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ANALYSIS OF VACUUM-ASSISTED RESIN TRANSFER MOLDING

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

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Vacuum-Assisted Resin Transfer Molding (VARTM) processes have become more and more important in recent years because of the promise of near-zero emissions, high-quality laminates and lower-cost tooling in making large, complex composite parts. The objective of this study is to establish a comprehensive analysis tool for process design and material selection in a new and promising VARTM technology — the SCRIMP process. In order to achieve this goal, a systematic analysis has been carried out to study the mold filling and resin cure. In mold filling analysis, two types of SCRIMP process, i.e. SCRIMP based on a high-permeable medium and SCRIMP based on grooves, have been investigated through both experimental and numerical analyses. The processability of the processing materials such as the fiber reinforcements, the peel ply and the high-permeable medium was investigated. The flow mechanism was explored through flow visualization. Based on experimental observations, leakage flow models based on control volume/finite element method (CV/FEM) or finite difference method (FDM) have been proposed for both processes to simplify the simulation of mold filling. The simplified models can serve as efficient tools for the design of resin distribution systems. In mold curing analysis, integrated analytical tools such as DSC, FTIR and RDA
were employed to probe the reaction mechanism and kinetics of vinyl ester resins cured at low temperatures. The influences of the promoter, initiator, retarder and inhibitor on the reaction mechanism and kinetics and the interaction between them were discussed. Combined with the reaction kinetics, a heat transfer model has been implemented to investigate the cure behavior in SCRIMP. In order to elucidate the fundamental reaction mechanism and the process and structure of the network polymer in monovinyl-divinyl systems represented by vinyl ester resins, a numerical simulation was performed for the copolymerization of model materials, ethylene glycol dimethacrylate (EGDMA) and methyl methacrylate (MMA). The model is able to generate some qualitative information which can not be obtained by traditional models, such as cyclization fraction, polymer size distribution.
To My Grandmother
I wish to express my sincere gratitude to my advisor, Dr. L. James Lee for his priceless guidance, advice and support throughout this work. I would like to thank Drs. Kurt Koelling and James Rathman as members of this dissertation committee. I would like to thank the polymer research group for their useful discussion and support. I also wish to thank those who are always behind me throughout the years of my study, especially my parents, my aunt Deyi Sun, my mentors Chi Chen and Yuchen Lou. Without their consistent encouragement, guidance and support, I would not have reached this step. Finally, special thanks go to my husband, Gaozhong, for his understanding, encouragement, support and sometimes stimulating discussions.
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CHAPTER 1

INTRODUCTION

1.1 Polymeric Composites

In recent years, many advanced materials have been invented for lightweight, structurally sound and cost effective replacement of conventional materials. The fiber reinforced polymeric composite is one of the major advanced materials, which has been widely used in various markets such as aerospace, defense, marine, transportation, sports and consumer products. The increasing popularity of polymeric composite materials is due to their many advantages, such as weight reduction which frequently ranges from 25 to 50% of the weight of conventional metallic designs, durability, corrosion resistance, excellent weight-to-performance ratios, design flexibility and low capital investment.

Generally, a polymeric composite consists of two components: the matrix and the reinforcement. The reinforcement, a discontinuous phase, usually has higher modulus and strength than the surrounding continuous matrix phase. The properties of the reinforcement (i.e. the structure and volume fraction) determine the mechanic properties of a composite material. In order to provide reinforcement, there generally must be a substantial volume fraction (~10% or more) of the discontinuous phase. Candidate
materials normally used as reinforcement are glass fiber, carbon fiber, etc. Ninety-nine (99) percent of all fibers used in the composite industry are glass fibers that are strong and stiff with a wide variety of properties achieved through proper selection of glass type, filament diameter, sizing chemistry and fiber forms. Fibers are silica-based glasses that contain several metal oxides, which can be tailored to create different types of glass fibers. Electrical or E-glass is the most commonly used and the most economical glass fiber for composites and accounts for 90 percent of all glass fiber reinforcements, while structural or S-type glass has higher strength and greater corrosion resistance than E-glass. Carbon fibers exhibit higher tensile strength and stiffness than glass fiber. However, because the cost of these fibers greatly exceeds that of glass fibers, they are typically reserved for high-tech applications demanding exceptional fiber properties for which the customer is willing to pay a premium.

The purpose of the composite matrix is to bind the fibers together by virtue of its cohesive and adhesive characteristics, to transfer load to and between fibers and to protect them from environments and handling. In other words, the matrix acts as a stress transfer medium for the reinforcement. The matrix generally determines the overall service temperature limitations of the composites, and may also control its environmental resistance. A good adhesion of the matrix to the fibers is crucial to the quality of the composite. The majority of the composites manufactured today use thermoset polymers as the matrix, since they offer better thermal stability and solvent resistance than thermoplastic polymers. The most common thermoset polymers include phenolic resins, unsaturated polyester resins, epoxies and polyurethanes. Each of them has particular advantages or limitations that direct its use. Polyurethanes are available as flexible foam, rigid foam, and non-cellular products. Flexible polyurethanes offer good cushion and light weight, while rigid polyurethanes provide light weight, dimension stability and good
insulation. Phenoic resins are the oldest members of the group and offer low price and proven performance. However, they tend to be brittle, can not be colored and have poor weather resistance. The unsaturated polyester resins, which have long been the workhorse for polymeric composites, are low cost and offer weather resistance, chemical resistance and a short cycle time. The limitation of the unsaturated polyester is the smoke generation upon combustion. Epoxy resins constitutes the partner workhorse to polyesters among thermosets, which provide impact strength, good electrical properties, good adhesion to fiber surface and excellent corrosion resistance. Vinyl ester resins, on the other hand, provide a product bridge between the low cost, rapid cure, and easily processed polyesters and the higher performance properties found in epoxies. Compared to polyesters, vinyl esters offer reduced water absorption and shrinkage as well as enhanced chemical resistance. Since vinyl esters cost somewhat more than polyesters, specific applications where vinyl esters surpass polyesters include chemically-corrosion environments and in structural laminates where a high degree of moisture resistance is desired (such as in boat manufacture).

1.2 Various Manufacturing Techniques for Polymeric Composites

Various processes exist for the manufacturing of polymeric composites. To select the best composite manufacturing process, one generally chooses the process that will provide an acceptable-quality component for the lowest cost through an environmentally safe way. Many methods are used to produce different type of composites and each of them has its own characteristics. Some of the methods are briefly described here for comparison.
Open-mold processes in one-sided molds such as spray-up and hand lay-up are the lowest tooling cost and most common processes for making large composite parts such as boat hulls and decks, automobile bodies and fenders, tubs and showers. In typical hand lay-up processing, glass fiber continuous strand mat and/or other fabrics such as woven roving are manually placed in the mold. Each ply is sprayed with catalyzed resin (viscosity of 1000 to 1500 cps). Then the resin is worked into the fiber with brushes and rollers to wet-out and compact the laminate and remove entrapped air. The chief advantages of the open processes are the low tooling cost, the unlimited size and shapes of the parts to be manufactured, the easy design changes, and the very low capital cost. However, there are many drawbacks. Typical glass fiber volume is only between 15 percent with spray-up and 25 percent with hand lay-up, which means the strength of the part manufactured is low. Also it is a labor-intensive process, and the quality of the parts is based on the skill of the operators. Moreover, Volatile Organic Chemicals (VOC) emission poses a serious problem to the safety of workers and the environment.

To control over fiber volume, laminate quality and VOC emissions, closed-mold processes such as Resin Transfer Molding (RTM) and Structural Reaction Injection Molding (SRIM) have become more and more important. RTM is a closed-mold low-pressure process that can make small to middle size composite parts with complex shape. In such a process, the fiber is preformed to the desired shape prior to molding. Then the dry preform is placed in the mold. After the mold is closed, the resin is injected into the mold cavity and the resin starts to cure. Finally, the cured part is taken out of the mold. RTM is prevalent in the electronics, recreational vehicle and consumer markets because it produces two finished sides and Class A finishes — the highest quality surface technically achievable. While various RTM processes are gaining favor in commercial
circles, the tooling costs can sometimes be prohibitive, especially when making large parts.

Attracted by the promise of near-zero emissions, high-quality laminates and lower-cost tooling, manufacturers are increasingly turning to Vacuum-Assisted Resin Transfer Molding (VARTM) processes to make large, complex parts. In these infusion processes, fibers are placed in a one-sided mold and a cover, either rigid or flexible, is placed over the top to form a vacuum-tight seal. A vacuum method is used to draw the resin into the structure through various types of ports. Compared to RTM, the tooling costs for VARTM are cut in half, which are especially significant when one deals with large parts. Therefore, VARTM processes are well suited for manufacturing large parts requiring complex structural properties. Many current applications are in the marine industry, ground transportation and infrastructure. Fiber content can run as high as 70 percent by weight, which means structural performance is also high. In addition, because VARTM is a close-mold process, styrene emissions are close to zero. This is extremely important because stricter control of styrene emissions is coming from both EPA and states adopting new ACGIH (American Conference of Governmental Industrial Hygienists) guidelines who will formally adopt 20 ppm as the new threshold limit value for styrene in May 1998. Numerous versions of VARTM processes have emerged in recent years. Most of them are still in the developmental stage.

1.3 Scope of Study

A common feature in the liquid composite molding processes is that polymerization and processing take place at the same time. Due to the reactive nature of these systems, they are often more complicated than the traditional thermoplastic
processing operations and conventional polymerization methods. For instance, combination of reaction into the processing step usually means reaction must occur in the bulk state. Quite often, the reactions are highly exothermic, making temperature control a difficult task. Most reactions are further complicated by the occurrence of multiple physical changes during molding, such as gelation in which materials change from a viscous fluid to a network gel with chemical or physical cross-linking, and glass transition or crystallization in which the reacting mixture changes from a rubbery material to a glassy polymer or from an amorphous material to a crystalline structure. These physical changes occur during the course of reaction and may certainly interact with the ongoing chemical reaction. For example, the gel transition effect may cause premature cessation and thus an incomplete reaction. Physical properties of the finished products depend not only on the raw materials used, but also on the processing method and processing conditions.

In each process, raw materials go through a set of elementary processing steps such as mixing, mold filling and curing. These steps are governed by the transport phenomena of the process and the behavior of the reactive materials such as resin flow, molecular diffusion, rheological changes and reaction kinetics, as shown in Figure 1.1. For instance, the change of resin viscosity can affect the flow pattern during mold filling and the molecular diffusion during curing. The flow pattern and the molecular diffusion, in turn, may determine the reaction rate and the final conversion. Much experimental and modeling work has been carried out by many researchers to understand the elementary processing steps and governing phenomena in various liquid composite molding processes.
Figure 1.1. A Schematic Diagram of Resin Transfer Molding
As mentioned earlier, although VARTM processes have already been used in industry for small quantity productions, they have not been thoroughly analyzed. Seemann Composites Resin Infusion Molding Process (i.e. SCRIMP), developed by Bill Seemann, Seemann Composites, is a new and promising VARTM process that has attracted considerable attention from the composite industry in recent years. The process now has more than 30 licensees and is growing fast. It has been involved in high-end military applications as minesweepers, mine countermeasures vessels and many other commercial applications including pleasure boats, windmill blades, boxcars. To become the 'Microsoft' of the composite industry, in other word, the operating system, is the ultimate goal of this process.

However, many techniques developed to date for the SCRIMP process are still based on experience or trial-and-error approaches. To develop a process and infrastructure that will enable SCRIMP to consistently yield quality composite parts in a manufacturing facility and further reduce the manufacturing costs and time to market is the major challenge of this process. Since SCRIMP applications are often for very large composite parts like sail boats, refrigerated cargo boxes and bridge decks, the raw materials used are in large quantity and expensive, and the molding process is often time consuming. To make SCRIMP more economically attractive, the process needs to be optimized and the product rejection rate has to be kept very low. This requires a thorough understanding of both mold filling and curing, and the development of efficient computation tools for process design and material selection. Our work focuses on three aspects of the SCRIMP process: resin characterization, analysis of mold filling and mold curing, which are shown in the small frame of Figure 1.1. In mold filling, knowledge of the resin flow, the pressure distribution, and the wetting of the fibers are essential for mold design and product quality control. Since SCRIMP processes are usually used to
manufacture very large parts. It is very important that mold filling be finished before the system viscosity reaches too high a value. Therefore, the influences of various molding conditions on mold filling should be analyzed, and a model which can be used to predict the flow pattern and filling time in the SCRIMP process is essential. Understanding of the reaction kinetics and mechanisms is equally important to the success of the overall process. The properties of the final products depend on reaction kinetics, rheological changes and micro-structure formation. The reaction kinetics may determine the final conversion in the curing stage and the process cycle time. The information of the heat of reaction and the rate of heat generation as a function of time and temperature is necessary for quantifying the heat transfer in the molding process. On the other hand, the reaction induced rheological changes would affect the flow pattern in the mixing and mold filling steps. Low temperature reaction often characterizes the SCRIMP process. Low temperature polymerization has its own characteristics due to the different curing agents used and the temperature at which the reaction occurs. For example, low temperature curing may lead to incomplete conversion which affects the quality of the final products. However, very little fundamental study has been done in this area. Therefore, a greater understanding of reaction kinetics and mechanism of low temperature polymerization is essential for better quality control of polymeric products produced by SCRIMP. In the molding process, viscosity increases with polymer formation and reaches an infinite level when material solidifies due to the network formation. Further reaction proceeds in the solid state. Understanding of the interactions between resin reaction and heat transfer can be critical to SCRIMP since different curing patterns have been speculated as a main reason for the fiber 'print through' problem in SCRIMP.

In summary, the ultimate goal of this research is to develop a comprehensive analysis tool for SCRIMP. In order to achieve this goal, there are several tasks to be
accomplished: (1) to understand the flow mechanisms in SCRIMP mold filling. (2) to develop mold filling simulation models that can be used as a tool for process design. (3) to investigate the reaction kinetics and mechanism of the low temperature free radical crosslinking polymerization for better quality control. and (4) to develop a cure model which can be used to simulate the cure behavior of the resin under various process conditions. In this dissertation, Chapters 3 and 4 focus on the mold filling analysis in two types of SCRIMP processes — SCRIMP based on a high-permeable medium and SCRIMP based on grooves. Chapter 3 presents the mold filling analysis in SCRIMP based on a high-permeable medium. Flow visualization of mold filling was carried out under various molding conditions. A three-dimensional Control Volume/Finite Element Method (CV/FEM) was adopted to solve the flow governing equations, i.e. the Darcy’s law, and the influences of the flow properties of various processing materials on filling time were investigated. Based on experimental observations and CV/FEM simulation, a simplified leakage flow model was also presented. Chapter 4 focuses on the mold filling analysis in SCRIMP based on grooves. It was found that compared to SCRIMP based on the high-permeable medium, SCRIMP based on grooves has the advantage of a much higher mold filling rate. The size of the groove, groove spacing, number of fiber layers and resin viscosity on mold filling were investigated and the flow mechanism was analyzed. A leakage flow model was also developed to simplify the simulation of the mold filling process in SCRIMP based on grooves, which greatly reduced computation time and yet provided simulation results that were in good agreement with experimental observations. Chapter 5 describes the results of a study on the reaction kinetics and mechanisms of vinyl ester resins cured at low temperatures and their cure behavior in the SCRIMP process. The influences of various curing agents such as promoter, initiator, retarder and inhibitor on reaction kinetics and mechanisms were studied by scanning and
isothermal DSC, FTIR and RDA. The monovinyl-divinyl systems are of great importance for elucidation of the process and structure of the network polymers. The polymerization of vinyl ester resins is not simple enough to be used as a 'model' material for studying the fundamental reaction mechanism. Therefore, in Chapter 6 we present a numerical simulation for the copolymerization of model materials, ethylene glycol dimethacrylate (EGDMA) and methyl methacrylate (MMA), which is capable of generating information that can not be obtained by traditional models, such as cyclization fraction, polymer size distribution. Finally, conclusions and recommendations are given in Chapter 7 for further study.
CHAPTER 2

LITERATURE REVIEW

2.1. Vacuum-Assisted Resin Transfer Molding (VARTM)

Despite the recent interest in the VARTM process, this technology was initially considered as a clean alternative to the hand lay-up process and has been used in industry as early as 1950 [Muskat, 1950]. However, before 1980’s, resins used for manufacturing composite parts were in favor of hand lay-up process (i.e. very high viscosity). The VARTM processes made little progress. In the beginning of 1980’s, the lower level emission for styrene vapor was imposed in the European Economic Community (EEC) countries, and the low cost manufacturing method and high quality composites became a concern. Thus, the VARTM processes were again highlighted. During this period, many patents were granted [Fourcher. 1982; Letterman, 1986; Palmer. 1982; Johnson. 1985; Myers, 1985; Comte, 1982]. For example, Comte [1982] patented his method and apparatus for producing a thin-walled, large size article of synthetic resin. Using an inner and an outer template, the synthetic resin was infused to the mold cavity via resin supply apertures, while a partial vacuum was maintained via air discharge apertures downstream of the synthetic resin front. The partial vacuum and the positive resin supply pressure were used in turn.
In the 1990’s, new environmental regulations under Title V of the 1990 Clean Air Act amendments took effect that require EPA to certify programs in every state to limit emissions of VOCs and hazardous air pollutants. A lower emission of styrene and production cost, and a higher production quality became more of a concern, which has expedited the development of VARTM technology in recent years. New advances in VARTM have occurred, primarily in the resin delivery technique. Seemann patented his methods for the manufacturing of medium-to-large parts in medium volume production setting. Three patents were granted, i.e. Plastic Transfer Molding Techniques for the Production of Fiber Reinforced Plastic Structures [Seemann, 1990], Plastic Transfer Molding Apparatus for the Production of Fiber Reinforced Plastic Structures [Seemann, 1991], and Unitary Vacuum Bag for Forming Fiber Reinforced Composite Articles [Seemann, 1994]. These patented manufacturing methods are called Seemann Composites Resin Infusion Molding Processes, or SCRIMP in short.

