is the same. This is because the higher viscosity PC OQ3820 introduces higher viscous heating. Also the melt temperature used in PC OQ3820 was 10\(^\circ\)C higher than that in PC OQ1030.
Figure 5.53 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the injection speed in LGP moldings of PC OQ1030.

Figure 5.54 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the injection speed in LGP moldings of PC OQ3820.
Figure 5.55 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the packing pressure in LGP moldings of PC OQ1030.

Figure 5.56 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the packing pressure in LGP moldings of PC OQ3820.
Figures 5.57 and 5.58 indicate a dependence of anisotropic shrinkages in LGPs as a function of the packing time for PC OQ1030 and PC OQ3820, respectively. Measurements and simulations show little variation of three shrinkages of LGPs made from both PCs with the packing times. In our previous study [90], the packing time was found to be the most significant factor in development of shrinkage of a PS strip. This contradiction cannot be explained by higher thermal conductivity of PC, see Table 3.1, introducing higher cooling rate. Also, the gate is very thin in the LGP mold. That means the gate freezes relatively faster than that in the strip cavity [90]. In fact, it was found that the gate freezes off at 2.16 and 2.54 s for PC OQ1030 and PC OQ3820, respectively, according to the simulation at processing condition Run #1.

In PS strip cavity, the gate freezes later allowing for more materials to be pushed into cavity during the packing stage. In case of LGP moldings, no more material can be forced into the cavity after gate freezes during the packing stage. Therefore, gate freezing does not allow a supply of an additional melt to compensate for the shrinkage. That explains the contradiction of why the shrinkage is not affected by the packing time in the present study. Actually, the LGP molding of PC OQ3820 at packing time of 2 s shows a slightly higher shrinkage because the gate freezing time is a little longer than the packing time.
Figure 5.57 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the packing time in LGP moldings of PC OQ1030.

Figure 5.58 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the packing time in LGP moldings of PC OQ3820.
Figures 5.59 and 5.60 indicate anisotropic shrinkage as a function of the mold temperature for PC OQ1030 and PC OQ3820, respectively. Again, the length and width shrinkages show limited variation due to a low level of molecular orientation introduced in LGP moldings of amorphous polymer. The thickness shrinkage increases with increasing mold temperature. This is due to a slower cooling rate resulting in hotter melt core and the specific volume being relatively higher compared to that of the lower mold temperature. Also, lower cooling rate causes a faster pressure relaxation and results in higher value of specific volume.

![Graph showing anisotropic shrinkage as a function of mold temperature](image)

**Figure 5.59** The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the mold temperature in LGP moldings of PC OQ1030.
Figure 5.60 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the mold temperature in LGP moldings of PC QO3820.

Figures 5.61 and 5.62 indicate anisotropic shrinkage as a function of the melt temperature for PC QO1030 and PC QO3820, respectively. Again, the length and width shrinkages show minor variation due to a low level of molecular orientation. The thickness shrinkage increases with increasing melt temperature. From comparison of Figs. 5.59 to 5.62, it is clear that the melt temperature has more significant effect on the thickness shrinkage than mold temperature at the increment of temperature change in this study. The thickness shrinkage of PC QO3820 is higher than that of PC QO1030 due to a higher melt temperature applied and more viscous heating introduced in case of PC QO3820.
Figure 5.61 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of the melt temperature in LGP moldings of PC OQ1030.

Figure 5.62 The measured (symbols) and simulated (lines) anisotropic shrinkage as a function of the melt temperature in LGP moldings of PC OQ3820.
5.6.2 Polystyrene

The following discussions demonstrate the influences of processing conditions on the anisotropic shrinkages for Runs #1 and #2 corresponding to different packing times, for Run #1 and Run #3 corresponding to different melt temperatures for PS 615. The details of processing conditions were listed in Table 3.3.

Figure 5.63 shows a comparison of anisotropic shrinkage at different processing conditions for PS 615. The length shrinkage is slightly higher than the width shrinkage as observed on both PCs and minor variation on both shrinkages are shown by varying processing conditions indicating a low level of molecular orientation. Also, the thickness shrinkage slightly increases with increasing melt temperature and significantly increases with reducing packing time. The difference of the influence of the packing time on the thickness shrinkage in case of LGP molding of PS in comparison with that of LGP made of both PCs is due to a longer gate freezing time in case of PS as also seen from the effects on the normal and transverse birefringence, as shown in Figs. 5.37 and 5.52.

The predicted thickness shrinkage at the processing condition of Run #2 shows an overestimation compared to the measured shrinkage. However, the reason for this discrepancy is not clear at this point.
Figure 5.63 The measured (symbols) and simulated (lines) anisotropic shrinkages as a function of processing conditions in LGP moldings of PS 615.

5.6.3 Conclusions

The numerical simulation of anisotropic shrinkage was carried out at various processing conditions of the LGP moldings made of two PCs and a PS. The results were compared to the measurements. A good agreement is reached between the simulations and measurements of anisotropic shrinkage at various processing conditions. Both PCs show similar tendency in shrinkage with respect to variation of processing conditions. However, a higher value of shrinkage on PC OQ3820 is observed due to its higher viscosity and higher applied temperature.
In addition, it is concluded that the shrinkage for amorphous polymers is influenced by volumetric shrinkage, flow-induced residual birefringence and heat transfer during the molding process, especially in the packing stage. Besides, the gate freezing effect was observed to be an essential factor in development of shrinkage. The effect of processing conditions on the development of shrinkage in case of PC in this study is found to be ranked from most to least: packing pressure, melt temperature, mold temperature, injection speed and packing time. In case of PS, the thickness shrinkage slightly increases with increasing melt temperature and significantly increases with reducing packing time. The packing time was found to be a critical parameter affecting the thickness shrinkage due to a longer gate freezing time in case of LGP molding of PS.

However, the results obtained from different processing conditions indicate that there is effect of multiple factors on shrinkage. This leads to complex effect of processing parameters on shrinkage due to coupling effect of various variables, cavity and material. However, the temperature and pressure history are most important factors influencing the development of shrinkage.

5.7 Contribution of Thermally-induced Birefringence

The thermally-induced birefringence is caused by the nonequilibrium density and the viscoelastic behavior of polymers during an inhomogeneous rapid cooling through the
glass transition temperature. The non-linear constitutive equation used to describe flow behavior is not valid to describe the development of the thermal stresses and birefringence during the transition from the rubbery to the glassy state. Since polymeric materials exhibit a small deformation during cooling from melt to the temperature below the glass transition temperature, a linear viscoelastic and photoviscoelastic constitutive equations were used to evaluate the evolution of thermally-induced birefringence. The mathematical modeling of the thermally-induced stresses and birefringence has been described in Section 5.1.2.