In the first patent, Seemann detailed the molding techniques. For example, a rigid mold half and a soft mold half, i.e. a vacuum bag, were used. Because the SCRIMP process is a low pressure process, the rigid mold half can be made of composites, nickel plate or wood, as long as the mold is vacuum tight. The soft mold half, i.e. the vacuum bag, is an air impervious plastic film, such as nylon, which is marginally sealed on the rigid mold to provide a chamber in which the fabric preform, peel ply and resin distribution medium are placed. The film is usually transparent, which may help to monitor the progress of mold filling. The resin distribution medium is a highly permeable layer. Its function is to facilitate the flow of liquid resin into the dry fabrics. The peel ply, which is placed between the fabric preform and the resin distribution medium, is to separate the composite part from the vacuum bag and the resin distribution medium such that the composite part can be easily demolded after it is completely cured. In a typical
SCRIMP process, the resin goes over the fiber and under the vacuum bag through these specially designed resin distribution systems. The resin only has to infuse through the thickness of the part. With both single skin and cored construction, the entire laminate is wet in one infusion step, eliminating weaker secondary bonds and the time and mess that accompany them. Cleaning solvents and the associated tool cleaning time are also completely eliminated. Reduced need for solvents coupled with the closed SCRIMP system can reduce volatile organic chemical (VOC) levels to well below the most stringent current or proposed standards. The patent described several types of resin distribution media, and also gave some application examples such as boat hulls, panels, and sandwich structures. The second patent concentrated on the boat hulls. A boat hull made by this process was 50 feet long, and the ratio of the fiber reinforcement to the resin was in the range of 70% to 75% by weight, compared with 50% by the hand lay-up method. The advantage over hand lay-up were low void content, low volatile emission and less labor. In the third patent, Seemann presented a reusable resin distribution medium which is made of silicon rubber. It functions as the high-permeable medium as well as the vacuum bag. There are many small channels on the inner surface of the reusable resin distribution medium, whose purpose is to facilitate the resin infusion into the fabrics. The advantage of this type over the typical one is its cost saving because the resin distribution medium can be used repeatedly.

As the market front-runner in VARTM, the SCRIMP process is becoming an important process for manufacturing very large composite parts because of its low cost, processing flexibility, high fiber-to-resin ratio, low void content, and consistency in production. There are many products and parts made by this technology. For example, the Northern Star insulated rail car which is 68 feet long, 12 feet high and 10 feet wide, is produced by Hardcore DuPont Composites in two pieces. The sidewalls, endwalls and
floor are all one piece: the roof is the other. The only joint is at the interface of the car body and the roof. Compared to steel boxcars which have hundreds of pieces, the composite boxcars have much better insulation due to its seamlessness and 5 inches of insulation laminated between composite skins, as well as toughness, light weight and corrosion resistance. The total weight of the rail car is about 15,450 lb. which is about 50% lighter compared to a steel one. The boat manufacturing industry has also been very successful in using SCRIMP. Conventionally, boats are built by hand lay-up or spray-up process mentioned above, which is therefore considered as a hazardous-waste generator. Workers are exposed to toxic emission, and the strength of boats is low because of the low fiber content and high void content. By using the SCRIMP process, very good weight control can be achieved and the emission of styrene can be reduced by 90%.

Numerous versions of VARTM have emerged in recent years and each has its own advantages [Hudson, 1996]. Besides SCRIMP, Ultra-violet VARTM (UV-VARTM) and Low Pressure Resin Infusion Molding (LPRIM) process are two examples. UV-VARTM is similar to most VARTM processes. The differences are in the resin distribution systems and the resin systems. Polypropylene resin supply tubes are strung from the resin source to the side of the mold. Each resin supply tube is outfitted with an on/off valve and then connected to a strip of spiral wrap, a permeable tube made of polypropylene. Under vacuum, the resin is pulled through the spiral wrap, allowing for distribution through the reinforcements. The UV-VARTM process offers the benefit of "cure on demand". A UV cure resin system uses a photo initiator. Cure doesn't begin until UV radiation is applied while for the SCRIMP process the resin systems rely on catalysts and promoters to induce cure and resins may gel before mold filling is finished. Cost of UV resins is a bit higher. The process is limited to light-permeable laminate which prevents the use of fabrics other than glass fiber, and limits the type of core to
certain types of honeycomb. Further, thicker laminates need several mold cycles. For now, the UV-VARTM has yet to be used for any large-scale commercial applications.

In the LPRIM process, a patented vacuum bag film, similar in texture to bubble wrap used for packaging, is attached to the edges of the mold. Pressure to get the resin into the fiber is generated by elevating the resin supply slightly off the ground. The slight pressure, combined with the vacuum bag texture, allows the resin to flow in and around the fiber reinforcements. Instead of resin supply tubes or some other distribution means, micro-fine foam cores are used to create channels for resin distribution. A slight vacuum, equivalent to about one bar of pressure, helps draw the resin through. While it’s lower than processes with higher pressures, fiber content remains high and it’s less costly to implement.

VARTM processes have attracted sufficient attention that suppliers have introduced new reinforcements and resins for the processes. Since VARTM is a soft mold process in which the fiber content of the molded parts is controlled by the vacuum level, it is very important to have appropriate types of fabrics to achieve high fiber content under vacuum. Brunswick Technologies Inc. developed super-heavy-weight stitched fabrics such as QM6408, TVM3408 and QM5005 for VARTM processes. The advantages of this type of fabrics include higher tensile strength than woven fabrics, reduction in labor costs because of one multi-layer fabric replacing several individual fabrics, and easier to wet out because of no fiber crimps. New series of polyester, vinyl ester and epoxy resins are formulated for SCRIMP and other VARTM processes which require resin systems of low viscosity and low curing temperature to allow for fabrication of large composite parts. Dow Chemical’s DERAKANE Vinyl Ester Resins, Shell Chemical’s EPON Epoxy Resin Systems are two examples.
2.2. Thermoset Polymers — Vinyl Ester Resins

Vinyl ester resins have long been recognized as the premium resin for fabrication of industrial fiber reinforced plastic (FRP) parts in demanding corrosion resistant applications. Vinyl ester resins were first introduced commercially in the early 1960s [May and Newey, 1965]. They are thermosetting resins produced by esterification of a polyfunctional epoxy resin with an unsaturated monocarboxylic acid, usually methacrylic or acrylic acid. The terminally unsaturated epoxy methacrylate resin is usually dissolved in an unsaturated monomer such as styrene to give a low viscosity liquid resin which can be cured by free radical polymerization at ambient or at elevated temperatures. One of the first commercial vinyl ester resins introduced were EPOCRYL resin by Shell in 1965, followed in 1966 by the DERAKANE vinyl ester resins manufactured by the Dow Chemical Company. It was not until the mid-1960s, however, that these products began to be used for applications demanding superior chemical resistance. Since that time product lines have been extended to improve heat, fire and impact resistance of the resins. Major manufacturers and sellers of vinyl ester resins currently are shown in Table 2.1.

Vinyl ester resins combine the superior thermal, mechanical and chemical resistance properties of epoxies with the rapid curing and ease of processing of unsaturated polyesters. Like unsaturated polyesters resin, vinyl ester resins are unsaturated oligomers dissolved in styrene and are cured with roughly the same catalyst systems. The major difference is in the oligomer chemistry. Vinyl esters are methacrylated epoxies. The epoxy molecule does not have a weak chemical link susceptible to chemical attack (corrosion), which is the major difference between polyesters and vinyl esters. Another significant difference is that unsaturation is limited to two sites at the end of each molecule. The latter characteristic gives vinyl esters a higher
failure strain than typical polyesters, which in turn gives vinyl ester laminates superior mechanical properties, impact damage resistance, and fatigue file. The advantage they have over epoxies is that they cure at room temperature but still have heat distortion temperature that approach 90°C without a postcure. Their excellent elevated temperature performance, high elongation, and fatigue resistance attributable to the epoxy backbone make them favored candidates for new structural composite applications. These resins are now being used to fabricate a variety of reinforced structures including pipe, tanks, boats and ducts where the SCRIMP process often finds its applications. In addition to these applications, vinyl ester resins are also finding use in coatings, adhesives, molding compounds, structural laminates, electrical applications and military/aerospace applications.

<table>
<thead>
<tr>
<th>Company</th>
<th>Trade Name</th>
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<tbody>
<tr>
<td>Dow Chemical</td>
<td>DERAKANE®</td>
</tr>
<tr>
<td>Ashland Chemical</td>
<td>Hetron</td>
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<tr>
<td>Koppers</td>
<td>Atlac. Dion</td>
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<tr>
<td>Interplastic</td>
<td>Co-Rezyan</td>
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Table 2.1. Major manufacturers and sellers of vinyl ester resins
[Blankenship et al, 1989]
Diverse vinyl ester resins can be produced by reacting different epoxide resins with various unsaturated acids as shown in Figure 2.1. In addition, considering the number and type of unsaturated monomers which can be combined with and which can be copolymerize with vinyl ester resins, the number of products is further extended. Some of the commercial variations include different epoxy resins that the vinyl ester resins are based on, such as bisphenol A epoxy resin, Novolac epoxy resin and modified vinyl esters using specialty epoxy resins, urethanes, or acid anhydrides in the resin cook. To a large extent, it is the choice of the epoxy resin that determines the mechanical, thermal and corrosion properties of the cure product. For example, vinyl esters made from bisphenol A diglycidyl ethers (DGEBA) are made in various molecular weights and styrene contents. Because the methacrylate crosslinking sites are on the end of the molecular chain, crosslink density decreases as the molecular weight increases. A vinyl ester made with a low molecular weight epoxy will have a high crosslink density. When cured, this material will have a high heat distortion temperature (HDT) and good solvent resistance, but will tend to be brittle. Resins made with high molecular weight epoxies will have lower crosslink density, less solvent resistance, lower HDT, but will be more resilient. Bromine can be incorporated into the epoxy resin to form tetrabromo-bisphenol A for the purpose of adding fire retardancy, which is provided by the restricted molecular motion caused by the large molecular size and mass of the bromine atoms. The toughness of epoxies can be increased by rubber modification, and some of the most commonly used additives are the butadine-nitrile liquid elastomers. Specialty vinyl ester resins can be made by chemically modifying epoxy resins from the hydroxyl and epoxide functionality present. For example, carboxylic acid functional VE resins are produced by reaction of the backbone hydroxyl groups with maleic anhydride. These resins can be thickened with divalent metal oxides and hydroxides for use in sheet molding (SMC) and
bulk molding (BMC) compounds. Urethane structures are incorporated into vinyl esters to increase flexibility, toughness and adhesion.

Resin handling characteristics, reactivity, processability and chemical resistance all are affected by the choice of unsaturated acid and diluent monomer. Vinyl esters intended for structural and corrosion resistant composite applications are made using methacrylic acid. Steric hindrance by the methyl group increases resistance of the resin to basic hydrolysis. The monomer added to the vinyl ester resin must satisfy many demands. Its properties such as vapor pressure, toxicity and reactivity affect handling and ease of processing, yet also must contribute to the required optimal properties in the finished part. Styrene by far is the dominant monomer for vinyl ester resins, due to its low cost, producing low viscosity resins at reasonable monomer concentrations and polymerizing readily with VE using either ambient or elevated temperature curing systems. Other polymerizable diluents which have been used include vinyl toluene, divinyl benzene and other similar styrenics, methyl methacrylate and various mono and poly-functional acrylate monomers. Because vinyl esters have more latitude for reformulation than polyester resins due to the higher performance of the epoxy backbone and the higher reactivity of the terminal unsaturation, the diluents mentioned above can be used in whole or in part to adjust performance, which establishes niches in some applications.

2.3 Material Characterization

2.3.1 Resin Chemistry and Kinetic Modeling

(1) Experimental Techniques

Kinetic measurements during the reactive processing are inherently difficult. Resin solidification due to chemical crosslinking, domain formation or crystallization
obviates most solution techniques like titration or standard size exclusion chromatography. High polymerization temperatures, high pressure and fast reaction rates further complicate the task.

Since most liquid molding polymerizations are fast and highly exothermic, one of the simplest ways to follow overall conversion is to monitor heat generation in the adiabatic condition. Several researchers have used the adiabatic temperature rise idea together with linear or non-linear regression methods to predict the kinetic parameters [Lee, 1979; Camargo, 1984]. Because the thermal conductivity of polymer is extremely low, an insulated disposable bucket can serve as a suitable adiabatic reactor. A fast responding thermocouple is used to follow the adiabatic temperature rise.

For the change of temperature with time in an adiabatic system, the heat balance can be expressed as equation (2.1)

\[ \rho C_p \frac{\partial T}{\partial t} = \Delta H k_0 \exp\left[-\frac{E_a}{RT}\right] C^n \]  

for an nth order reaction. If we assume that thermophysical properties are constant, the extent of reaction is directly proportional to the heat generated.

\[ \alpha = \frac{T_{ad} - T}{\Delta T_{ad}} \]  

Substituting equation (2.2) into equation (2.1), a linear form can be derived as shown in equation (2.3).
\[
\ln \left( \frac{\partial T}{\partial t} \right) = \ln \left( K_0 C_{\text{at}}^{n-1} \Delta T_{\text{ad}} \right) - \frac{E_a}{RT} + n \ln \left( \frac{T_{\text{ad}} - T}{\Delta T_{\text{ad}}} \right)
\]  

(2.3)

The variables \( \partial T / \partial t, 1 / T \) and \( (T_{\text{ad}} - T) / \Delta T_{\text{ad}} \) can be evaluated from the temperature vs. time curve of the adiabatic polymerization. By using non-linear curve fitting, one can obtain the order of reaction, \( n \), the activation energy \( E_a \), and the frequency coefficient \( K_0 \).

For slower reactions or systems which are not reactive at room temperature but are activated at elevated temperatures, differential scanning calorimetry (DSC) has been used extensively in the kinetic measurement. DSC and adiabatic temperature rise method have the advantages of simplicity, less limitation, and the capacity to yield simultaneously information regarding kinetics, energetics, and thermal properties. However, both methods only measure overall heat release and cannot differentiate between multiple reactions or between reaction and physical changes such as crystallization. They are also less sensitive at high conversions. Kinetic information obtained tends to be less accurate due to empiricism and lack of details in the kinetic sense.

Spectroscopic methods like infrared, ultraviolet or nuclear magnetic resonance can be much more specific to particular bond formation. The recent development of computer assisted FT-IR spectroscopy has enabled accurate monitoring of fast and complex polymerizations. Several researchers [Ishida and Scott, 1986; Yang and Lee, 1987] have successfully used FTIR to follow fast bulk polymerization. The disadvantages of spectroscopic methods are that the sample preparation and data analysis are more time consuming compared to the thermal methods.

(2) Kinetic Modeling
An ideal kinetic model should be simple enough to be combined with process simulation model for predicting the mold filling and curing behavior. Yet, the model should be able to describe both the kinetic changes of the reacting material and the physical phenomena such as gelation and vitrification effects. Furthermore, if the model is to be used for material design, the effect of major chemical ingredients on the reaction kinetics, and consequently, the physical properties or the defects of the molded product, need to be addressed. Obviously, it would be difficult to develop a single model which could fulfill all the above mentioned requirements. An alternative approach is to have several levels of models.

The simplest kinetic model for describing the isothermal cure of reactive resins is given by the familiar n-th order rate expression

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n$$  \hspace{1cm} (2.4)

where $\alpha$ is conversion, $d\alpha/dt$ is rate of reaction, $K$ is the temperature dependent rate constant and $n$ is the kinetic exponent. This model assumes a maximum initial reaction rate, and consequently, is not capable of realistically describing the curing reaction when a rate peak in the isothermal cure is observed. In many studies of reactive processing [Pusatcioglu et al. 1979; Han and Lem, 1984], the following kinetic expression proposed by Kamal and Sourour [1973] has been found to correlate well with isothermal kinetic data:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^n)(1 - \alpha)^n$$  \hspace{1cm} (2.5)
The kinetic exponents, m and n, are usually assumed to be independent of temperature and rate constants; $K_1$ and $K_2$ are assumed to have an Arrhenius temperature dependency.

The parameters of these two models can be easily determined from rate profiles measured by conventional analytical tools. For applications where the primary objective of modeling is to estimate the overall curing rate, reaction exotherm and temperature profile for a given resin, these models are often adequate because they are simple, yet provide a reasonable prediction. The limitation of these general purpose models is that they are not based on the resin chemistry, and therefore, their parameters may not reflect the functions of the resins and curing agents in the reaction. Consequently, the predictive capability is limited.

The second level of kinetic models is based on the reaction mechanism of a given resin. The resin chemistry and the major elementary reactions are considered in the modeling. For example, for the modeling of the curing of unsaturated polyester resins, several simplified models based on the generally accepted free radical polymerization mechanism have been proposed [Stevenson. 1986]. However, this level of kinetic models does not consider the effect of diffusion on the reaction. This limitation often results in an over-prediction of reaction rate and conversion at later stage of cure. This led to the development of several kinetic-diffusion models in recent years [Huang and Lee, 1985]. For this level of modeling, several material properties, such as glass transition temperatures and thermal expansion coefficients of monomer and polymer need to be known in order to determine rate constants from measured reaction rate or conversion profiles. For systems like styrene or methyl methacrylate homopolymerization, such information can be found in the literature or can be determined experimentally. For more complicated reaction systems, this may present some practical difficulties.
The kinetic-diffusion effect may play a major role in many reaction systems. In the kinetic modeling of poly(urethane/isocyanurate) formation, researchers [Vespoli and Alberino, 1985; Viola and Schmeal [1994] have found difficulties describing the behavior of their systems at large isocyanate indices by using the second level of kinetic models. Viola and Schmeal [1994] used statistical methods to correlate the kinetic data by adding some empirical factors in the reaction heat of trimerization. Kinetic-diffusion models may be needed for such reactive systems. Unsaturated polyester and vinyl ester resins gel early in the polymerization and most of the polymerization occurs under diffusion control. Hence, kinetic-diffusion models are the only relevant tool to analyze these reaction systems.

2.3.2 Rheological Changes and Modeling

(1) Experimental Techniques

The rheological changes which occur during processing of thermoset polymers are enormous. Understanding these rheological changes can be critical to the processing of thermoset polymers. In liquid composite molding, the reaction system generally starts at a low viscosity. The viscosity increases with conversion and reaches an infinite level when the material solidifies either by chemical crosslinking or physical changes, such as phase separation or crystallization. Further reaction occurs in the solid state, which may increase the polymer modulus to a desired level before demolding. During the process, mold filling must be finished before the system viscosity reaches too high a value. This process is then followed by a curing stage in which the material reacts to a sufficient mechanical strength before being ejected.

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Non-Newtonian effects appear to be small for polymers built up from branched monomers, except near the gel point. Most viscosity models for reactive resins neglect the non-Newtonian effects because the temperature and network formation effects tend to dominate the rheological changes. However, for crosslinking of long chains or if particulate fillers are present, shear thinning and time dependent effects can be pronounced even at the beginning of the reaction.

The rheological changes of reactive polymers are mainly measured by two methods. In the first method, the resin in its liquid state is subjected to shear flow in various rheometers. The measured viscosity increases with increasing extent of reaction until the stress reaches the limit of the instrument or until the material breaks. A Brookfield viscometer or similar devices [Wang and Lee, 1990] are often used in the adiabatic reactor to measure the viscosity rise. Since the measuring probe can be disposable and the viscometer is portable, these viscometers are quite appropriate for measuring viscosity changes in fast cure processes. However, due to its empiricism, the measured results are less accurate from the rheological point of view. The Haake rheometer and Rheometrics Mechanical Spectrometer are often used to measure viscosity changes of slower reactions. Measurements in liquid state give reliable data since the shear flow field and resin temperature can be well controlled.

In the second method, small amplitude oscillatory shear gives the components of the complex modulus during polymerization. The viscous behavior of the reactive liquid dominates the initial part of the reaction. The loss modulus, $G''$, is large while the storage modulus, $G'$, is small. With increasing molecular weight, the loss modulus increases while the storage modulus rises sharply until it intersects and then exceeds the loss modulus. Several researchers [Winter and Muthukumar, 1986; Chamber and Winter.
1987] have suggested that the intersection of $G'$ and $G''$ marks the time of gelation for crosslinking polymers when the stress relaxation at the gel point follows a power-law (i.e. $G'(\omega) = G''(\omega) \sim \omega^{1/2}$ where $\omega$ is frequency) and the temperature is much higher than the glass transition temperature. However, for many crosslinking systems the relaxation exponent at the gel point may have a value not equal to $1/2$ [Chamber and Winter, 1987; Winter, 1988]. Winter and coworkers [1989] proposed a general expression at gel point. $G'(\omega) \sim G''(\omega) \sim \omega^\gamma$. If $\gamma = 1/2$, $G'(\omega) = G''(\omega)$ and $G'$-$G''$ crossover is the gel point. If $\gamma \neq 1/2$, the instant of gelation occurs when $G'(\omega)$ is parallel to $G''(\omega)$. A Fourier transform dynamic mechanical analysis method was developed [Winter and Scanlan, 1989] where the dynamic response at several frequencies is measured simultaneously. The resulting stress is decomposed into the individual frequency responses by a discrete Fourier transform. Such analysis allows for the determination of the gel point for a reacting system.

(2) Modeling

Roller [1975, 1986] has reviewed several studies regarding the rheology of curing thermoset polymers. In these studies, viscosity changes during processing are expressed as a function of time and temperature:

$$\eta = K \exp\left(\frac{E_v}{RT}\right) \exp\left(k(T)t\right) \tag{2.6}$$

This model is useful for correlating experimental data measured at different temperatures. It, however, does not provide any insight into the network structure and properties of the resin. Since the viscosity model is based on the overall curing kinetics, the model parameters are batch specific, i.e. once the resin composition is changed, the parameters have to be reevaluated.
The next level of modeling is to convert viscosity versus reaction time to viscosity versus conversion using independently measured kinetic data. Such a correlation corrects for the effect of reaction rate due to various catalyst concentrations and reaction temperature. A typical expression is [Castro and Macosko, 1982; Richer and Macosko, 1980]:

\[ \eta = \eta_\infty \exp(E_\eta / RT) \left( \frac{\alpha_{gel}}{\alpha_{gel} - \alpha} \right)^{f(\alpha, T)} \] (2.7)

where \( \alpha_{gel} \) is the gel conversion and \( \alpha \) is the conversion. This model, however, still does not incorporate any molecular structure.

From conversion data, the corresponding molecular weight can be calculated using appropriate theories. Thus, the viscosity changes during polymerization can be expressed as a function of weight-average molecular weight and an Arrhenius temperature dependence [Lipshitz and Macosko, 1976; Macosko and Miller, 1976]:

\[ \eta = K \exp(E_\nu / RT) \left[ \frac{M_w}{(M_w)_0} \right]^{f(T, M_w)} \] (2.8)

This model brings the structure parameters, Mw, into the viscosity correlation. The function f, however, needs to be fitted empirically.

For copolymerization such as poly(urethane/isocyanurate) formation, the second level of viscosity modeling is usually not enough since the competition between reactions changes with the ratio of the reactive components. Conversion alone does not reflect this information, and therefore the third level of viscosity modeling is necessary.
2.3.3 Theories of Network Formation

During thermoset polymerization, complex branched molecules are formed. The development of these three dimensional structures determines processing properties such as viscosity, gel point and the final properties of the network: modulus, damping, ultimate strength, permeability, etc. The theoretical models that describe network formation in terms of structural changes as a function of the extent of reaction can be divided into two categories, branching theory (BT) [Flory, 1953] and simulation in n-dimensional space.

The process of structure build-up during polymerization is affected by both the mobility of the structures and the reaction kinetics. BT models are based on the premise that the mobility of the structures is very fast compared with their reaction rates. Simplification in model formulation is achieved by recognizing that several combinations in the structures are statistically random. Thus the models could be formulated in terms of either the probability generating functions (pfg) [Gordon, 1962] or the expectation values [Macosko and Miller, 1976] of the relevant random variables. These models are briefly reviewed below.

(a) Flory-Stockmayer Model:

Flory [1953] and Stockmayer [1943] proposed a model for the network formation. Their model provides an adequate description for the formation of networks via step reactions and for crosslinking of linear chains. It started with the assumptions of equal and independent reactivity of the same type chemical groups and no intramolecular reactions. Based on these assumptions, the classical Flory-Stockmayer gelation theory derived the weight average molecular weight before the gel point and the gel conversion of a monovinyl-divinyl system as follows:
where $\alpha$: conversion of total vinyls;

$\alpha_c$: critical conversion at the gel point;

$\rho_c$: crosslinking density, i.e., the ratio of initial vinyls on divinyls over the total initial vinyls;

$\lambda_w$: primary polymer chain length, which can be determined by the initial propagation and termination rates;

$M_w$: weight average molecular weight of polymer chains;

$(M_w)_0$: weight average molecular weight of primary polymer chains.

(b) Cascade Model

For the chain crosslinking (co)polymerizations, the assumptions of equal and independent reactivity and no intramolecular reaction are often not fulfilled. The strong cyclization causes the formation of inhomogeneities consisting of densely crosslinked regions surrounded by less densely crosslinked regions. The Flory-Stockmayer model, thus, was extended by Gordon et al. [1962, 1967, 1978] by taking into account unequal reactivity and substitution effects within monomer units and by a mean field treatment of very restricted cyclization. Gordon showed that molecular weight averages could be
calculated directly using the theory of stochastic branching (cascade) processes and its method of probability generating functions [Gordon, 1962].

Although Gordon's techniques are quite general, they have not been widely applied to network problems. The use of vectorial probability generating function approach makes formulation of specific equations for the molecular weight average difficult. It requires breaking down of the reactive monomers somewhat artificially and usually yields equations in matrix form.

(c) Recursive Model:

Macosko and Miller [1976] proposed a recursive method for the modeling of the reaction-structure relationships of polymeric networks. The basic principles used were the recursive nature of the branching process and the law of total probability of expectation which can be stated as follows:

\[
E(Y) = E(Y|A)P(A) + E(Y|A^c)P(A^c)
\]  \hspace{1cm} (2.11)

Where A is an event and A^c is its complement; Y is a random variable; E(Y) is its expectation and E(Y|A) is its conditional expectation given that the event A has occurred.

Many important nonlinear stepwise polymerizations can be treated using the recursive model [Lipshitz and Macosko, 1976; Musatti, 1975]. It also can be extended to treat nonideal effects such as unequal reactivity of functional groups [Miller and Macosko, 1978] and substitution effect, (i.e. changes in reactivity with reaction) [Miller and Macosko, 1980]. Ladin and Macosko [1984] further accounted cyclization in the recursive model for a vinyl \((A_2)\)-divinyl \((A_4)\) copolymerization.
BT models can absorb the majority of chemical information, such as functionality, reactivity, reaction paths, etc. However, the models cannot deal exactly and directly with existing spatial correlations due to cyclization or excluded volume. Much attention has been paid recently to an alternative approach in which network formation is simulated in an n-dimensional space. The most prominent method is the percolation model [Stauffer, 1985] which is usually associated with a lattice, and uses a Monte Carlo technique to form bonds at random between the lattice sites. In this model, sites that are joined to one another by bonds are clusters, and at any stage of the bond-forming process there is a distribution of clusters having different sizes and connectivity.

The percolation model is able to explain spatial effects such as cyclization and excluded volume. In addition, the percolation model can show inhomogeneity in the system and can provide a qualitatively proper description of the high extent of cyclization for bulk chain growth polymerizations [Boots et al. 1985; Manneville and de Seze, 1981]. Manneville and de Seze [1981] first introduced this simulation method of free radical polymerization of multifunctional monomers. They used a cubic lattice with each site on the lattice representing either a di- or tetra-functional monomer. Mobility of polymer and monomer is not included, besides, all the radicals were activated prior to the polymerization. which is referred to as "fast initiation." Earlier modifications of this model [Herrmann and Landau, 1984; Bansil et al., 1984] were the addition of a solvent or the addition of monomer movement. "Fast initiation" was still performed and no polymer mobility was incorporated in these models. Although the simulation results gave reasonable trends of polymerizations of multifunctional monomer, the predicted kinetic chain lengths were shorter and the predicted gel conversion was higher than the experimented data.
Boots and Pandey [1984] embodied a more realistic initiation algorithm by allowing randomly selected monomer initiated to a radical at a constant rate. This method of initiation did not consider different initiator type or the exponentially decay rate of initiation. Nevertheless, their model was an improvement over "fast initiation" models. Boots and Dotson [1988] later established a model which took into account polymer diffusion. Only one active radical presented in the system, and thus termination took place through the trapped radical.

Bowman and Peppas [1991] developed a model which considers multiple occupations of monomers, initiator decomposition, and different conformations of monomers. However, they did not check the mobility of every molecule in the system. In addition, the kinetic information was not used in the simulation to determine the probabilities of each event, i.e. propagation, termination and cyclization. Recently, Chiu and Lee [1995b] developed a model which incorporates translational diffusion of monomers and polymers, and segmental diffusion of polymers.

Although much progress has been made in the percolation techniques, the method is still far from being able to absorb major information on the laws for making bonds, such as the reactivity, reaction paths and the conformation rearrangement which occurs in the formation of successive bonds. In addition, the free radical copolymerizations, which are important in VARTM, have not been studied using this type of models.

2.4 Analysis of Isothermal Mold Filling

The mold filling process of liquid composite molding has been analyzed both microscopically and macroscopically. Most work involving the microscopic flow mechanism is done experimentally. Because of the computational limitation and the lack
of comprehensive physical models, the analysis was carried out by simplifying the fiber mat as a set of parallel tubes or permeable capillaries.

In macroscopic studies, the basic concerns are the resin flow through the fiber mats in a mold cavity, heat transfer between the resin, fibers, and tools, as well as the resin cure (i.e. chemical reaction). Darcy's law for flow through porous media is the most commonly used equation for describing flow through the fibrous reinforcements. Darcy's law assumes plug flow and therefore does not account for any drag effects from the walls of the mold. Eckler and Rust [1987] have reported that under most production conditions the flow resistance from the walls is much smaller than that of the porous media and can therefore be ignored. The exception to this is when the mold cavity is very thin and the porosity of the reinforcement is high.