In addition, the presence of the mold wall changes the strains and birefringence development during cooling dramatically (constrained boundary). Because of the adhesion between polymer and wall, the stresses will not be equilibrated. The thermal expansion coefficient of polymer is, in general, considerably higher than that of the metal mold wall. Therefore, during cooling process only tensile stresses will be built up until the polymer is released from the wall (free quenching boundary). The thermal expansion of wall is considered to be small enough such that it is neglected in this study.

5.7.1 Polystyrene

Figure 5.64 exhibits the development of the gapwise distribution of the thermally-induced birefringence at different times calculated by a combination of
constrained and free quenching at location B of LGP molding made of PS 615 in Run #1. Figure 5.65 displays the corresponding calculated gapwise temperature distribution at various times during molding. The transient thermally-induced birefringence calculated by a combination of constrained and free quenching can be differentiated as following.

The first curve at time of 0.02 s indicates an immediate growth of the thermally-induced birefringence taking place near the wall. This is caused by the freezing effect at the mold wall. Then, the thermal birefringence growth propagates towards the center when the cavity pressure calculated by simulation is applied. However, the thermal birefringence in the center region is still negligible at this point, since the core is still hot, as shown in Fig. 5.65. The constrained quenching algorithm was applied at this stage leading to the lateral strains caused by melt pressure. The curve of 3.8 s indicates the time when pressure drops to zero. Then the free quenching condition was applied. At this instant, the thermal birefringence in the center region starts to develop due to the fact that the melt temperature is reduced to the value being close to $T_g$. The birefringence in the wall region does not relax since the tensile stress was developed before this point. Such calculation continues until cooling time of 30 s. Then a convective boundary condition was applied to evaluate the temperature field until equilibrium state. The final thermally-induced birefringence indicates a parabolic shape in the core region, since the free quenching...
condition was applied. This results in compressive stress while the core region is still in the melt state. A very similar birefringence distribution can be seen in the core region by comparing results obtained in the free quenching. However, a higher birefringence in the core region was observed in combing constrained quenching due to only tensile stress was developed during the constrained cooling. In the wall region, the equilibrated birefringence curve indicates some relaxation taking place in extended wall region, except at the wall. This is due to the boundary condition of $T = T_w$ was assumed. Besides, the equilibrated birefringence curve exhibits all negative values of the thermally-induced birefringence. In contrast, in case of free quenching, a negative birefringence in the core region and positive birefringence in the wall region was observed. The difference between behaviors of the thermal birefringence in molding and free quenching is due to the presence of the tensile stresses in the wall region in constrained quenching case.

Figure 5.66 exhibits a comparison of the calculated residual thermally-induced birefringence in the gapwise direction at different locations of LGP molding made of PS 615 in Run #1. In this case, the thermal birefringence varies slightly with locations. Such a tendency had been observed in studies of the residual thermal stresses by Hieber [149].
Figure 5.64 The transient thermally-induced birefringence calculated by a combination of constrained and free quenching at location B of LGP made of PS 615 in Run #1. The free quenching curve was calculated at an initial temperature of 130°C to 25°C water [119].

Figure 5.65 Transient temperature calculated during the injection molding of LGP at location B of PS 615 for Run #1.
Figure 5.66 Comparison of calculated residual thermally-induced birefringence in the gapwise direction at different locations B and C in LGP molding made of PS 615 in Run #1.

Figures 5.67 and 5.68 show a comparison of the gapwise distribution of the calculated residual thermally-induced birefringence at locations B and C, respectively, of LGP molding obtained at different processing conditions for Run #1 and #2 corresponding to different packing times, for Run #1 and Run #3 corresponding to different melt temperatures for PS 615. The details of processing conditions were listed in Table 3.3. Among three conditions, very minor differences of the thermal birefringence are observed. However, a slightly lower birefringence was observed at processing
condition of Run #2, which is the condition with lowest packing time of 2 s. This implies that processing condition of Run #2 has shorter time of cooling at constrained conditions than that of Runs #1 and #3. This indicates that the duration of constrained cooling could be the dominating factor in determination of the thermally-induced birefringence. Therefore, a lower value of the thermal birefringence in the core region is observed at processing condition of Run #2 due to a shorter duration of constrained cooling than that found in other moldings. However, in case of PS, the main contribution to the thermal birefringence occurs in the wall region.

![Figure 5.67 Comparison of calculated gapwise distribution of the thermally-induced birefringence at location B for different processing conditions of PS 615.](image)

Figure 5.67 Comparison of calculated gapwise distribution of the thermally-induced birefringence at location B for different processing conditions of PS 615.
Figure 5.68 Comparison of calculated gapwise distribution of the thermally-induced birefringence at location C for different processing conditions of PS 615.

The calculated thermally-induced birefringence is added to the flow-induced birefringence to obtain the total residual birefringence in the LGP molding. Figure 5.69 shows comparison of the experimental and calculated total residual birefringence in the gapwise direction at locations B and C of LGP molding obtained in Run #1 of PS 615. At position B, the measured and predicted total birefringence in the gapwise direction is slightly higher than that of location C, since it is more close to the gate. Predictions are in a qualitative agreement with the measurements. However, the predicted total
birefringence at position C is in a better agreement with the measurement. This may be due to the effect of extensional flow which is less significant at this location than that near the gate. Also, it is noted that in case of PS the contribution of the thermal birefringence to the total birefringence is minor except in the wall region. However, a high value of the thermally-induced birefringence at the wall is caused by the instant freezing at the wall.

Figure 5.69 Comparison of the gapwise distribution of measured residual birefringence and calculated residual flow-, thermally-induced and total birefringence at locations B and C in LGP molding at processing condition of Run #1 of PS 615.
5.7.2 Polycarbonates

Figure 5.70 exhibits the gapwise distribution of the transient thermally-induced birefringence calculated by a combination of constrained and free quenching at location B of LGP molding of PC OQ1030 in Run #1. Figure 5.71 displays the corresponding calculated gapwise temperature distribution at different times during molding. At the earlier stage of development thermally-induced birefringence is very similar to that found in the PS case, as shown in Fig. 5.64. The birefringence at time of 0.08 s indicates an immediate growth of the thermally-induced birefringence taking place near the wall. This is caused by the freezing effect at the mold wall. Then, at constrained quenching time of 1 s, the thermal birefringence growth propagates towards the center when the calculated cavity pressure is increased and further cooling occurred. The gapwise temperature distribution at this time is shown in Fig. 5.71.