Fluid flow partially bounded by a free surface, which is observed in the transient mold filling process, also occurs in numerous industrial applications as well as natural phenomena, such as coating, die casting, coastal sea water intrusion, tide movement, etc. It is difficult to describe free-surface flows with an accurate mathematical model. The main difficulties are as follows: 1) unknown location of the free surface a priori; 2) undetermined shape of the free surface a priori; 3) a stress singularity at any three-phase contact line, i.e. the intersection of the free surface and the solid boundary [Huh, 1969].

Since the complete analytic description of flows with a free surface is still not available, numerical simulation is considered as an alternative way to investigate the free-surface flow. Most RTM modeling dealt with isothermal mold filling [Michaeli et al., 1989; Coulter and Gucer, 1988; Um and Lee, 1990; Young et al. 1991a, 1991b]. These models considered two-dimensional isothermal mold filling in RTM by applying Darcy's law and either the finite element method [Michaeli et al., 1989], the finite difference
method with numerical mapping [Coulter and Guceri, 1988] or the boundary element method [Um and Lee, 1990].

The finite element method is an approximation procedure for solving differential equations of boundary and/or initial-value type in engineering and mathematical physics. The procedure employs subdivision of the solution domain into many smaller regions of convenient shapes, such as triangles and quadrangles, and uses approximation theory to quantitize behavior on each finite element. Suitably disposed coordinates are specified for each element, and the action of the differential equation is approximately replaced using values of the dependent variables at these nodes. Using a variational principle, or weighted-residual method, the governing differential equations are then transformed into finite-element equations governing each isolated element. These local equations are collected together to form a global system of boundary conditions. The nodal values of the dependent variables are determined from solutions of this matrix equation system.

Young et al. [1991a, 1991b] used the control volume/finite element method (CV/FEM) to simulate both 2-D and 3-D isothermal mold filling in RTM and SRIM. The entire flow field is divided into a number of three-node triangular elements. The control volume is formed based on the nodes of adjacent elements. Each element is divided into three sub-areas by the lines connecting the centroid of the element of the midpoint of each side. A control volume is composed of several sub-areas, which have a common node at the center of the control volume. Darcy's law is used to describe the resin flow and the continuity equation is integrated along the boundary of a control volume. A set of linear algebraic equations with the node pressure as variables are formed. After the pressure field is determined, the velocity field can be evaluated according to Darcy's law. For a selected time increment, the volume of resin flow into each flow front control
volume \((0 < f < 1)\) is calculated based on the velocity field. The calculated volume of resin inflow is added to the original volume of resin in the flow front control volume. If the total resin volume in a control volume is equal to the volume in a control volume, that control volume is considered full. After the value \(f\) is updated, another pressure computation is performed for all the control volumes, which are considered full. The procedure is repeated until the whole mold is filled. In Young's study, the anisotropic behavior of the fiber mat was also considered. He proposed a flow front mesh refinement method to better predict the resin flow in the moving front region. The nonisothermal mold filling process were analyzed to demonstrate the efficiency of this mesh refinement method.

Han et al. [1993] investigated the deformation of fiber mats caused by resin flow during mold filling. Two models are developed to simulate the flow pattern including the deformation of a fiber mat. He proposed two simplified models to treat the fiber free region as part of the fiber bed with an "equivalent" permeability. He studied the relationship among flow rate, pressure and deformation of a fiber mat.

For the simulation of mold filling in VARTM, the author has not found any publication. VARTM is often used to make large-size parts. If one uses the conventional CV/FEM to model the resin infusion process, it would create far too many nodes and elements to be solved by using reasonable computer memory and CPU time. Therefore, a simplified model is needed for the simulation of mold filling in VARTM.

2.5. Analysis of Mold Curing

Curing in the mold is governed not only by the behavior of the reactive materials such as rheological changes and reaction kinetics, but also by the transport phenomena of the process. The highly exothermic reactions often make temperature control a difficult
task and heat transfer an important factor to consider during mold filling and curing. Nonisothermal mold curing may affect dimensional accuracy, surface quality and physical properties of the molded parts.

The heat generated in LCM is produced by the polymerization exotherm. The polymerization can usually be activated in two ways: mixing activated systems or thermally activated systems. For the mixing activated systems, two or more reactive monomers or prepolymerms are impingement mixed in a mixing chamber. These reactions are often highly reactive step growth polymerizations. The mixed fluid reacts rapidly and forms a solid part shortly after mold filling. The thermally activated reactions may involve chain growth or step growth polymerizations. These reactants can be mixed slowly and injected into the mold at a lower temperature. Crosslinking reaction is usually initiated in the mold cavity by heat transfer from the mold walls or by initiators and promoters.

Because of the reaction exotherm and the energy conducted from the mold walls and convected by the flow, heat transfer cannot be neglected during the filling and curing stage of LCM processes. Moreover, resin viscosity changes as a function of temperature and conversion. Before the reaction starts, viscosity is temperature dependent and decreases with increasing temperature. However, when the crosslinking polymerization occurs, viscosity may become conversion sensitive and increase rapidly with increasing conversion. The interaction between fluid flow, heat transfer, reaction conversion, and resin viscosity complicates the governing equations. Deliberate material characterization and numerical simulation are needed.

There is very little work appearing in literature on the nonisothermal mold filling and curing in LCM processes. Lin [1991] developed a numerical scheme to simulate the
non-isothermal RTM process, and an experimental method to measure the volumetric heat transfer coefficient. However, in VARTM, mold filling is usually carried out at room temperature and the filling time is relatively short comparing to the curing time (i.e. minutes vs. hours). By adjusting the amount of inhibitor and/or initiator, little reaction would occur and heat transfer can be neglected during mold filling. But after mold filling is finished and the reaction starts, heat transfer can no longer be neglected, especially in the molding of thick composites. Curing near the cosmetic surfaces often occurs last and thus causes the fiber “print through” problem. Compared to the open-mold processes, fabrication of thick composites is one of the limitations of VARTM. In order to optimize the process design and processing conditions, an integrated study of kinetics, chemorheology and heat transfer in the mold filling and curing stage is necessary for VARTM.
CHAPTER 3

MOLD FILLING ANALYSIS IN SCRIMP BASED ON A HIGH-PERMEABLE MEDIUM

SYNOPSIS

Mold filling in SCRIMP based on a high-permeable medium is complicated because of the considerable difference in the permeabilities of the fiber reinforcement, the peel ply and the high permeable medium. The objectives of this study are to understand the flow mechanism through flow visualization experiments and to present models that can be used to predict the filling time and flow pattern. Permeabilities of a stitched fiber mat, a high-permeable medium and a peel ply were measured. Flow visualization of SCRIMP mold filling was carried out under various molding conditions. A three-dimensional Control Volume/Finite Element Method (CV/FEM) was adopted to solve the flow governing equations, i.e. the Darcy’s law, and the influences of the flow properties of the high-permeable medium, the fiber reinforcement and the peel ply on filling time were investigated. Based on experimental observations and CV/FEM simulation, a simplified leakage flow model was also presented. The comparison of experimental and simulation results showed good agreement.
3.1 Introduction

In recent years, Vacuum-Assisted Resin Transfer Molding (VARTM) has become more and more popular in the composite industry for making large size composite parts at low cost. For open-mold processors, VARTM is particularly attractive since it also can reduce emissions of volatile organic chemicals (VOCs) [Laxarus, 1996]. SCRIMP, the acronym for Seemann Composites Resin Infusion Molding Process, is a new and promising VARTM process that meets increasingly stringent environmental regulations and is capable of delivering composite parts that exhibit excellent properties [Seemann, 1990, 1991, 1994]. It has been applied in several commercial applications, from repairing bridges to making sailboats and refrigerated cargo boxes, and is being considered for various civil and marine infrastructure, aerospace, defense and automotive applications. The process uses only a single rigid mold, which is laid up with fiber reinforcements and covered with a vacuum bag made of air impervious films such as nylon or silicone film. Resin is infused into the mold cavity through patented resin distribution systems solely under vacuum [Seemann, 1990, 1991, 1994]. Besides low tooling cost and extremely low VOC emissions, advantages also include processing flexibility, low void content, consistency in production and the ability to mold very large parts – up to 186 m² and 0.15 m thick with reinforcements to achieve glass contents up to 75-80% by weight [Plastics Tech., 1995].

There are varieties of the SCRIMP process, depending on the resin distribution systems used to facilitate the resin infusion. Figure 3.1(a) shows the SCRIMP process
Figure 3.1. Resin distribution systems used in SCRIMP.
(a) high-permeable medium; (b) grooves
based on a high-permeable medium. This type of SCRIMP is commonly used because of the design flexibility and the availability of the processing materials such as the high-permeable medium, the peel ply, and the vacuum bag film. Figure 3.1(b) shows the SCRIMP process based on the grooves cut in a low-density core to facilitate the resin infusion. The core is part of the final product, which can reduce the weight of the composite part.

Although SCRIMP has already been used in industry for small quantity productions, the process has not been thoroughly investigated. Many techniques developed to date are based on experience or trial-and-error approaches. Mold filling is one of the critical phases in determining the overall success of the process. In this stage, the reactive resin flows into the fiber preform under vacuum to wet out the dry fiber preform. Resin reaction may occur during this stage, which leads to a sharp increase in the viscosity of the liquid resin (i.e. gelation). This viscosity increase may result in incomplete mold filling, especially in making large parts. Therefore, understanding the flow mechanism and the capability of designing and predicting the filling time are essential to the SCRIMP process. The prediction can help the molder to select the type and amount of reactants such as initiator, promoter, inhibitor and retarder in order to adjust the gel time of the resin. The objectives of this study are to understand the flow mechanism through flow visualization experiments and to present models that can be used to predict the filling time and flow pattern. This chapter presents experimental and simulation results of SCRIMP based on a high-permeable medium, and Chapter 4 focuses
on SCRIMP based on grooves. Experimental results [Li, S. 1997] are quoted here for further analysis, discussion and comparison with the numerical simulation.

3.2 Experimental

3.2.1 Materials

Three non-reactive fluids were used for permeability measurements and mold filling experiments: DOP oil (viscosity 43 cp at 24.4°C), Mobil Extra Heavy oil (viscosity 320 cp at 26.2°C) and Mobil BB oil (viscosity 530 cp at 23.5°C). A stitched glass fiber mat, QM6408, from Brunswick Technologies, Inc. was used as the reinforcement in all experiments. The high-permeable medium used in this study is a knitted fabric with a high porosity. Because of the twist at the link, the porosity of the high-permeable medium changes little under compression.

3.2.2 Permeability Measurements

The flow of the liquid resin in the fiber reinforcement, the high-permeable medium, and the peel ply can be complicated because the permeability is significantly different among these materials.

3.2.2.1 The Fiber Reinforcement (QM6408)

In-Plane Permeability: The effective planar permeability of the fiber mat can be measured via the radial flow method [Wang et al. 1994]. The fiber mat was cut into a disc shape with 133 mm in diameter. A hole with a diameter of 19 mm was punched at the center of the disc. Certain layers of fiber samples were placed into a mold cavity. By
changing either the number of fiber layers or the thickness of the cavity, different porosities of the fiber preform were achieved. During the experiment, a constant flow rate was provided by an Instron machine and a pressure transducer was used to measure the pressure at the inlet of the mold cavity. DOP oil was used as the measurement fluid. The measured effective planar permeability for QM6408 as a function of porosity is summarized in Figure 3.2. It can be seen that for QM6408, the permeability is about 50 to 60 darcy as the porosity of the fiber mat is around 0.47 to 0.49 (i.e. under the full vacuum condition).

Trans-plane Permeability: The permeability in the thickness direction can be determined using either a unidirectional flow method or the three-dimensional computer simulation method [Wu et al. 1994]. The first method measures the steady state inlet pressure for a fabric stack under a constant flow rate in the thickness direction. The application of Darcy’s law can be made to determine the transverse permeability. However, it is no easy to measure the permeability accurately this way because channeling flow and fiber deformation may occur, particularly at high pressure. Therefore, the second method, i.e. the three-dimensional flow measurement and simulation method, was employed. This method utilizes a three-dimensional flow experiment at constant flow rates, and compares the measured inlet pressure with numerical simulation. When the in-plane permeabilities are known, the trans-plane permeability can be back calculated using the three-dimensional flow simulation. The DOP oil was also employed as the measurement fluid. Circular fiber samples with 133
Figure 3.2. Effective permeability of QM6408 fiber mat as a function of porosity
mm in diameter without hole in the center were used. The permeabilities measured using this method are 1.5 darcy for a porosity of 0.47 and 10 darcy for a porosity of 0.49. 10 darcy is taken as the transverse permeability for the QM6408 fiber mat, $K_{t}$, under full vacuum.

3.2.2.2 The High-Permeable Medium

In order to determine the contribution of the flow in the high-permeable medium to the resin infusion into the fiber preform, the permeability of the high-permeable medium needs to be known. It is assumed that the high-permeable medium is isotropic so that only the in-plane permeability needs to be measured.

Permeability of the High-Permeable Medium Stacked on a Glass Platform: The set-up used to measure the permeability of the fiber preform can not be employed to measure the permeability of the high-permeable medium since the permeability of the latter is very high. This high permeability leads to a very small pressure drop for the sample with 133 mm in diameter, which is difficult to measure accurately using the previously mentioned permeability set-up. Therefore, another method (an unsteady state method) was employed for this case. In this method, the flow length versus time was recorded for a unidirectional flow. Then the permeability of the high-permeable medium was determined using the analytical solution for the unidirectional flow. The high-permeable medium was cut into strips with 0.11 m in width and 0.81 m in length. The Extra Heavy oil with viscosity of 410 cp at 22.5°C was used as the measurement liquid. In order to study the effect of the number of layers of the high-permeable medium on the
permeability, two sets of experiments were conducted: seven layers of the high-permeable medium in one set and one layer in the other set. The experimental set-up with visualization equipment is shown in Figure 3.3. The high-permeable medium strips were placed on a glass platform and sealed with a vacuum bag. Since both the bottom glass platform and the top vacuum bag are transparent, the bottom and top filling images can be captured by a CCD camera through two tilted mirrors. When the vacuum was applied, the strips were compressed against the glass platform and the liquid flowed in the direction of the strips when the valve at the inlet was opened. At the same time, the CCD camera and the VCR recorded the flow front location as a function of time.

The distance from the inlet to the flow front and the corresponding time were measured from the recorded image. For the one-dimensional flow, Equation (3.1) can be used to calculate the permeability of the high-permeable medium:

$$t = \frac{\mu \phi}{2kP_0} s^2$$  (3.1)

Where $s$ is the distance from the inlet to the flow front, $t$ is the corresponding time, $\mu$ is the viscosity of the measurement fluid, $P_0$ is the inlet pressure (1 atm in this experiment) and $\phi$ is the porosity of the high-permeable medium, which is 0.85-0.88. By plotting $t$ vs. $s^2$, the permeability can be calculated from the slope. Figure 3.4 shows such plots for one-layer and seven-layer samples, and the permeabilities calculated are 5500 and 4900 darcy for one-layer and seven-layer samples respectively. Initially, it was thought that the

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Figure 3.3. Experimental set-up for flow visualization.
Figure 3.4. Flow length as a function of filling time for the high-permeable medium stacked on glass platform
permeability for one-layer sample should be smaller than that for seven-layers because of the additional frictional force caused by the wall of the mold cavity. However, the experimental results showed the opposite trend. This may be attributed to the nestling effect, which is defined as the reduction of porosity due to the inlay of fibers or fiber tows between adjacent layers. In the SCRIMP production, the high-permeable medium is placed on a soft peel ply and the fiber preform rather than on a rigid glass platform. The arrangement may affect the permeability because the effective porosity may change under vacuum. Therefore, another set of experiment, which mimics the SCRIMP production, was carried out to measure the permeability of the high-permeable medium in this arrangement.