A significant difference in PC case compared to the case of PS is that the predicted pressure does not relax to zero during the packing stage, since the cooling takes place much faster than in PS. The pressure is not able to relax completely before the temperature is reduced below $T_g$. Accordingly, a constrained quenching calculation continues at time of 5 s. At constrained quenching time of 5 s, the thermal birefringence in the center region tremendously increases, since the temperature of core region is
already lower than the $T_g$, as shown in Fig. 5.71. In such a case, the development of the thermally-induced birefringence may eventually reach a constant value throughout the gapwise direction since only tensile stress acts on polymer. This birefringence stays until the constraint is removed [208-211].

![Graph showing the gapwise distribution of the transient thermally-induced birefringence calculated by a combination of the constrained and free quenching assumption at location B of LGP molding of PC1030 in Run #1.](image)

Figure 5.70 The gapwise distribution of the transient thermally-induced birefringence calculated by a combination of the constrained and free quenching assumption at location B of LGP molding of PC1030 in Run #1.
After 5 s, the free quenching condition was applied. At this instant, only relaxation happens due to the fact that the melt temperature throughout the gapwise direction is below $T_g$. Again, such calculation continues until cooling time of 30 s. Then a convective boundary condition was applied to evaluate the temperature field until equilibrium state. The final thermally-induced birefringence indicates a nearly constant value in the core region and increases to slightly high value in the wall region. This tendency implies that the free quenching condition does not play an important role at this location.

![Figure 5.71 The predicted gapwise distribution of temperature calculated at different times during molding at location B of LGP molding of PC OQ1030 in Run #1.](image)
Figures 5.72 and 5.73 display a comparison of the gapwise distribution of the calculated residual thermally-induced birefringence at various locations in LGP moldings of PC OQ1030 and PC OQ3820 at processing conditions of Run #1, respectively. Interestingly, both PCs show a similar tendency. However this tendency is completely different than that found in PS, as shown in Fig. 5.66. At position B of LGPs made of two PCs pressures were still employed after the temperature reduced below $T_g$. At the same time, at position C of LGPs made of two PCs, curves demonstrate a parabolic shape of the thermal birefringence curve in the core region with birefringence increasing towards the wall region with a maximum being at the wall.

This parabolic shape of thermal birefringence in the core region is apparently due to an earlier release of pressure since the position C is further away from the gate. It means if the constraint is released as soon as skin solidified, the distribution of birefringence in the core region of LGP will be similar to that of the free quenching. Therefore, the duration of constrained quenching is clearly the most important factor in defining the shape and magnitude of the thermally-induced birefringence. In addition, at the same location both PCs are found to have similar level of birefringence in the core region and the surface.
Figure 5.72 Comparison of calculated residual thermally-induced birefringence in the gapwise direction at locations B and C in LGP molding made of PC OQ1030 in Run #1.

Figure 5.73 Comparison of calculated residual thermally-induced birefringence in the gapwise direction at locations B and C in LGP molding made of PC OQ3820 in Run #1.
Figures 5.74 and 5.75 exhibit comparison of the gapwise distribution of measured residual birefringence and calculated residual flow-, thermally-induced and total birefringence of $\Delta n_{13}$ and $\Delta n_{23}$, respectively, at locations B and C in LGP molding of PC OQ1030 in Run #1. The predicted total residual birefringence is in a fair agreement with the measured birefringence of $\Delta n_{13}$ and $\Delta n_{23}$. In Fig. 5.74, the calculated residual total birefringence $\Delta n_{13}$ of PC OQ1030 shows positive values throughout the gapwise direction due to a positive stress-optical coefficient of PC in the melt and solid state. Also, the total birefringence $\Delta n_{13}$ at location B in LGP made of PC OQ1030 exhibits a maximum being at position $z/b = 0.64$. The calculated total birefringence $\Delta n_{13}$ at location C indicates that the majority of birefringence contribution came from the thermally-induced birefringence since a presence of weak flow at the location further away from the gate. However, a lower predicted total birefringence compared to that of measurement was observed. This may be due to that one relaxation time of $\tau_r = 0.05$ s was used to describe the volume relaxation behavior, as described in Section 4.4. Due to the lack of experiments concerning the volume relaxation of PCs, one relaxation time was used to predict the thermally-induced birefringence. To reach a better prediction, a further investigation on the volume relaxation behavior of PCs is required. Fig. 5.75 shows that the contribution of the flow-induced birefringence to calculated total birefringence of
\( \Delta n_{23} \) is minor in comparison to that of the thermal contribution. This is due to the locations B and C have stronger flow in direction of 1 than that in direction of 2. Accordingly, the flow-induced birefringence \( \Delta n_{23} \) at position B and C was observed nearly negligible. Therefore, the thermally-induced birefringence in the 2-3 plane gives the major contribution to the total birefringence especially at the positions further away from the gate. However, the effect of the thermally-induced birefringence was not significant in the LGP molding of PS.

![Figure 5.74](image)

Figure 5.74 Comparison of the gapwise distribution of measured residual birefringence and calculated residual flow-, thermally-induced and total birefringence of \( \Delta n_{13} \) at locations B and C in LGP molding of PC OQ1030 in Run #1.
Figure 5.75 Comparison of the gapwise distribution of measured residual birefringence and calculated residual flow-, thermally-induced and total birefringence of $\Delta n_{23}$ at locations B and C in LGP molding of PC OQ1030 in Run #1.

Figure 5.76 depicts a comparison of the gapwise distribution of measured residual birefringence and calculated total birefringence of $\Delta n_{13}$, at locations B and C in LGP molding of PC OQ3820 in Run #1. The calculated flow- and thermally-induced birefringences are shown in Fig. 5.43 and 5.73, respectively. At location B, the predicted total birefringence indicates a higher maximum further away from the wall than that at location C. This higher maximum at location B is due to the fact that more melt was
introduced in the packing stage as explained in Fig. 5.43. In the wall region, the predictions show higher values of birefringence comparing to measurements. However, the measurement of birefringence near the wall is not possible to carry out, since a dark field in this region in a polarized microscope is not observed. Therefore, no data is reported at the gapwise position of $z/b > 0.96$.

Figure 5.76 Comparison of the gapwise distribution of measured residual birefringence and calculated residual flow-, thermally-induced and total birefringence of $\Delta n_{13}$ at locations B and C in LGP molding at processing condition of Run #1 of PC OQ3820.
5.7.3 Conclusions

The thermally-induced birefringence was calculated by a combination of constrained and free quenching assumption for PS and two optical grades of PCs. The temperature and pressure calculated from simulation were used to determine the time to switchover from constrained to free quenching. The constrained quenching was imposed for duration of time when the pressure is non zero. The calculated thermally-induced birefringence was added to the flow-induced birefringence to obtain the total birefringence.

In case of PS, the final thermally-induced birefringence indicates a parabolic shape in the core region, since the free quenching occurs in this region. Also, the thermally-induced birefringence indicates minor effect of the flow direction. A similar observation was made on the calculated thermally-induced stress carried out by Ghoneim and Hieber [149]. However, they did not investigate the thermal birefringence. The packing time slightly decreases the thermal birefringence due to a shorter duration of constraint. The total birefringence shows that the thermal birefringence in PS molding plays minor role compared to that of the flow-induced birefringence.
In case of PCs, the thermally-induced birefringence indicates a nearly constant value in the core region and slightly high value in the wall region. Also, the thermal birefringence is strongly dependent on the flow direction. This is due to the fact that pressure does not relax to zero at the position closer to the gate, but does drop to zero at the position further away from the gate. It indicates that the moment of release of constraint is the most important factor in affecting the development of the thermally-induced birefringence. In fact, the thermally-induced stress and birefringence will be a constant through the thickness and equal to the cavity pressure, if the constrained condition is maintained until thermal equilibrium [211]. It is also found that the birefringence $\Delta n_{23}$ is mainly determined by the thermally-induced birefringence since the flow in the direction of 2 is weaker than that in direction of 1.
CHAPTER VI

LUMINANCE OF INJECTION MOLDED V-GROOVE LGP

An edge-lit LGP is designed to convert a linear light sources (such as a cold cathode fluorescent lamp, CCFL), or some point sources (such as light emitting diodes, LEDs) from the side to the front of LGP with highest possible illumination by the microstructures located in the bottom of LGP. The objectives of LGP design include low power consumption, large area with a minimal thickness, high brightness, uniform luminance, and desirable viewing angles. Therefore, the major concern in the manufacturing of LGP is the light transmission through the LGP, termed luminance. However, a relation between molding conditions and luminance performance has never been reported.
6.1 The V-groove Patterns and the Melt Filling Depth Measurements

A surface profiler (TENCOR Instruments, Alpha-Step 100) was used to measure the depth of V-grooves of LGP moldings. The measurements were carried out at nine positions on the LGP moldings as indicated on Fig. 6.1. Initially, three LGP moldings, obtained at the same processing conditions (Run #1 of PC OQ3820 in Table 3.2), were used for measurements of the depth of V-grooves of LGP moldings. These measurements indicated a standard deviation of 1.4\% for the depth of the grooves. Therefore, all subsequent measurements of the depth of the grooves of LGP moldings obtained at other conditions were carried out using one sample.

Figure 6.1 The planar geometry of a LGP with the positions where the measurement of the depth of melt filling in V-grooves was carried out. Unit: (mm).
6.2 Luminance Measurements

The experimental setup for luminance measurement is shown in Fig. 6.2. All measuring components were mounted on an optical bench (ORIEL 11200). A light emitting diode of blue light (LED, Nichia NSCB215) was mounted on the side of a LGP. To avoid loss of light, the light source housing is covered with a reflective film (Enhanced Specular Reflector, ESR, 3M Vikuiti\textsuperscript{TM}). The housing containing the LGP was installed on a rotational stage to collect the luminance at various viewing angles. The light source was placed in the hole made in the housing. Walls of the hole were also covered with the same film to ensure that all the light is guided out of the front surface of LED. Luminance was measured by a luminance meter (Minolta, LS110) mounted at a distance of 50 mm away from the LGP. To avoid the influence of environmental light on luminance measurements all measuring components and path of light were covered by a black paper to attain zero luminance reading when light was off. It should be noted that triggering the luminance meter manually introduced luminance fluctuations. To avoid these fluctuations, the overall control of the luminance meter was carried out by a computer through a parallel port. By rotating the stage with the LGP housing, the luminance as a function of the viewing angle was recorded by the computer.
Figure 6.2 The layout (a) and photograph (b) of luminance measuring device.
To ensure the reproducibility of measurements, two additional tests were performed. Figure 6.3 exhibits the luminance as a function of viewing angle measured three times at the processing condition Run #1 of PC OQ3820. Nearly overlapped results were observed. This ensures a good reliability on any single measurement. In addition, three different LGP moldings, obtained at the Run #1 and #11 of PC OQ3820, were also used to investigate the reproducibility of measurements. Figure 6.4 (a) and (b) show such comparisons of Run #1 and #11 for PC OQ3820, respectively. It indicates a standard deviation of 2.7% for the luminance measurements.

Figure 6.3 Reproducibility study: luminance as a function of viewing angle measured using the same sample for three times, at condition of Run #1 for PC OQ3820.
Figure 6.4 Reproducibility study: luminance as a function of viewing angle measured using three different samples made at the same processing condition of (a) Run #1 and (b) Run #11 for PC OQ3820.
Therefore, all subsequent measurements of the luminance of the LGP moldings obtained at other processing conditions were made using one sample since the reproducibility of the luminance measurements indicate a low deviation.

6.3 Results and Discussions

The complex viscosity of two PCs as a function of frequency at different temperatures is shown in Figs. 3.2 and 3.3. At high temperatures both PCs show a typical Newtonian behavior in a wide range of frequencies and a shear thinning behavior at high frequencies. At low temperatures both PCs show a Newtonian behavior only at low frequencies and a non-Newtonian behavior in wide range of higher frequencies. It is also seen that at the same temperature PC OQ1030 shows the complex viscosity about one order magnitude lower than that of PC OQ3820. Based on the simulation of cavity filling at molding Run #1 in Table 3.2, the maximal shear rate at the gate at the end of cavity filling was $1.9 \times 10^4$ s$^{-1}$ and $3.5 \times 10^4$ s$^{-1}$ for PC OQ1030 and PC OQ3820, respectively. This indicates that cavity filling of both PCs occurs in the shear thinning region.
6.3.1 Depth of Melt Filling of V-grooves

The local pressure and temperature distribution during melt filling stage of injection molding determines the formation of V-grooves in the injection molded LGP since the cooling starts from the mold wall. As melt front propagates, the pressure and temperature tend to reduce.