**Permeability of the High-Permeable Medium Stacked on a Peel Ply and Fiber Mat:** Three layers of fiber mat were placed on the glass platform. A very thin Mylar film (0.01 mm), which is impermeable to the liquid, was placed on the fiber preform. Thus, no liquid flows in the thickness direction, which ensures the flow is unidirectional. Then one layer of peel ply was laid on the top of the Mylar film, and one layer of the high-permeable medium was stacked on the top of the peel ply before adding the vacuum film. The measurement liquid was the Extra Heavy oil with a viscosity of 400 cp at 23.0°C. The plot of t vs. s^2 is shown in Figure 3.5, and the permeability of 2800 darcy was calculated from the slope according to Equation (3.1). This value is much less than 5500 darcy measured earlier. The difference results from the nestling effect. Since the in-plane permeability of the fiber mat is 50 to 60 darcy under full vacuum in SCRIMP mold
Figure 3.5. Flow length as a function of filling time for the high-permeable medium stacked on peel ply and fiber mat.
filling, the flow rate in the horizontal direction of the fiber preform should be much less than that in the high-permeable medium.

3.2.3 Flow Visualization of SCRIMP Mold Filling

In the SCRIMP experiments based on the high-permeable medium, the fiber preform was directly placed on the glass platform. A layer of high-permeable medium was placed under the vacuum bag and a peel ply was laid between the high-permeable medium and the upper surface of the fiber preform. The assembly is illustrated in Figure 3.6. The length of the fiber preform is 0.65 m and the width is 0.11 m. During the experiment, the vacuum pump was turned on to pull the air out of the mold. At the same time, any air leakage at the edge was checked. Then the resin was allowed to flow in from the resin container. The applied vacuum force compacted the fibers and helped the resin penetrate and wet-out the fiber preform.

Figure 3.7 shows the typical flow front patterns obtained from the experiments. Three layers of fiber mats and the Extra Heavy oil with viscosity of 325 cp at 26.0°C were used in this experiment. The flow patterns at both the bottom and the top surfaces of the fiber preform are like plug flow, which are in agreement with Darcy's law. There is a clear lead-lag distance between the top and bottom flow fronts because of the difference in the permeability of the fiber preform and the high-permeable medium. This lead-lag leads to a transverse flow in the thickness direction. Although the permeability in the high-permeable medium region is almost 50 times that in the fiber preform region, the flow front in the former is only about 6 cm ahead of that in the fiber region. It was
Figure 3.6. Experimental set-up for SCRIMP based on a high-permeable medium
Figure 3.7. Typical flow patterns obtained from Exp.2 with three layers of fiber mat and fluid of viscosity 325 cp. (a) t = 67 s, (b) t = 271 s, (c) t = 410 s, (d) t = 695 s. ↓ marks the flow front position on the top.
observed from experiments that except a slight decrease at the beginning, this lead-lag
distance remained nearly constant during the filling process.

In order to evaluate the importance of the high-permeable medium in mold filling,
two experiments were conducted, i.e. Experiments 8 and 9 in Table 3.1. In both
experiments, two-layers of fiber mats and DOP oil with viscosity of 40 cp at 25.8°C were
used. In one experiment, one layer of peel ply was stacked on the top of the fiber
preform, followed by one layer of high-permeable medium, while in the other
experiment, no peel ply and high permeable medium were used. As shown in Table 3.1,
the filling time for the experiment with the high-permeable medium is about 105 s, which
is almost 7 times less than that without the high-permeable medium (750 s). It is very
clear that the high-permeable medium is essential to SCRIMP mold filling.

The purpose of the peel ply is to separate the composite part from the high-
permeable medium and the vacuum bag, so that the composite part can be easily
demolded after it is completely cured. However, the presence of the peel ply may affect
mold filling in several ways. First, it increases the flow resistance in the
thicknessdirection, which may lengthen the mold filling time. On the other hand, the peel
ply decreases the nestling effect of the fiber preform on the high-permeable medium and
therefore increases its permeability. This may facilitate mold filling. The overall effect
depends on these two competing factors. Experiments were carried out to investigate this
effect. Three layers of fiber mats and the Extra Heavy oil were used. In one experiment, a
peel ply was laid between the high-permeable medium and the fiber preform. In another
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Table 3.1. The molding conditions and filling time of SCRIMP experiments based on a high-permeable medium.
experiment, no peel ply was used. As listed in Table 3.1, the filling time without the peel ply (i.e. Experiment 3) is longer than that with the peel ply (i.e. Experiment 2). This indicates that for one layer of peel ply, its nestling effect on the permeability of the high-permeable medium is more significant than the added flow resistance in the thickness direction.

The molding conditions and filling time of various SCRIMP experiments based on the high-permeable medium are summarized in Table 3.1.

3.3 MOLD FILLING SIMULATION

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

Mold Filling in SCRIMP is governed by the continuity equation and Darcy’s equation as follows:

\[ \nabla \cdot \bar{V} = 0 \quad (3.2) \]

\[ \bar{V} = -\frac{K}{\mu} \nabla P \quad (3.3) \]

Where \( \bar{K} \) is the permeability tensor, which is a function of space coordinates. Its local value can be the permeability in the fiber preform region or that in the high-permeable medium region. The governing equations can be solved by various numerical methods, such as CV/FEM [Young et al. 1991a, 1991b], in which the entire flow field is discretized into a number of three-node triangular elements. Each element is divided into three sub-areas by the lines connecting the centroid of the element to the midpoint of
each side. The control volume is formed based on the nodes of adjacent elements. The continuity equation is then integrated along the boundary of a control volume and a set of linear algebraic equations with the node pressure as variables are formed. The solution of the pressure field is used to calculate the velocity in each element according to Equation (3.3). For a time increment, the volume of resin flow into each flow front control volume is calculated based on the velocity field. The control volume filling status is updated and these are used to determine the flow domain for calculations in the next time step. The detailed computation procedure can be found elsewhere [Young et al. 1991a, 1991b]. In SCRIMP based on the high-permeable medium, the properties of the fabrics (i.e. the high-permeable medium, the peel ply and the fiber preform) vary a lot in the thickness direction. Hence, a 3D CV/FEM model [Young et al. 1991b] needs to be applied to simulate the flow in different regions.

The permeabilities of the high-permeable medium and the fiber preform have been measured experimentally. However, it is not easy to measure the permeability of the peel ply. The peel ply is often a thin, low porosity fabric with very low permeability. Using the previously mentioned permeability set-up, this low permeability leads to a large pressure drop, which tends to cause fiber deformation and movement during measurement. Therefore, the permeability of the peel ply was estimated by using the 3D CV/FEM to search for the best-fit value for the measured filling time and lead-lag distance from one mold filling experiment. Since the peel ply is laid between the high-permeable medium and the fiber preform, the trans-plane permeability of the peel ply.

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$K_{pz}$, plays a more important role than its in-plane permeability in mold filling. It is assumed that the in-plane permeability of the peel ply is equal to that of the fiber preform and only the trans-plane permeability needs to be fitted. Experiment 2 in Table 3.1 which used three layers of fiber mat and the Extra Heavy oil was chosen for this purpose since it provides a very distinct lead-lag distance. With the permeability of the high-permeable medium equal to 2800 darcy, the in-plane permeability of the fiber preform equal to 60 darcy and the trans-plane permeability of the fiber preform equal to 10 darcy, Figure 3.8(a) shows the experimental lead-lag distance profile and the calculated lead-lag distance profiles with different $K_{pz}$ values of the peel ply. Figure 3.8(b) shows the filling time as a function of $K_{pz}$. As can be seen, the lead-lag distance is a strong function of $K_{pz}$ while $K_{pz}$ has almost no influence on the mold filling time when it is greater than a certain value. The search gives $K_{pz}$ a value of to 0.03 darcy for this peel ply under full vacuum.

With all the parameters known, CV/FEM can then be used to predict the mold filling time under various molding conditions. It can be seen from Table 3.1 that the simulation gives a reasonable prediction of the filling time.

Mold filling in SCRIMP is a two-regional flow, i.e. flow in the high-permeable medium region and flow in the fiber preform region. It is important to understand the effect of the permeabilities of these two regions on the mold filling time. Figure 3.9(a) shows the calculated filling time using CV/FEM vs. the permeability of the high-permeable medium in the range of 60 to 10000 darcy. Figure 3.9(b) shows the calculated
Figure 3.8. (a) Lead-lag distance and (b) filling time as a function of $K_z$ of the peel ply. $K$ of high-permeable medium = 2800 darcy, $K_x = K_y$ of fiber preform = 60 darcy, $K_z$ of fiber preform = 10 darcy. □: Experiment 2 in Table 3.1
Figure 3.8 continued

![Graph showing filling time vs. Kz of the peel ply (darcy)](image)

(b)
Figure 3.9. Filling time as a function of the permeability of (a) high-permeable medium and (b) fiber preform. Thickness of fiber preform = 0.006 m, viscosity of fluid = 325 cp, $K_z$ of the peel ply = 0.03 darcy, $K_x = K_y$ of fiber preform = 60 darcy, $K_z$ of fiber preform = 10 darcy, $K$ of the high-permeable medium = 2800 darcy. □: Experiment 2 in Table 3.1
Figure 3.9 continued

(b)
filling time vs. the permeability of the fiber preform in the range of 0.5 to 100 darcy, which covers the permeability of most commercially used fiber reinforcements. In both figures, the permeability changes about two orders of magnitude. It can be clearly seen that the filling time is a strong function of the permeability of the high-permeable medium, while it is not very sensitive to the change in the permeability of the fiber preform. Figure 3.10(a) describes the velocity distribution near the flow front position calculated from 3D CV/FEM for Experiment 2. It can be seen that the velocity in the high-permeable region is hundreds to thousands times larger than that in the fiber region. Most of the resin in the fiber preform comes from the high-permeable region.

For large parts with complicated geometry, 3D CV/FEM would take too much computation time. Since the flow rate is substantially different in the high-permeable medium, the peel ply and the fiber preform, the conventional 2D CV/FEM can not be applied either. However, experimental results and the 3D CV/FEM simulation indicate that if the permeability of the fiber preform is much less than that of the high-permeable medium and the length along the flow direction is much larger than the thickness of the composite part, it can be assumed that there is no flow in the fiber preform and the peel ply in the in-plane direction. All the resin in the fiber preform is leaked from the high-permeable medium in the thickness direction. With these assumptions, a leakage flow model based on 2D CV/FEM can be developed to predict the SCRIMP mold filling of large parts with complicated geometry using a reasonable computation time.
Velocity magnitude: max: 0.002495 m/s; min: 5.51e-07 m/s

Figure 3.10. (a) Velocity distribution near the flow front calculated using CV/FEM. (thickness of fiber preform = 0.006 m, viscosity of fluid = 325 cp, K of the high-permeable medium = 2800 darcy, Kz of the peel ply = 0.03 darcy, Kx = Ky of the fiber preform = 60 darcy, Kz of the fiber preform = 10 darcy). (b) Leakage flow model for SCRIMP based on the high-permeable medium.
3.3.2 Leakage Flow Model for SCRIMP Based on a High-Permeable Medium

The assumptions stated above lead to a physical model for SCRIMP mold filling shown in Figure 3.10(b). The flow in the high-permeable medium is considered as a 2-dimensional in-plane flow with a leakage flow in the thickness direction to the fiber preform. The fiber preform and the peel ply are treated as sinks that receive the resin leaked from the high-permeable medium. The detailed procedure of 2D CV/FEM can be found elsewhere [10]. Only the modification of this method to accommodate the leakage flow is discussed here.

In the leakage flow model, the flow field of the high-permeable medium is divided into a number of three-node triangular elements. Figure 3.11 shows typical two-dimensional triangular elements and a control volume. In the conventional 2D CV/FEM [Young et al. 1991b], the following equation is written for all control volumes in the flow field:

\[
\sum_{i=1}^{m} \left[ \frac{h_x}{2A} \begin{bmatrix} n_x & n_y \end{bmatrix} \right] + \left[ I_{bc} \begin{bmatrix} n_x & n_y \end{bmatrix} \right] \begin{bmatrix} \beta_1 & \beta_2 & \beta_3 \\ \lambda_1 & \lambda_2 & \lambda_3 \end{bmatrix} \begin{bmatrix} P_1 \\ P_2 \\ P_3 \end{bmatrix} = 0
\]

(3.4)
Figure 3.11. Typical two-dimensional triangular elements and a control volume
Where $A$ is the area of an element, $h_z$ is the thickness of the high-permeable medium, $l_{ac}$ and $l_{bc}$ are the length between points $a$ and $c$, and $b$ and $c$. The definition for other variables in Equation (3.4) can be found elsewhere [Young et al. 1991]. With a leakage flow from the control volume of the high-permeable medium to the fiber preform and the peel ply, a new term is added to Equation (3.4):

$$
\sum_{i=1}^{m} \left( \frac{h_z}{2A} l_{ac} \begin{bmatrix} n_x & n_y \end{bmatrix} + l_{bc} \begin{bmatrix} n_x & n_y \end{bmatrix} \right) \begin{bmatrix} s_{xx} & s_{xy} & \beta_1 & \beta_2 & \beta_3 \\ s_{yx} & s_{yy} & \lambda_1 & \lambda_2 & \lambda_3 \end{bmatrix} \begin{bmatrix} P_1 \\ P_2 \\ P_3 \end{bmatrix} \right) + Q_{\text{leak}} = 0
$$

(3.5)

where

$$Q_{\text{leak}} = \int \frac{K_{\text{lump}} P}{\mu} \frac{dS}{L}$$

(3.6)

Where $dS$ is the surface integral of the control volume, $L$ is the total length of the flow front in the peel ply and the fiber preform and is a function of time and location, $K_{\text{lump}}$ is the lumped permeability of the peel ply and the fiber preform in the thickness direction.

To simplify the calculation, it is assumed that the average pressure in the control volume can be approximated by $P_1$. Therefore, the leakage flow from this control volume can be calculated according to the following equation:

$$Q_{\text{leak}} = \frac{K_{\text{lump}} P_1}{\mu} \frac{m}{L} \sum_{i=0}^{3} A_i$$

(3.7)
$K_{\text{jump}}$ can be derived as follows. The pressure drop in the thickness direction of the peel ply and the fiber preform consists of two parts, $\Delta P_{\text{peel}}$ in the peel ply and $\Delta P_{\text{fiber}}$ in the fiber preform:

$$P_t = \Delta P_{\text{peel}} + \Delta P_{\text{fiber}} \quad (3.8)$$

According to mass balance and Darcy's law, we have

$$u = \frac{K_p \Delta P_{\text{peel}}}{\mu L_p} = \frac{K_f \Delta P_{\text{fiber}}}{\mu L_f} \quad (3.9)$$

Where $L_p$ is the thickness of the peel ply and $L_f$ is the length of the flow front in the fiber preform. The superficial velocity $u$ can also be expressed as:

$$u = \frac{K_{\text{jump}}}{\mu \frac{P_t}{L_f + L_p}} = \frac{K_{\text{jump}} P_t}{\mu L} \quad (3.10)$$

Combining Eqs.(4.8-10), $K_{\text{jump}}$ can be solved:

$$\frac{1}{K_{\text{jump}}} = \frac{\chi}{K_p} + \frac{1 - \chi}{K_f} \quad (3.11)$$

Where

$$\chi = \frac{L_p}{L} \quad (3.12)$$
Equation (3.5) can be written for all control volumes in the flow field of the high-
permeable medium. Together with the appropriate boundary conditions, the pressure in
the flow field can be solved. Boundaries of the flow domain in mold filling include the
mold walls, inlets and flow front. At the mold walls there is no flow in the direction
normal to the wall, which means that the first derivative of pressure normal to the wall is
zero. A specified pressure is assigned to the inlet nodes (e.g. 1 atm under full vacuum).
The node pressures in the partially filled flow front control volumes are set to zero. With
these boundary conditions, the set of linear algebraic equations developed can be solved
to determine the pressure field in the high-permeable medium. The leakage flow to the
fiber preform can then be computed according to Equation (3.7). Both the leakage flow
and the flow in the high-permeable medium are regarded as quasi-steady state processes
by assuming a steady state condition at each time step. The selection of a time increment
for each quasi-steady state is based on the constraint that each time increment allows only
one control volume or a certain volume (e.g. one-fifth) of a fiber sink to be filled,
depending on which one needs less time. The new flow front position in fiber sinks can
then be updated according to the leakage flow rate and the time increment. At a given
location, the leakage flow stops when the sink is filled.