Therefore, the measuring positions of the melt filling depth were taken based on the melt front propagation which is measured by preparing short-shot moldings as shown in Fig. 6.5. The experimental procedure for preparing short shot moldings was described in Section 3.4. As indicated in Fig. 6.5, the position 9 is considered as the last filling position. It also indicates that the direction of melt fronts propagation tends to be parallel at positions 1, 3 and 7, but variable at the other positions. The sequence of melt filling from the earliest to the last filling point can be sorted as position 1, 2, 3, 4, 5, 6, 7, 8, and 9, respectively.
Figure 6.5 Melt front propagation during filling stage of injection molding (Run #1 of PC OQ3820) as obtained by short shot experiments.

Figures 6.6 to 6.15 depict the depth of melt filling as a function of distance from edge for the LGP moldings of two PCs obtained at various processing conditions. Figs. 6.6 and 6.7 show such a measurement in LGP moldings obtained at different injection speed for PC OQ1030 and PC OQ3820, respectively. In general, the depth of melt filling increases with increasing injection speed. This is due to a short filling time at higher injection speed causing higher local temperature and pressure. However, this effect is more significant in the measurements of PC OQ3820 than that found in PC OQ1030.
because the polymer melt of a lower viscosity of PC OQ1030 can penetrate deeper into
the V-groove leading to more complete filling.

Accordingly, the depth of V-groove patterns in the LGP moldings made of high
viscosity PC OQ3820 at processing condition of Run #1 is shallower at most positions
along the width of the LGP away from the edge than that of PC OQ1030.

![Figure 6.6](image_url)

Figure 6.6 The depth of melt filling as a function of distance from edge for the LGP
moldings of PC OQ1030 obtained at different injection speeds. The numbers 1 to 9
correspond to positions in Fig. 6.1.
Figure 6.7 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ3820 obtained at different injection speeds.

Figures 6.8 and 6.9 exhibit the depth of melt filling as a function of distance from edge for the LGP moldings at different packing pressures for PC OQ1030 and PC OQ3820, respectively. In the LGP made of low viscosity PC OQ1030, no significant effects of the packing pressure were observed, as seen in Fig. 6.8. However, the positions 1, 3, and 7 of Run #4 in Fig. 6.9 display shallower filling depth. This may indicate that the depth of melt filling in the direction parallel to the flow direction could be improved by applying a higher packing pressure, but this effect is not significant at other locations.
Figure 6.8 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ1030 obtained at different packing pressures.

Figure 6.9 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ3820 obtained at different packing pressures.
Figures 6.10 and 6.11 exhibit the depth of melt filling as a function of distance from edge for the LGP moldings at different packing times for PC OQ1030 and PC OQ3820, respectively. No considerable effects of the packing time were observed. However, similar to the effect of packing pressure, more variations were observed at locations parallel to the flow direction, but the effect was not as significant as that of injection speed. The latter is due to the fact that the depth of melt filling is mainly determined by the melt filling stage of injection molding.

Figure 6.10 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ1030 obtained at different packing times.
Figure 6.11 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ3820 obtained at different packing times.

Figures 6.12 and 6.13 exhibit the depth of melt filling as a function of distance from edge for the LGP moldings at different mold temperatures for PC OQ1030 and PC OQ3820, respectively. A tremendous variation of the depth of melt filling was observed. Clearly, an increase of the mold temperature results in a deeper filling of the V-grooves. This is due to the fact that PC melt can penetrate deeper into the micro patterns at a higher mold surface temperature during the melt filling stage of injection molding process.
Figure 6.12 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ1030 obtained at different mold temperatures.

Figure 6.13 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ3820 obtained at different mold temperatures.
Figures 6.14 and 6.15 exhibit the depth of melt filling as a function of distance from edge for the LGP moldings at different melt temperatures for PC OQ1030 and PC OQ3820, respectively. Evidently, a higher melt temperature also leads to an enhancement of melt filling. This is due to lower viscosity caused by higher melt temperatures. However, this effect is more significant in the LGPs made of PC OQ3820 than that found in PC OQ1030, because the polymer melt of a lower viscosity of PC OQ1030 can penetrate deeper into the V-groove leading to more complete filling.

![Graph](image)

Figure 6.14 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ1030 obtained at different melt temperatures.
Figure 6.15 The depth of melt filling as a function of distance from edge for the LGP moldings of PC OQ3820 obtained at different melt temperatures.

As indicated by Han et al. [176], the degree of filling of microstructure is strongly affected by the direction of melt front propagation with respect to the layout of V-grooves. The degree of filling was defined as the ratio of the depth of melt filling and the depth of V-groove patterns on the mold surface. The degree of filling can be significantly improved when the direction of the V-grooves layout is parallel to the melt flow direction and deteriorates with increasing angles to the direction of melt flow.
Fig. 6.16 depicts the variation of the degree of filling with the melt front propagation direction. It clearly indicates that this directional effect of filling of the V-grooves is not significant at a higher mold temperature, such as occurs at processing condition of Run #1 carried out at a mold temperature of 100°C. However, for the LGPs made of processing condition of Run #8 at a low mold temperature of 80°C, a sudden deterioration of the degree of filling starts to occur at position 5 with both PCs. A further deterioration of the degree of filling was observed in the LGP made of higher viscosity PC OQ3820. In addition, a slight increase of the degree of filling at position 7 was also observed due to the fact that the direction of the V-grooves layout was along the melt flow direction. This observation indicates that the degree of filling is affected by the layout of V-grooves with respect to the flow direction at the melt front, but this effect is not significant for a lower viscosity PC OQ1030.
Figure 6.16 Variation of the degree of filling of V-grooves with the melt front propagation at nine positions in LGP indicated in Fig. 6.1.

6.3.2 Luminance

The following measurements depict the measured luminance as a function of viewing angle in LGP moldings made of two PCs and obtained at different processing conditions.

6.3.2.1 Polycarbonates

Fig. 6.17 exhibits a comparison of luminance of LGPs obtained at different injection speeds. It indicates that the luminance increases with increasing injection speed. This is
due to a short filling time introduced by higher injection speed causes higher local temperature and pressure resulting in a higher depth of melt filling of V-groove. For PC OQ1030, a convex shape of luminance curve was observed and a maximum of luminance peak happens at 9° of viewing angle. Besides, the luminance measurements of PC OQ1030 display higher values compared to the LGP of PC OQ3820 made at the same processing conditions. In addition, for Run #1 of PC OQ3820, the result exhibits no maximum. That indicates no concentration of light is delivered at this processing condition.

Figures 6.18 and 6.19 depict experimental data on luminance as a function of viewing angle in LGP moldings made of two PCs and obtained at different packing pressures and times, respectively. It is seen that the luminance of LGPs made from the same grade PC is not strongly affected by these processing parameters with exception of the LGP made of low viscosity PC in Run #4 corresponding to the lowest packing pressure. This is due to the fact that after the cavity is completely filled, PC melt cannot penetrate deeper into micro grooves, since polymeric melt becomes frozen on the mold surface as soon as it penetrates into micro grooves. Therefore, maintenance of the packing pressure have little effect on deeper penetration of the melt into these micro
grooves, as indicated by the measurements of depth of filling in Figs. 6.8 to 6.11.

Behavior of luminance in LGP made of different PCs show different trends. In particular, the LGP made of the low viscosity PC shows a maximum of luminance at a specific angle, while the LGP made of the high viscosity PC instead shows a continuous decay of luminance resulting in a poor optical performance.

![Figure 6.17 Luminance as a function of viewing angle for the LGP moldings of PC OQ1030 (open symbols) and PC OQ3820 (filled symbols) obtained at different injection speeds.](image)

From our previous study [92], an increase in the packing pressure and time introduces an additional birefringence peak in the core region of LGP moldings in addition to the
birefringence peak near the wall, thus increasing optical retardation in the thickness direction. The packing pressure also prevents the LGP from global shrinkage in all three directions. Therefore, one can conclude that global dimension of the LGP and optical retardation seems to have very little effect on luminance, as long as the depth of V-grooves filling, as shown below, has a similar level.

Figure 6.18 Measured luminance as a function of viewing angle for the LGP moldings of PC OQ1030 (open symbols) and PC OQ3820 (filled symbols) obtained at different packing pressures.
Figure 6.19 Measured luminance as a function of viewing angle for the LGP moldings of PC OQ1030 (open symbols) and PC OQ3820 (filled symbols) obtained at different packing times.

Figure 6.20 depicts experimental data on luminance as a function of viewing angle in LGP moldings made of two PCs and obtained at different mold temperatures. The luminance increases with increasing mold temperature. For the Run #8 of PC OQ1030, it indicates no concentration of light due to a poor melt filling of micro grooves as observed in Fig. 6.12. However, comparing luminance at this condition to that of Run #1 of PC OQ3820, a similar luminance performance was observed, but the mold temperature for Run #1 of PC OQ3820 is 20°C higher than that of Run #8 of PC OQ1030. Therefore, it is
concluded that the viscosity plays an essential role in luminance performance of injection molded LGPs.

Also, it is noted in Fig. 6.20 that there is a sudden decrease of luminance at a mold temperature of 120°C for PC OQ3820 having the glass transition temperature of 147°C. This is due to the fact that at mold temperatures close to $T_g$ the V-grooves were smashed during demolding. The existence of such damage is detected by an optical microscope. Photographs are shown in Fig. 6.21. It is clearly seen from the photograph depicted in Fig. 6.21(a) and denoted as the top view, that the sharp V-grooves were stuck in the mold during demolding. This explains why the luminance of the LGP obtained at this condition shows lower optical performance than that obtained at other conditions.

Figure 6.22 depicts experimental data on luminance as a function of viewing angle in LGP moldings made of two PCs and obtained at different melt temperatures. The luminance increases with increasing melt temperature but this effect seems to be more significant on PC OQ3820 than that found on PC OQ1030. This maybe due to the reduced viscosity with increasing melt temperature which is more effective in PC OQ3820 since it has higher viscosity.
Figure 6.20 Measured luminance as a function of viewing angle for the LGP moldings of PC OQ1030 (open symbols) and PC OQ3820 (filled symbols) obtained at different mold temperatures.
Figure 6.21 Damage of V-groove in LGP made of PC OQ3820 due to a high mold temperature (120°C) as detected by an optical microscope. (a) top view; (b) side view.
These results are very important in understanding the performance of LGP moldings. Clearly, the present study indicates that the optical retardation and the global dimensional specification of LGPs do not play a major role in their luminance. This is possibly due to the fact that the optical grade PCs do not introduce as much optical retardation as conventional grades. In addition, since the luminance is provided by the internal reflection from the V-groove patterns on the bottom of the LGP, the melt filling of these microstructures, including their depths and shapes, are evidently the most important
factors in optical performance of the LGP moldings. Accordingly, even though the high
viscosity PC OQ3820 may introduce more viscous heating and is thus molded at a higher
melt temperature, the LGPs made from the low viscosity PC OQ1030 show higher values
of luminance. This is due to the fact that the melt filling of the microstructures in LGPs
made from low viscosity PC OQ1030 is better than that of high viscosity PC OQ3820
under the same processing conditions.

6.3.2.2 Polystyrene

The following discussions demonstrate the influences of processing conditions on
the luminance for Run #1 and #2 corresponding to different packing times, for Run #1
and Run #3 corresponding to different melt temperatures for PS 615. The details of
processing conditions were listed in Table 3.3. Figure 6.23 depicts the measured
luminance as a function of viewing angle in LGP moldings made of PS 615 obtained at
different processing conditions. Among three conditions, the luminance show global
maximum at -20° and minimum at +20°. This indicates that the concentration of light is
achieved at these processing conditions. This tendency is similar to that found in some
processing conditions of the high viscosity PC OQ3820. However, the luminance
measured at the highest melt temperature, Run #3 (20°C higher than in Run #1), indicates
a tendency of developing light concentration but such melt temperature effect is not as significant as in PC OQ3820 as shown in Fig. 6.22.

Figure 6.23 Measured luminance as a function of viewing angle for the LGP moldings of PS 615 obtained at different processing conditions.

Furthermore, to investigate the influence of viscosity, two viscosity curves at 280°C of PC OQ3820 and 250°C of PS 615 are extrapolated according to Figs. 3.2 and 3.4 along with shift factors as indicated in Fig. 6.24. It is seen that the viscosity of PS 615 at 250°C is lower than that of PC OQ3820 at 280°C at any frequency. This indicates that even though PS 615 shows better penetration to form the V-groove pattern due to its lower
viscosity, PS 615 (Run #3) shows lower luminance than that found in PC OQ3820 (Run #1). It is apparently due to the relatively large phenyl group on the side of molecular chain creating the optical obstacle resulting in deterioration of luminance. Therefore, from this observation, the polystyrene doesn’t seem to be a proper material for this light-guide application.