Table 3.2 shows the comparison of the filling time and CPU time for the leakage
flow model and the 3D CV/FEM model in unidirectional flow cases. The condition for
the flow simulation is the same as Experiment 2 in Table 3.1 (i.e. three layers of fiber mat
and fluid viscosity of 325 cp). The inlet is set at one end of the high-permeable medium.
Table 3.2. Comparison of the leakage flow model and the 3D CV/FEM model for SCRIMP based on a high-permeable medium.
The filling time calculated from the leakage flow model, i.e. 1087 s, is very close to that obtained from the 3D/FEM model, i.e. 1088 s, when the in-plane permeability of the fiber preform is equal to zero. This result verifies that the leakage flow model is numerically correct. Since the leakage flow model is based on the assumption that there is no flow in the in-plane direction of the fiber preform, the change of the in-plane permeability of the fiber preform does not affect the filling time calculated from this model. The 3D CV/FEM model, on the other hand, is able to reveal the effect of the fiber preform permeability on the filling time. Since the filling time changes only about 13% when the permeability of the fiber preform changes from zero to 60 darcy, the leakage flow model can still provide a reasonable estimation of the mold filling time for SCRIMP based on the high-permeable medium. The computation time needed by the leakage flow model is more than 10 times less than that by the 3D CV/FEM model in this case.

3.4 CONCLUSIONS

Mold filling is a critical step in the SCRIMP process. In this study, we investigated SCRIMP based on a high-permeable medium. Permeabilities of major processing materials, i.e. a stitched fiber reinforcement, a high-permeable medium and a peel ply, were measured under different molding conditions. Flow visualization of SCRIMP mold filling was also carried out. It was found that the high-permeable medium played an important role in determining the mold filling time. A peel ply laid between the high-permeable medium and the fiber preform can not only help demolding
but also speed up mold filling. A 3D CV/FEM model was applied to simulate the mold filling process, which elucidates the influences of the flow properties of the high-permeable medium, the fiber preform and the peel ply on the mold filling time. The simulation results indicate that mold filling time is a strong function of the permeability of the high-permeable medium, but is not sensitive to the permeability of the fiber preform. Based on the experimental observations and the 3D CV/FEM simulation, a simplified leakage flow model was developed to simulate the three-dimensional SCRIMP mold filling. In this model, the resin flows into the mold cavity through the high-permeable medium only. The fiber preform is impregnated by resin leaked from the high-permeable medium. The leakage flow model greatly reduces the computation time and yet provides a reasonable estimation of the mold filling time in SCRIMP based on a high-permeable medium.
CHAPTER 4

MOLD FILLING ANALYSIS IN SCRIMP BASED ON GROOVES

SYNOPSIS

Compared to SCRIMP based on the high-permeable medium, SCRIMP based on grooves has the advantage of a much higher mold filling rate. This chapter analyzes the influences of various molding conditions on mold filling and presents models which can be used to predict the filling time and flow pattern in SCRIMP based on grooves. Mold filling experiments were carried out to investigate the effect of various factors such as the size of the groove, groove spacing, number of fiber layers and resin viscosity on mold filling. A leakage flow model was developed to simplify the simulation of the mold filling process in SCRIMP based on grooves. An 'equivalent permeability' was introduced to represent the average flow capacity in the grooves. Compared with the Control Volume/Finite Element Method (CV/FEM) model, the leakage flow model greatly reduced computation time and yet provided simulation results that were in good agreement with experimental observations.

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4.1. Introduction

SCRIMP [W.H. Seemann, 1990, 1991] based on a high-permeable medium has been used to manufacture complicated composite parts in recent years. This method, however, has two disadvantages. First, the processing materials such as the peel ply and, in some cases, the high-permeable medium can not be reused. After demolding, they have to be disposed, which not only generates solid waste but also increases the production cost. Second, the mold filling rate is relatively low. SCRIMP based on grooves is able to overcome these two drawbacks. The grooves are cut on a low-density core. The core is part of the final product, which can reduce the weight of the composite part. Since the grooves have much higher permeability than the high-permeable medium, the mold filling rate is considerably higher than that in SCRIMP based on the high-permeable medium. In addition, neither the high-permeable medium nor the peel ply are needed in this type of SCRIMP.

The previous chapter, i.e. Chapter 3, has presented experimental and simulation results of mold filling in SCRIMP based on a high-permeable medium. This chapter focuses on SCRIMP based on grooves. The objectives are to analyze the influences of various molding conditions on mold filling and to present computationally efficient models which can be used to predict the filling time and flow pattern in the groove type of the SCRIMP process. Since SCRIMP applications are often for very large composite parts, hundreds or thousands of grooves may be involved in actual production. It is
impractical to carry out the Control Volume/Finite Element Method (CV/FEM) simulation because of the large number of meshes required. Therefore, a leakage flow model was developed to accommodate such cases. The previous model proposed by Ni [1996] could only handle very thin parts. The leakage model proposed in this study is able to handle thin parts as well as thick parts. Mold filling experiments were carried out to investigate the flow mechanism and to verify the modeling results.

4.2. Experimental

The set-up for flow visualization is the same as that used in Chapter 3, i.e. Figure 3.3. In the groove type of SCRIMP experiments, a 91.44 cm x 40.64 cm grooved acrylic plate was used as the 'core', and placed on the glass platform. One feeding channel and three groups of grooves were cut on the plate surface, as shown in Figure 4.1. The inlet channel is 12.7 mm wide and 6.3 mm deep. It is connected to the resin container and perpendicularly linked to all three groups of grooves. Each groove is 0.3175 cm wide and 40.64 cm long. The left-side and the middle groups of grooves are 0.3175 cm deep, and the right-side group of grooves are 0.635 cm deep. The groove spacing of the middle group is 5.08 cm, and that of the other two groups is 2.54 cm. The groove spacing between each group is 7.62 cm.

The outlet channel connected to the vacuum pump is 6.35 cm away from the end of the grooves. The location of the outlet affects the filling time. If the outlet channel is
Figure 4.1. Mold dimensions and groove distribution of the 13-groove SCRIMP experiment.
connected to the grooves directly, the majority of the resin will flow from the grooves to the outlet rather than flowing into the fiber preform because of the large difference in the permeability of the fiber preform and the outlet channel. It would take a much longer time for the resins to impregnate the fabrics. Therefore, the outlet should be at a distance from the grooves. For thin composite parts, the distance between the end of the grooves and the outlet should be larger than two times the spacing between the grooves. For thick composite parts, this distance is related to the composite thickness and the transverse permeability of the fabrics. Thus, the distance should be larger than that in thin composite parts.

The schematic of the assembly of the experiment is show in Figure 4.2. The plate with grooves was first placed on the glass platform. A certain number of layers of fiber mat were then stacked on the plate. Finally, the entire assembly was covered by a vacuum bag. During the experiment, the vacuum pump was turned on to pull the air out of the mold. At the same time, any air leakage at the edge was checked. Then the resin was allowed to flow in from the resin tank. The applied vacuum force compacted the fibers and helped the resin penetrate and wet-out the fiber preform. Four fluids were used in the experiment: DOP oil (viscosity 43 cp at 24.4°C), Mobil Extra Heavy oil (viscosity 320 cp at 26.2°C), Mobil BB oil (viscosity 530 cp at 23.5°C) and water. A stitched fiber mat, QM6408 from Brunswick Technologies, Inc., with effective in-plane permeability of 60 darcy, transverse permeability of 10 darcy and thickness of 0.2 cm per layer under full vacuum, was used in all experiments.
Figure 4.2. Schematic of the assembly of SCRIMP experiment.
Ten runs of the experiments, as listed in Table 4.1, were carried out with different layers of fiber mats and fluids. Figures 4.3 and 4.4 are snapshots of the resin infusion process on both the top and the bottom surfaces for one-layer and ten-layer fiber preforms respectively. As can be seen, in both cases the grooves were filled first, then the resin infused from the filled grooves into the fiber preform. For the one-layer fiber preform, the flow fronts on the top and bottom surfaces were almost identical. However, for the ten-layer fiber preform, when the bottom surface was almost filled, the top surface was still dry.

It was observed from the experiment that the fluid flowed faster in the larger grooves than in the smaller grooves. However, the grooves wider than 6 mm either would waste too much resin or tend to cause the fiber preform to cave into the grooves under the vacuum force. On the other hand, grooves smaller than 3 mm are not easy to machine. Therefore, the ideal groove size is usually between 3 ~ 6 mm.

As can be seen from Table 4.1, for the same mold geometry and the same fiber type, the filling time depends on the fiber preform thickness and the fluid viscosity. When the same fluid was used, the filling times for the one-layer fiber preform were very close to those for the two-layer fiber preform, but much shorter than those for the ten-layer fiber preform. This phenomenon is related to the flow mechanism and will be explained later. Fluids with different viscosity used in the filling process led to different filling times. Table 4.2 shows the effect of fluid viscosity on the filling time. For one- and two-
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Table 4.1. The molding conditions and the filling times of SCRIMP experiments based on grooves.
Figure 4.3. Snapshot of SCRIMP experiment at 5 seconds with one-layer fiber mat and DOP oil.
Figure 4.4. Snapshots of SCRIMP experiment at 11 seconds with 10-layer fiber mats and DOP oil.
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<td>9</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>DOP Oil</td>
<td>53</td>
<td>17</td>
<td>9</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>Mobil Oil</td>
<td>509</td>
<td>96</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>Extra Heavy</td>
<td>476</td>
<td>74</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
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<td>DOP Oil</td>
<td>53</td>
<td>18</td>
<td>6.7</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>Extra Heavy</td>
<td>351</td>
<td>75</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>BB Oil</td>
<td>492</td>
<td>101</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Extra Heavy</td>
<td>351</td>
<td>75</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>10</td>
<td>Extra Heavy</td>
<td>322</td>
<td>275</td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>BB Oil</td>
<td>492</td>
<td>630</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2. Effect of fluid viscosity on the filling times of SCRIMP experiments based on grooves.
layer fiber preforms, when the high viscosity fluids were used, the filling time was almost linearly proportional to the fluid viscosity, following Darcy’s law. However, when the low viscosity oil and water were used, the filing time was no longer linearly proportional to the fluid viscosity (i.e. Darcy’s law is not valid). Because the low viscosity fluids ran through the grooves and inlet channels at high speeds, the inertial force played an important role during the groove filling process. For ten-layer fiber preform, the filling time shown in Table 4.2 is not linearly proportional to the viscosity even at high fluid viscosity. It can be explained by the difficulty in determining the exact filling time because of the non-uniform filling pattern at the top surface, which results from the non-uniformity of the fiber preform.

Several small-scale SCRIMP experiments were also carried out with a mold of 3 grooves as illustrated in Figure 4.5(a). The gaps between grooves are 2.54 cm and 5.08 cm respectively. The cross section of the groove is 0.3175 cm x 0.3175 cm. The fiber preforms used had the same size as those used in SCRIMP based on the high-permeable medium. Therefore, the experimental results from these two methods can be compared directly. The Extra Heavy oil was used in all the experiments and the filling times as a function of the number of fiber layers and viscosity are shown in Table 4.3. Compared with SCRIMP based on the high-permeable medium, SCRIMP based on grooves needs much less time to fill the mold cavity. For example, it took only 60 seconds for the grooves to fill 3 layers of fiber mats, while for SCRIMP with the high-permeable
Figure 4.5. (a) Mold dimension and groove distribution of 3-groove SCRIMP experiment, (b) Typical meshes generated for CV/FEM simulation
<table>
<thead>
<tr>
<th>Fiber mat layers</th>
<th>Viscosity (cp)/Room Temp. (°C)</th>
<th>Filling time (s)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Leakage flow</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>337/25.5</td>
<td>27</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>268/29.0</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>351/25.0</td>
<td>60</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>328/25.9</td>
<td>75</td>
<td>64</td>
</tr>
<tr>
<td>5</td>
<td>307/27.0</td>
<td>85</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 4.3. Comparison of the filling times from the small-scale SCRIMP experiments and the leakage flow model.
medium, the filling time was 960 seconds. Considering the viscosity difference in the two experiments (i.e. 351 cp vs. 325 cp), SCRIMP based on grooves is almost 17 times faster than SCRIMP based on the high-permeable medium. This result is attributed to the difference in the permeability of different resin distribution systems, i.e. the high-permeable medium and the grooves. The average flow capacity in the groove region can be represented by an 'equivalent permeability'. $K_{eq}$, which can be calculated from the following formula [Ni et al., 1997]:

$$K_{eq} = \frac{1}{HW} \sum_{n=1,3,5,...} \left\{ \frac{8}{n\pi\beta_n^3} \left[ W - \frac{\sinh(\beta_n W)}{\beta_n} - \frac{1 - K\beta_n^2 - \sqrt{K} \beta_n \sinh(\beta_n W) - \cosh(\beta_n W)}{\beta_n \cosh(\beta_n W) - 1} \right] \right\}$$

(4.1)

where $\beta_n = \frac{n\pi}{H}$. $H$ and $W$ are the depth and width of the groove respectively. $K$ is the permeability of the fiber preform and $\alpha$ is an empirical parameter which is related to the boundary condition. With a given groove size of 0.3175 cm x 0.3175 cm, the equivalent permeability calculated according to Equation (4.1) is between 356,000 darcy and 441,000 darcy as $\alpha$ varies from 1 to 0.01. Since the permeability of the high-permeable medium is around 2800 darcy, the permeability of the groove is almost 127 times larger.

90
This explains the large difference in the filling time between two types of SCRIMP processes.

4.3. Simulation of Mold Filling

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

Mold Filling in SCRIMP is governed by the continuity equation and Darcy’s equation as follows:

\[ \nabla \cdot \vec{V} = 0 \]  \hspace{1cm} (4.2)

\[ \vec{V} = -\frac{\mathbb{K}}{\mu} \nabla P \]  \hspace{1cm} (4.3)

Where \( \mathbb{K} \) is the permeability tensor, which is a function of space coordinates. Its local value can be the fiber permeability in the preform region or the equivalent permeability in the groove region. The governing equations can be solved by various numerical methods, such as CV/FEM [Young et. al., 1991; Wang et. al., 1994]. CV/FEM requires that the entire flow field be discretized into a number of three-node triangular elements. In SCRIMP based on grooves, it means mesh inside the groove area as shown in Figure 4.5(b). Generally, the groove size is between 3 ~ 6 mm, and the distance between two grooves is ranged from 2.5 cm to 7.5 cm. For very large parts such as cargo boxes and
sailboats, this would create far too many nodes and elements to be solved by using reasonable computer memory and CPU time. It can be concluded that a simplified model is needed for such cases.

4.3.2. Leakage Flow Model for SCRIMP Based on Grooves

The leakage flow model for SCRIMP based on grooves is based on the experimental observation that the flow always fills the grooves first, and then infuses from the filled grooves to the fiber area. The basic idea is similar to that of the leakage flow model developed for SCRIMP based on the high-permeable medium. In this approach only the flow in the grooves is calculated. Since the grooves often have small cross-sections, the flow inside can be assumed as a one-dimensional flow, which can be solved using line elements. The fiber preform around the grooves is considered as sinks that receive the resin leaked from the grooves. As soon as the sink becomes full, the local leakage flow stops. The solution procedure of the leakage flow model for SCRIMP based on grooves is as follows:

1. Describe the flow in the grooves as a one-dimensional porous flow, whose equivalent permeability is obtained using the corresponding close-form solution, i.e. Equation (4.1).
2. Divide the fiber area between two neighboring grooves into blocks, as shown in Figure 4.6(a). Each block is treated as a sink, receiving the fluid diffused from the groove segments.