Figure 6.24 Comparison of complex viscosity vs. frequency curves at 280°C of PC OQ3820 and at 250°C of PS 615.
6.3.3 Luminance as a Function of Melt Filling

Figs. 6.25 and 6.26 indicate the average luminance over -20° to 20° viewing angles versus the degree of filling averaged over nine positions on the LGPs made of PC 1030 and PC 3820, respectively. Fig. 6.25 shows the results for LGP made of low viscosity PC OQ1030 at various molding conditions.

![Graph showing average luminance over -20° to 20° viewing angles versus degree of filling](image)

Figure 6.25 Average luminance over -20° to 20° viewing angles versus average degree of filling of V-grooves over nine points indicated in Fig. 6.1 in LGPs made of PC OQ1030.

Clearly, for the majority of the LGP moldings the average luminance shows a linear relationship with the degree of filling. However, there are two points that deviate from
this linear relationship in Fig. 6.26 for the LGPs made of high viscosity PC OQ3820. These two LGPs were obtained at the highest mold and melt temperatures. Such a deviation can be due to the differences in the degree of filling of V-grooves at various positions that is more significant in the LGP made of high viscosity PC OQ3820 than that of low viscosity PC OQ1030, as indicated by Fig. 6.27.

Figure 6.26 Average luminance over -20° to 20° viewing angles versus average degree of filling of V-grooves over nine points indicated in Fig. 6.1 in LGPs made of PC OQ3820.

Fig 6.27 shows the difference of melt penetration at the highest injection speed, mold temperature and melt temperature at position 9 of LGPs made of high viscosity PC OQ3820. The measurement of the shape of V-groove was carried out by means of an
optical microscope after slicing LGP samples in the thickness direction. It indicates that the shape of V-grooves was strongly distorted at this position. However, such a significant distortion at the position was not observed in LGPs made of low viscosity PC OQ1030, as indicated in Fig 6.28.

Figure 6.27 Shape of V-grooves in the LGP mold and LGP moldings obtained at the highest injection speed, mold temperature and melt temperature at position 9 of LGP made PC OQ3820.
Figure 6.28 Shape of V-grooves in the LGP mold and LGP moldings obtained at the highest injection speed, mold temperature and melt temperature at position 9 of LGP made PC OQ1030.

6.4 Conclusions

The experimental investigation of luminance and depth of melt filling of V-grooves in LGP moldings was carried out at various processing conditions. It was found that the injection speed and mold temperature have the most significant effect on the depth of filling of micro patterns. An increase of these parameters leads to LGPs exhibiting a better luminance. This is due to the fact that the higher injection speed generates higher
local pressure and at the same time leads to more viscous heating causing increased penetration of the melt into V-grooves. Also, when the PC melt fills micro patterns at higher mold temperatures, freezing occurs more slowly leading to a higher degree of melt filling. However, a limitation on mold temperature was also observed. It should not be too close to the $T_g$ of the polymer since distortion of the V-grooves in moldings occurs during demolding. An increase of the melt temperature has a moderate effect in increasing luminance. The effect of melt temperature on luminance is much stronger in high viscosity PC OQ3820 than in low viscosity PC OQ1030. In contrast with what is known concerning the strong effect of packing pressure and packing time on intensity and distortion of light in CDs due to increased optical retardation, these parameters have very little effect on luminance in LGPs. This is possibly due to the fact that in LGPs the effect of V-groove filling on their luminance surpasses the effect of optical retardation. Therefore, the packing effect could be a factor affecting LGP luminance at very short filling time in case of ultra high injection speeds. It should be also noted that the formation of the V-grooves is mainly completed in the melt filling stage.

An ultra high injection speed had been proven to provide a better melt filling of microscale prisms made of PMMA, as reported by Han et al. [176], because of high
viscous heating and cavity pressure during transcription molding at ultra high injection speeds. Based on the current study, use of a low viscosity PC can provide a 90 to 93% degree of melt filling of V-grooves at a regular injection speed and a lower melt temperature. Therefore, LGPs made of low viscosity PC exhibit better luminance than those made of the high viscosity one. It was also found that the degree of filling is affected by the layout of V-grooves with respect to the direction of melt front, but this effect is not significant in low viscosity PC. The low viscosity PC seems to be less sensitive to the processing conditions and can easily reach the required level of optical performance. The depth of melt filling was found to play an important role in the luminance performance of the LGPs. Further studies should be directed to find a quantitative effect of local pressure and temperature history on the depth of melt filling of V-grooves.
CHAPTER VII

SUMMARY

7.1 Conclusions

A rheo-optical instrument has been built to simultaneously measure the strain-optical coefficient function and the Young’s relaxation modulus function. The relaxation modulus and the strain-optical coefficient were found to be sensitive to the level of the imposed elongational strain such that these functions exhibit a nonlinear behavior even at low strains at room temperature. The linear viscoelastic and photoviscoelastic constitutive equations were used to convert these functions in the linear region to the stress-optical coefficient function. It was found that the stress-optical coefficients in rubbery state of optical grade PCs are lower than that of a general purpose PC, while in the glassy state the values are almost the same. The observed differences in the behavior of PCs are probably caused by the presence of different side groups in these polymers.
The linear viscoelastic and photoviscoelastic constitutive equations along with the first order rate equation for volume relaxation have been applied to predict the residual birefringence in quenched PC slabs from the measured mechanical and optical relaxation functions on two PCs. The predictions are in a qualitative agreement with the measured thermal birefringence in quenched slabs. However, to obtain a quantitative agreement with the measured residual birefringence, further investigation of the volume relaxation behavior of PCs is required.

The flow-induced birefringence and anisotropic shrinkage of LGPs were simulated by using a combination of a CV/FEM/FDM technique, a nonlinear viscoelastic constitutive equation and orientation functions as well. The two-dimensional triangular finite element mesh was created over the mold cavity and a fan gate entrance. The one-dimensional tube element was used for the entire delivery system (nozzle, sprue and runners). An unconditionally stable upwinding scheme was introduced to improve the efficiency of the viscoelastic simulation. A significant time saving was achieved due to an elimination of subdivision of the time step. The numerical solutions for pressure field, flow-induced birefringence and anisotropic shrinkage were obtained, accordingly. The results were compared to measurements.
The effect of various processing conditions on the development of the normal birefringence, $<\Delta n_{12}>$, of PCs can be ranked from most to least: packing pressure, mold temperature, melt temperature, injection speed and packing time. However, the packing time is a significant factor in case of LGP moldings made of PS due to a longer gate freezing time. A higher value of the normal birefringence of PC OQ3820 in comparison with PC OQ1030 was observed due to a higher stress-optical coefficient of PC OQ3820 and also higher normal and shear stresses achieved during the cavity filling caused by its higher viscosity. It is concluded that the simulation is able to predict the level of the residual normal birefringence but unable to describe the exact shape of curves especially the formation of a maximum of the normal birefringence. This may be due to the elongational flow behavior in the gate area.

In case of the transverse birefringence, both PCs and a PS exhibit distinct pattern in development of $\Delta n_{13}$. The PC OQ1030 indicates a highly pronounced maximum of $\Delta n_{13}$ further away from the wall than that found in PC OQ3820. However, the PC OQ3820 develops a significant residual flow-induced birefringence near the wall which was not observed in PC OQ1030 due to low viscosity of PC OQ1030 leading to a faster relaxation near the wall. Due to a slower cooling rate, the development of transverse birefringence $\Delta n_{13}$ for PS at location further away from the gate shows considerable maximum of $\Delta n_{13}$ compared to that of both PCs. Also, the PC OQ1030
shows an opposite tendency in developing the maximum birefringence further away from the wall in variations of melt temperature than that found on PS and PC OQ3820 because of a dominating relaxation process of birefringence. In addition, the length of packing time provides a tremendous impact on the development of birefringence due to a slower cooling rate of PS. However, this was not observed in both PCs due to the shortest packing time on both PCs was set to be closed to the gate freezing time.

In case of anisotropic shrinkage, a good agreement was reached between the simulations and measurements at various processing conditions. Both PCs show similar tendency in shrinkage with respect to variation of processing conditions. However, a higher value of shrinkage on PC OQ3820 was observed due to its higher viscosity and higher applied melt temperature. In addition, it is concluded that the shrinkage for amorphous polymers is influenced by volumetric shrinkage, flow-induced residual birefringence and heat transfer during the molding process, especially in the packing stage. Besides, the gate freezing effect was observed to be an essential factor in shrinkage. The effect of processing conditions on the development of shrinkage in case of PC in this study was found to be ranked from most to least: packing pressure, melt temperature, mold temperature, injection speed and packing time. In case of PS, the thickness shrinkage slightly increased with increasing melt temperature and significantly increases with reducing packing time. The packing time
was found to be critical in the influence of the thickness shrinkage due to a longer gate freezing time in case of LGP molding. The results obtained from different processing conditions indicate that there was effect of multiple factors on shrinkage. This leads to complex effect of processing parameters on shrinkage due to coupling effect of various variables, cavity and material. However, the temperature and pressure history are better variables influencing the variation of shrinkage.

The thermally-induced birefringence was calculated by a combination of constrained and free quenching assumption for PS and two PCs. The temperature and pressure calculated from simulation were used. The constrained quenching was imposed for duration of time when the pressure is non zero. In case of PS, The thermally-induced birefringence indicated a parabolic shape in the core region, since the free quenching condition was applied. Also, the thermally-induced birefringence indicated minor variation with flow direction. The packing time slightly decreased the thermal birefringence due to a shorter duration of constraint. The total birefringence showed that the thermal birefringence plays minor role compared to that of the flow-induced birefringence. In case of PCs, the thermally-induced birefringence indicated a nearly constant value in the core region towards the wall and slightly high value in the wall region. Also, the thermal birefringence is strongly dependent on locations along the flow direction. This is due to the fact that pressure does not relax
to zero at the position closer to the gate, but does drop to zero at the position further away from the gate. It indicated that the moment of release of constraint is the most important factor in affecting the development of thermally-induced birefringence. It was also found that the birefringence $\Delta n_{23}$ was mainly determined by the thermally-induced birefringence since the direction of 1 has stronger flow than that of direction 2.

The experimental investigation of luminance and depth of melt filling of V-grooves in LGP moldings was carried out at various processing conditions. It was found that the injection speed and mold temperature had the most significant effect on the depth of filling of micro patterns. An increase of the melt temperature had a moderate effect in increasing luminance. The effect of melt temperature on luminance is much stronger in high viscosity PC OQ3820 than in low viscosity PC OQ1030. However, it was found that the effect of packing pressure and packing time have very little effect on luminance in LGPs. The results also indicated that the LGPs made of low viscosity PC exhibited the best light concentration and the highest luminance while LGPs made of PS showed lowest optical performance. It was also found that the degree of filling is affected by the layout of V-grooves with respect to the direction of melt front, but this effect is not significant in low viscosity PC. The low
viscosity PC seemed to be less sensitive to the processing conditions and could easily reach the required level of optical performance.

7.2 Recommendations for Future Work

Based on theoretical and experimental findings in the present study, the following future studies are recommended:

(1) The minimizing functional scheme [178] could be applied in solving Eqs. (5-46) and (5-54) instead of under-relaxation scheme to increase the convergent speed so that the viscoelastic simulation of injection molding would be possibly applied to practical applications.

(2) The algorithm for finite element mesh generation should be carried out to optimize the calculating domain.

(3) The thermally-induced birefringence should be incorporated into anisotropic shrinkage calculation.

(4) A warpage approximation should to be considered.
REFERENCES


[58] D. Huilier, C. Lenfant, J. Terrisse and R. Deterre, “Modeling the Packing Stage in


299

Products: Flow- and Thermally Induced Stresses in Amorphous Thermoplastics”, PhD

(1963)

Shear and Elongational Flow of a Low-density Branched Polyethylene Melt”, Rheol.
Acta, 15, 136-142, 1976

[96] M. H. Wagner, “Prediction of Primary Normal Stress Difference from Shear
Viscosity Data using a Single Integral Constitutive Equation”, Rheol. Acta, 16, 43-50,
1977


477-489, 1992


during the Mold Filling Stage and the Frozen-in Orientation in the Injection Molding of

[101] N. Santhanam, “Analysis of Residual Stresses and Post-molding Deformation in

300


302


306


Numerical Methods in Fluids, 23, 923-936, 1996