3. Calculate the pressure distribution in each groove and the leakage flow from the groove to the neighboring fiber sinks, by using an iteration method.

Update the flow front positions in the grooves and in the sinks at every time interval.

According to Figure 4.6(b), the mass balance in the segment of groove is:

\[ Q_{in} = Q_{out} + Q_{leak} \]  \hspace{1cm} (4.4)

\[ Q_{out}, \text{ and } Q_{in} \text{ can be expressed as follows according to Darcy's Law:} \]

\[ Q_{out} = u_{i+1,n} A_n = \frac{K_{eq}}{\mu} \frac{p_{i+1,n} - p_{i,n}}{dl} A_n \]  \hspace{1cm} (4.5)

\[ Q_{in} = u_{i,n} A_n = \frac{K_{eq}}{\mu} \frac{p_{i,n} - p_{i-1,n}}{dl} A_n \]  \hspace{1cm} (4.6)

Where \( A_n \) is the cross-section area of the nth groove. \( Q_{leak} \), the leakage flow from the grooves to the fiber area as shown in Figure 4.6(c), can be estimated according to the flow patterns in the fiber preform. Mold filling in the fiber preform consists of flows in
Figure 4.6. The schematic of the leakage flow model
the thickness direction of the fiber preform and into the spacing between grooves, as shown in Figure 4.7(a). After the resin reaches the top surface of the fiber preform, this two-dimensional flow gradually changes to a one-dimensional flow as shown in Figure 4.7(b). A lead-lag distance, \( a \), can be used as a simple criterion to estimate whether the flow is 1-D or 2-D.

The lead-lag distance is defined as the distance from the nearest uniform flow front to the edge of the groove. If this distance is small compared to the groove spacing, the majority of the flow in the fiber is one-dimensional. The flow in the fiber region, therefore, can be regarded as 1-D flow without introducing too much error. On the other hand, if the lead-lag distance is close to or greater than the groove spacing, the flow in the fiber preform is two-dimensional during most of or the entire filling process. Ni et al. [1997] derived an analytical formula to estimate the lead-lag distance:

\[
a = \frac{1 - \left( \frac{K_z}{K_x} \frac{W}{2h} \right)}{\sqrt{\frac{\pi}{2}}} + \left( 1 - \left( \frac{K_z}{K_x} \frac{W}{2h} \right)^2 + \frac{\pi}{2} \right) \left( \frac{K_z}{K_x} \frac{W}{2h} \right) + o\left( \frac{a}{h} \right)
\]  

(4.7)

Where \( h \) is the thickness of the fiber preform, \( W \) is the groove width, \( K_x \) is the permeability along the flow direction and \( K_z \) is the permeability across the thickness direction. According to this close-form solution, if the ratio of the trans-plane to the in-
Figure 4.7. Schematic of the 2-D and 1-D flow.
plane fiber preform permeability is 0.167 (i.e. $K_z=60$ darcy and $K_z=10$ darcy from previous chapter), the thickness for one-layer preform is 0.2 cm and the half width of the groove is 0.16 cm, then the lead-lag distance for the one-layer preform is calculated to be 0.6 cm and that for the ten-layer fiber preform is 6 cm. Since the groove spacing in SCRIMP is generally between 2.5 cm to 7.5 cm, the filling of the ten-layer fiber preform is always two-dimensional, while for thin fiber preforms, such as one or two-layer fiber preforms, the filling may be considered as a one-dimensional flow problem.

This also explains the experimental observation in Table 4.1 that the filling times for the one-layer fiber preform are very close to those for the two-layer fiber preform, but much shorter than those for the ten-layer fiber preform. As mentioned earlier, mold filling for SCRIMP based on grooves consists of flows in the grooves, in the thickness direction of the fiber preform and into the spacing between the grooves. For thick composite parts, flow in the thickness direction is often very slow due to the small transverse permeability of the fiber preform and thus this flow mostly controls the mold filling time. On the other hand, for thin composite parts, filling the gaps between grooves is the rate-controlling step in mold filling. In the experiments listed in Table 4.1, the groove spacing ranged from 2.5 cm to 7.6 cm. For one-layer or two-layer fiber preforms, the thickness of the fiber preform is very small. The lead-lag distances, 0.6 cm for one-layer fiber preform and 1.2 cm for two-layer fiber preform calculated from Equation (4.7), are much less than the largest groove spacing of 7.6 cm. Therefore, the mold filling time was mostly
controlled by the 1-D flow that filled those 7.6 cm gaps. This is why the thickness of the thin fiber preforms has little influence on the filling time in our experiments. For thin composite parts with very long grooves, the time for the resin to fill the grooves would probably determine the filling time.

From the above discussion, it can be concluded that if the fiber mat is very thin and the lead-lag distance is much shorter than the groove spacing, the flow in the thickness direction can be neglected and the leakage flow is simplified to a one-dimensional problem. \( Q_{\text{leak}} \) can be simply expressed as:

\[
Q_{\text{leak}} = \frac{K_x}{\mu} \frac{P_{1,n}}{d_{\text{fill}}} hdl
\] (4.8)

Where \( P_{1,n} \) is the pressure in the nth groove and ith node, \( d_{\text{fill}} \) is the distance from the filling front to the center of the groove and dl is the length of the groove segment as shown in Figure 4.6(b). In the beginning of the filling, \( d_{\text{fill}} \) is zero. In order to initiate the calculation, \( d_{\text{fill}} \) can be assigned as an arbitrary small number. It is found that the initial value of \( d_{\text{fill}} \) has little influence on the filling pattern and final filling time.

If the fiber preform is thick and the lead-lag distance is greater than or equal to the groove spacing, the leakage flow is considered as a two-dimensional problem. In this case, the flow front shape in the X-Z plane would be an ellipse with a plug flow inserted in the middle before the fluid reaches the top surface of the fiber preform or merges with
another flow front. A schematic of the flow front is shown in Figure 4.7(a) and the elliptic shape can be described by Equation (4.9) [Wang et al, 1994]

\[
\frac{x^2}{p^2} + \frac{z^2}{q^2} = 1
\]  

(4.9)

where the ratio of the two axes of the ellipse, \( \frac{q}{p} \), is equal to the square root of the ratio of the permeability components along the two principal directions, i.e. \( \sqrt{\frac{K_z}{K_x}} \). \( Q_{\text{leak}} \) can be approximated by the following equation:

\[
Q_{\text{leak}} = \sum \frac{K(\theta)}{\mu} \frac{P_{i,n}}{r(\theta)} r(\theta) d\theta dl
\]

(4.10)

Here:

\[
r(\theta) = \frac{1}{\sqrt{\sin^2 \theta / p^2 + \cos^2 \theta / q^2}}
\]

(4.11)

\[
K(\theta) = \frac{1}{\cos^2 \theta / K_x + \sin^2 \theta / K_z}
\]

(4.12)

where \( K(\theta) \) is the directional permeability [Bear, 1972] and \( \theta \) denotes the angle between the flow direction and the principle X axis as shown in Figure 4.7(a).
In the leakage flow model, after the flow front reaches the top surface, the flow component to that direction, i.e. the Z component, has to be changed to the X direction. Consequently, the fluid flows fast there and the flow front shape would gradually convert from an ellipse into a rectangle, i.e. the plug flow. The position where the plug flow starts can be calculated according to Equation (4.7). The $Q_{\text{leak}}$ is calculated according to Equation (4.10). In the leakage flow model, after the flow front reaches the top surface, the flow front is updated assuming that it moves at a speed proportional to its distance to the plug flow, i.e. $d_{i,n,k}$, as shown in Figure 4.7(c). In other words, $Q_{\text{leak}}$ is distributed along the thickness direction according to $d_{i,n,k}$.

4.3.3 Comparison of Leakage Flow Model with CV/FEM and Experimental Results

The leakage flow model is first compared with the conventional CV/FEM method using a simple case: a one-groove mold with groove spacing of 2.54 cm on both sides. Other conditions are the one-layer of fiber preform with $K_x = K_y = 60$ darcy and $K_z = 10$ darcy, and the fluid of viscosity of 270 cp. The filling patterns from CV/FEM, represented by the pressure distribution, are shown in Figure 4.8(a), and those from the leakage flow model are shown in Figure 4.8(b). The filling times calculated are 17.9 s from the CV/FEM model and 16.5 s from the leakage flow model. It can be seen that a reasonable agreement is found between the two simulation models. It took only 1 minute to run the leakage flow modeling, while the CV/FEM simulation took about 20 minutes.
Figure 4.8. Flow patterns obtained from (a) CV/FEM and (b) the leakage flow model for one groove and one layer of fiber mat.
The leakage flow model was then used to simulate the small-scale SCRIMP, and compared with the actual filling pattern taken from the experiment. For the one-layer and four-layer fiber preforms, the comparisons of the flow patterns are shown in Figures 4.9-12. A good agreement is found for the case of one-layer fiber preform. For the case of four-layer fiber preform, the prediction of the flow pattern near the bottom side (i.e. the side with grooves) is very good, while the prediction of the flow pattern near the top side agrees reasonably well with the experimental result. Due to the non-uniformity of the fiber mat, the flow patterns captured from experiments are not uniform, especially for thick fiber preforms. However, it still can be seen that the flow front positions obtained from experiment and simulation are almost the same. The simulated filling time also agrees reasonably well with the experimental data as shown in Table 4.3.

4.4 Conclusions

Mold filling in SCRIMP based on grooves is much faster than that in SCRIMP based on a high-permeable medium. Mold filling experiments showed that the resin always filled the grooves first and then infused from the grooves to the fiber preform. The mold filling time was controlled by the flows in the grooves, in the thickness direction to the fiber preform and into the spacing between the grooves. For thin composite parts with large groove spacing, the flow between the groove spacing dominated the mold filling time. For thick composite parts, flow through the thickness direction dominated the filling time. The leakage flow model was able to simulate the mold filling process in
SCRIMP based on grooves. Compared with CV/FEM, the leakage flow model greatly reduced the computation time and yet provided simulation results that were in good agreement with the experimental observation.
Figure 4.9. Flow patterns obtained from the SCRIMP experiment with 3 grooves, 1 layer of fiber mat. (a) $t = 2.0s$, (b) $t = 4.0s$, (c) $t = 7.0s$, (d) $t = 19.0s$
Figure 4.10. Flow patterns obtained from the leakage flow model with 3 grooves, 1 layer of fiber mat. (a) $t = 1.8s$, (b) $t = 3.5s$, (c) $t = 6.8s$, (d) $t = 17.8s$
Figure 4.11. Flow patterns obtained from the SCRIMP experiment with 3 grooves, 4 layers of fiber mat. (a) $t = 2.0s$, (b) $t = 6.5s$, (c) $t = 14.0s$, (d) $t = 39.0s$
Figure 4.12. Flow patterns obtained from the leakage flow model with 3 grooves, 4 layers of fiber mat. (a) $t = 1.9$s, (b) $t = 5.2$s, (c) $t = 16.8$s, (d) $t = 40.9$s
CHAPTER 5

LOW TEMPERATURE CURE OF VINYL ESTER RESINS

5.1. Introduction

VARTM processes usually require that the resins start reaction at room temperatures. Styrene containing resins, such as unsaturated polyester (UP) or vinyl ester (VE) resins coupled with room temperature curing agents, have been widely used in this type of processes. Therefore, the reaction mechanism and kinetics of unsaturated polyester or vinyl ester resins and their processability at low temperatures have attracted considerable attention from the composite industry.

Curing of styrene with unsaturated polyester or vinyl ester resins is a chain cross-linking co-polymerization of monovinyl-divinyl systems. The kinetics of the resins are normally very complex because many reactive processes occur simultaneously. Taking vinyl ester resins as an example, in the initiation stage, the initiator decomposes chemically, giving out free radicals that can react with the inhibitor, which can act as a retarder of the polymerization or as an inhibitor, reacting with all the radicals that have
formed until it is exhausted. In the propagation or polymerization stage the initiator radicals can react with the styrene or with the vinyl ester. From this moment, the chains of polymer will grow and cross each other, according to three possible reactive processes: styrene-vinyl ester co-polymerization, styrene homopolymerization, and vinyl ester homopolymerization. In the termination stage, there are multiple reactive processes, and all the free radicals in the reaction medium can recombine, thus ending the growth of chains. If the temperature is sufficiently high in the reaction medium there may be thermal decomposition of the initiator [Salla et al, 1988] which can lead to other processes of polymerization. Besides the complexity of the curing process due to the large number of reactive processes, there are other parameters that increase the complexity of the curing of vinyl ester resins, such as the phenomena of gelation and vitrification, the change from chemical kinetic control to control by diffusion in the advance of the curing, and the possibility of forming different chemical or morphological structures [Yang and Lee, 1988]. Therefore, in many cases the calorimetric curve obtained by DSC is very complex, with several exothermic peaks, corresponding to different and clearly differentiated reactive processes. In other cases, it may be impossible to distinguish reaction processes that occur simultaneously.

For chain cross-linking co-polymerizations with high concentration of divinyl monomers, the gelation starts early at 1 to 5% conversion [Yang and Lee, 1987], and most of the polymerization occurs under diffusion control. Incomplete conversion of the reactive groups is often observed when densely cross-linked networks are prepared at low
temperatures [Kloosterboer and Lippits, 1984; Moore, 1978]. The final extent of reaction
increases with temperature and so does the crosslinking density of the polymer [Moore.
1978; Kloosterboer et al. 1984]. In recent years, our lab has been carrying out extensive
studies on the reaction kinetics, microstructure formation and shrinkage control of
[1986a, 1986b] found that changing the initiator and inhibitor, the reaction profile can be
tailored to provide desirable molding characteristics. However, among the studies of the
cure kinetics of unsaturated polyester or vinyl ester resins, most of the work focused on
high temperature applications, such as compression molding of sheet molding compound
(SMC), injection molding of bulk molding compound (BMC), and resin transfer molding
(RTM). There is very little work concerning the polymerization at ambient or low
temperatures.

Low temperature polymerization has its own characteristics due to the different
curing agents used and the temperature at which the reaction occurs. A typical room
temperature curing resin contains most or all of the ingredients in Table 5.1 [Juska and
Puckett, 1997]. For example, a promoter has to be used to induce the chemical
decomposition of the peroxide at low temperatures by means of a chemical reduction
[Barton and Borsig, 1988]. Other curing agents, such as retarder, inhibitor and initiator,
are also needed to adjust the resin pot life, gel time and cycle time [Dow Chemical,
1994]. The diffusion control effect at low temperatures undoubtedly becomes more
profound. These factors would make the reaction mechanism of low temperature
<table>
<thead>
<tr>
<th>Component</th>
<th>Wt %</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomer</td>
<td>45-65</td>
<td>Determines thermal, mechanical and chemical properties of resin</td>
</tr>
<tr>
<td>Solvent</td>
<td>35-55</td>
<td>Coreactive monomer; reduces resin viscosity</td>
</tr>
<tr>
<td>Promoter</td>
<td>0.3</td>
<td>Decomposes the initiator</td>
</tr>
<tr>
<td>Copromoter</td>
<td>0.1</td>
<td>Helps decompose the initiator</td>
</tr>
<tr>
<td>Initiator</td>
<td>1.25</td>
<td>Initiates chemical reactions that cure resin</td>
</tr>
<tr>
<td>Retarder</td>
<td>0.2</td>
<td>Reduces resin exotherm and extends gel time</td>
</tr>
<tr>
<td>Inhibitor</td>
<td></td>
<td>Delays the onset of curing reactions</td>
</tr>
<tr>
<td>Thixotrope</td>
<td>1-3</td>
<td>Prevents drainage prior to gel</td>
</tr>
<tr>
<td>Wax</td>
<td>0.4</td>
<td>Prevents air inhibition, reduces VOC emission</td>
</tr>
<tr>
<td>Air release</td>
<td>0.1</td>
<td>Reduces the void content</td>
</tr>
</tbody>
</table>

Table 5.1. Ingredients in a vinyl Ester/Polyester Resin Formulation
polymerization differ from that of high temperature reaction. From both fundamental and application points of view, it would be very valuable to understand the interaction between the promoter, initiator, retarder and inhibitor and their influences on the reaction kinetics of the free radical cross-linking polymerizations at low temperatures. The work presented in this chapter is to serve this purpose. Vinyl ester resins were chosen as the resin materials. Various analytical methods such as DSC, FTIR and RDA were integrated to characterize this complicated curing process. DSC measurements were performed in both isothermal and scanning modes to reveal the effect of the concentration of various curing agents on the reaction profiles. FTIR was used to differentiate the reaction of styrene and vinyl ester C=C bonds. RDA was also employed to follow the network formation during polymerization.

Based on these experimental analyses, a cure model combining resin kinetics and heat transfer was developed to analyze the cure behavior in the SCRIMP process. Although a typical SCRIMP process is often carried out at ambient temperature, the temperature profile inside the curing parts can be quite complicated because of reaction exotherm and heat transfer to the surroundings. Resins cured in thick sections can experience an unacceptable temperature increase because the heat of reaction is generated over a short time period. The rise in temperature further accelerates the reaction rate, and the process can easily go out of control. This can lead to resin degradation to the point that it will turn yellow or brown or will even ignite. In less serious cases, the temperature increases causes excessive resin shrinkage, resulting in unacceptable print-through of
fabric and core. Sometimes fiber/matrix debonding will occur, possibly because the resin shrinks away from the fiber. This condition is known as jackstrawing or fiber glinting and is evidenced by white streaks of fiber in the cured laminate. The cure model developed in this study can be used to serve as a design and analysis tool in terms of the choice of resin material, resin distribution system, tooling material and ambient temperature, etc.

5.2. Experimental

5.2.1. Materials

Two vinyl ester resins of different styrene content were used in this study. One is the DERAKANE 411-350 resin provided by Dow Chemical, which is a mixture of 55 weight percent of epoxy based vinyl ester with an average molecular weight of 970 g/mole and 45 weight percent of styrene monomers. The mole ratio of styrene to vinyl ester C=C bonds is 3.8. The other was prepared from the DERAKANE 411-350 resin by using vacuum to remove a certain amount of styrene contained in the resin so that the vinyl ester content increased to 67% (i.e. the styrene content decreased to 33%). The mole ratio of styrene to vinyl ester C=C bonds is about 2.3 for this resin. From now on, the commercial DERAKANE 411-350 resin will be referred as 55% VE resin and the latter as 67% VE resin in this study. Additives such as inhibitors, which had been previously added to the resin system, were not removed. Cumene hydroperoxide (CHP) in a solution form (Akzo Nobel Chemical) was used as the initiator, and a solution of 6.0 wt % of cobalt naphthenate (CoNap) from Huls America was used as the promoter. 2,4-Pentanedione (industry grade) from Union Carbide was used as the retarder.
Benzoquinone (BQ) from Aldrich Chemical Company was used as the inhibitor. In this study, all descriptions of curing agent concentrations are expressed as wt % based on the vinyl ester resins. The descriptions of cobalt concentrations are expressed as wt % of the promoter solution mixed into the vinyl ester resins. The detailed composition of each run is listed under corresponding figures.

5.2.2. Instrumentation

A differential scanning calorimeter (Thermal Analyst Instruments, DSC 2910) was used to follow the overall reaction rate profiles. The reactions were conducted in volatile aluminum sample pans which may stand at least two atmosphere internal pressure after sealing. After the reactants were quickly mixed, 5-10 mg of the mixture was placed in the DSC pan. In the isothermal runs, the DSC was set at a prescribed temperature and the isothermal run was continued until no further reaction exotherm could be detected. Samples were then reheated from room temperature to 275°C in the scanning mode with a heating rate of 5°C/min to measure the residual reactivity left in the isothermally reacted samples. The total heat of reaction during cure was calculated from the areas under both isothermal and residual scanning DSC curves. DSC cure was also carried out in the scanning mode from room temperature to 275°C at heating rates varied from 1 to 4°C/min. The total heat of the reaction was also calculated from the area under the scanning curve. The difference between the values obtained from the two methods was within the experimental error and an average was taken which is 364 J/g for the 55% VE resin and 300 J/g for the 67% VE resin. The heat of polymerization has been
determined to be 67.4 kJ/mol [Tong and Kenyon, 1947] for styrene and to be 57.8 kJ/mol for methyl methacrylate [Sawada, 1991]. A simple average for the 55% VE resin used in this study would be 357 J/g and 293 J/g for the 67% VE resin, which are very close to the values obtained in this study.

An FTIR spectrometer (Nicolet, Magna-IR 550) with a resolution of 4 cm⁻¹ in the transmission mode was applied in this study to make further investigation of the reaction kinetics of styrene and vinyl ester C=C bonds. A temperature chamber was designed to control the reaction temperature isothermally. After the sample was prepared, one drop of mixture was pasted between two sodium chloride plates without any spacer, which were then mounted on the preheated sample holder located in the FTIR instrument. Four consecutive scans from 4000 to 500 cm⁻¹ were taken and averaged at each sampling time. The sampling interval varied from 2 to 4 minutes depending on the reaction rate. All IR spectra in this study were shown in absorbance, and the measurement was ended when no changes were observed in the absorbance peak area. A software, OMINIC Macros, was used to perform sampling at a specific time automatically.

FTIR is based on the peak changes of functional groups or characteristic linkages during the reaction. Figure 5.1(a) shows typical FTIR spectra of a vinyl ester resin during the reaction. There are several peaks that may change during reaction. The absorbance of the peaks at 945 cm⁻¹ and 910 cm⁻¹ indicates the change of the vinyl ester and styrene C=C bonds, respectively. Because a small background absorbance of the vinyl ester
Figure 5.1(a). FTIR spectra change during reaction (55% VE, 1.5% CHP, 0.1% CoNap, w/o 2,4-P and BQ @ 35°C)
Figure 5.1(b). FTIR spectra before and after subtraction
Figure 5.1(c). Calibration curve for FTIR [Li et al, 1998]
backbone overlapped with the absorbance at 945 cm\(^{-1}\), all spectra were subtracted by a spectrum of the completely cured sample (Figure 5.1(b)). Furthermore, to compensate for changes of thickness and opacity in the sample during curing of vinyl ester resins, the phenyl peak of styrene at 700 cm\(^{-1}\) was used as an internal standard.

The calibration curves for styrene C=C bonds and vinyl ester C=C bonds has been established by Li et al [1998] by preparing a series of vinyl ester resin solutions with different weight ratios of vinyl ester to styrene, which confirmed that both peak height and peak area followed Beer's Law (Figure 5.1(c)). In this study, all the spectra analyses are based on the changes of peak area. Therefore, the conversions of styrene vinyl and vinyl ester vinylene groups can be calculated from the change of the normalized absorbances.

\[
\alpha = 1 - \frac{\bar{A}_t}{\bar{A}_o}
\]  \hspace{1cm} (5.1)

Where \(\bar{A}_o\) and \(\bar{A}_t\) are normalized absorbances of the functional groups before the reaction and after a reaction time \(t\) respectively.

The rheological properties of the resins as a function of shear and reaction were measured using a modified Rheometrics Dynamic Analyzer (RDA) in the steady shear mode. Water bath was used in order to reduce the styrene evaporation that could otherwise become very serious because of the oven heating method. A pair of parallel plates with a diameter of 50 mm were used as the sample cell to measure the viscosity.
change during reaction. The gap between the two plates was set at 1.0 mm. To better control the evaporation, a Couette device with cup diameter of 34 mm, bob diameter and length of 32 mm was used as the sample cell to measure the initial viscosity of the resin.

5.3. Results and Discussion

5.3.1. Heating Rate Effects on Scanning Reaction Rate Profiles

The scanning cure of 55% VE resin was performed at four different heating rates: 1, 2, 3 and 4°C/min with 1.5% weight percentage of initiator and 0.3% weight percentage of promoter. In all the cases, it was observed that the reaction started right after mixing at room temperature and the reaction rate showed multiple peaks or shoulder (Figure 5.2). Under lower scanning rates, e.g. 1°C/min, the reaction profile showed one main peak, a shoulder and a long plateau. As the scanning rate increased from 2 to 4 °C/min, the reaction rate profiles changed to two main peaks and a shoulder at the high temperature end (except for the case of 2°C/min). The positions of these peaks moved little with the change of heating rate, i.e. around 60°C for the first peak, 100°C for the second peak and 140°C for the shoulder, which implies that the reaction mechanisms corresponding to those peaks remain the same. However, for the case of 1°C/min, because the shoulder appeared at a much lower temperature (i.e. 65°C), it may involve a different mechanism compared to that for the second peak (i.e. 100°C) appearing under higher heating rates. Aella et al [1985] have also noted multiple peaks in the scanning DSC of Co³⁺/MEKP-initiated styrene/unsaturated polyester resins and suggested that the first peak was due to
Figure 5.2. Reaction rate vs. temperature at different scanning rates (55% VE, CHP/CoNap=5, 1.5%CHP, w/o 2,4-P and BQ)
the copolymerization of the styrene with polyester fumarate unsaturation, while the latter was caused by styrene homo-polymerization. If a peak is related to the styrene homo-polymerization, it would reduce or even disappear with the decrease of styrene content. The scanning cure of 67% VE resin which has a lower styrene content was then carried out at all heating rates from 1 to 4°C/min. The comparison with those of the 55% VE resin is given in Figure 5.3. It can be seen that at a heating rate of 1°C/min, the shoulder disappeared as the styrene content decreased. However, for a heating rate of 2°C/min, the second peak also vanished as the styrene content decreased. On the other hand, as the heating rate increased to 4°C/min, although the strength of the second peak decreased with the decrease of the styrene content, the peak still existed and its position stayed almost the same, i.e. 100°C. This comparison does not give us conclusive evidence that the shoulder appearing under the heating rate of 1°C/min is purely caused by the homo-polymerization of styrene monomers.

From the reaction rate profiles obtained under various heating rates, one can see that the reaction kinetics of the vinyl ester resin is very complicated and there are several reaction mechanisms that may be involved in the course of reaction. As we observed, depending on the heating rate and resin composition one mechanism or the other might prevail or disappear. In VARTM processes such as SCRIMP, the reaction often starts at room temperature without external heating. The temperature rise inside the composite parts is solely due to the reaction exotherm of the resin, which is the result of not only resin reaction but also the heat transfer, thickness of the parts and the existence of resin.
Figure 5.3. Effect of resin composition on scanning reaction rate (1.5%CHP, 0.3% CoNap, w/o 2,4-P and BQ)

(a) 1°C/min 
(b) 2°C/min 
(c) 4°C/min
rich area, etc. The temperature inside the composite parts could reach as high as 200°C [Puckett]. Therefore, in order to have an overall perception of the reaction going on during the process, it is necessary to understand the reaction mechanisms involved in both the low temperature region and the high temperature region. In the following study, we will elucidate those mechanisms through the scrutiny of the effect of various curing agents such as the promoter, initiator, inhibitor and retarder on the reaction kinetics and rheology. The heating rate of 2°C/min was employed for all the scanning reactions.

5.3.2. Promoter Concentration Effects on Reaction Kinetics

Li et al [1998] studied the promoter effect on the isothermal reaction rate profiles by using DSC and FTIR. For the purpose of comparison and discussion, some experiments were repeated and more experiments were added. The results [Li et al 1998] which are related to this study are quoted. Figures 5.4 (a) and (b) illustrate the effect of varying the promoter concentration on the isothermal reaction rate and conversion profiles obtained by DSC at 35°C. The concentration of cumene hydroperoxide (CHP) was kept constant at 1.5 wt %, and the vinyl ester resin used is the commercial one with a molar ratio of styrene to vinyl ester vinylene C=C bonds of 3.8. In all the cases from 0.075 wt % to 3 wt % promoter concentration, the reaction started from the very beginning without any observable induction period. The reaction rate increased with the increase of the promoter concentration. The reaction rate profiles display two overlapped peaks at lower promoter concentrations and a large peak followed by a shoulder at higher
Figure 5.4(a). Isothermal reaction rate vs. time as a function of promoter concentration (55% VE, 1.5%CHP, w/o 2,4-P and BQ @35C)
Figure 5.4(b). Conversion vs. time as a function of promoter concentration (55% VE, 1.5%CHP, w/o 2,4-P and BQ @ 35C)
promoter concentrations. When the promoter concentration varied from 3.0% to 0.10%, i.e. the ratio of CHP to CoNap from 0.5 to 15, the final conversion remained almost the same (Figure 5.4(b)). However, if the promoter concentration is a little less than 0.10%, i.e. 0.075% (CHP/CoNap=20), the final conversion began to decrease. Further lowering the promoter concentration to 0.05% (i.e. CHP/CoNap=30), there was no reaction observed at 35°C. It can be concluded that whether the reaction occurs at this low temperature is very sensitive to the level of promoter. There exists a critical promoter concentration (between 0.05% and 0.075% in this case) to induce the decomposition of hydroperoxide through redox mechanism at room temperatures. A critical amount of promoter also exists for the reaction to reach the maximum final conversion at that temperature, i.e. 0.1% in this case. It can be seen that these two critical concentrations are very close. In the vicinity of the critical promoter concentrations, the reaction rate and conversion are very sensitive to the subtle change in the promoter concentration. Hence, it is very important to employ a promoter concentration above the critical values mentioned above, which is between 0.075% and 0.1%. On the other hand, once the promoter concentration exceeds this value, further increase of the promoter concentration does not influence very much the final conversion as well as the time to reach that conversion, although the maximum reaction rates vary a lot. In fact, at too high a promoter concentration, such as 3.0% shown in Figure 5.4, the reaction rate becomes slower than that for 1.5% promoter concentration. This observation can be explained as follows.
The dominant catalyst systems used for ambient fabrication processes based on the chain growth polymerization are metal promoters in conjunction with hydroperoxides and peroxides. The decomposition of hydroperoxides by millimolar amounts of transition-metal ions, such as $\text{Co}^{2+}$, $\text{Mn}^{2+}$, and $\text{Fe}^{2+}$, is quite rapid even at room temperatures. The products in non-reactive solvents can be rationalized by the following redox reactions [Barton and Borsig, 1988]:

\[
\text{ROOH} + M^{n+} \rightarrow \text{RO}^* + M^{(n+1)+} + \text{OH}^-
\]  \hspace{1cm} (5.2)

\[
\text{ROOH} + M^{(n+1)+} \rightarrow \text{ROO}^* + M^{n+} + \text{H}^+
\]  \hspace{1cm} (5.3)

Followed in turn by radical-chain decomposition in competition with

\[
\text{RO}^* + M^{n+} \rightarrow \text{RO}^- + M^{(n+1)+}
\]  \hspace{1cm} (5.4)

The propagating radicals may be lost in similar side reactions:

\[
P_m^* + M^{n+} \rightarrow P_m^- + M^{(n+1)+}
\]  \hspace{1cm} (5.5)

\[
P_m^* + M^{(n+1)+} \rightarrow P_m^- + M^{n+}
\]  \hspace{1cm} (5.6)

Where R-OOH and M represent the hydroperoxide and cobalt species respectively. According to Equations (5.2) and (5.3), the cobalt catalyst is never consumed since it is constantly regenerated, and therefore only a small amount, e.g. as low as 0.1% in our
system is required in resin cure. Metal ions in large excess, however, compete effectively for RO* or propagating radicals (i.e. Equation (5.4) — (5.6)). This explains why the reaction at 3.0% promoter concentration is slower than that at 1.5% promoter concentration, and relatively low concentrations of metal ions are optimal for catalyzing the decomposition of the initiator.

In order to understand the mechanisms behind this complicated rate profile, Li et al [1998] used FTIR to follow the change of the styrene and vinyl ester C=C bonds separately. They found that in the beginning, the vinyl ester C=C bonds reacted much faster than that of styrene C=C bonds. However, after most of the vinyl ester vinylene groups were consumed, the reaction rate of styrene C=C bonds remained high. This is why the total reaction rate profile showed a second peak (or a shoulder). In other words, the second peak is mainly a result of the homopolymerization of styrene. Figure 5.5(a) give the FTIR measurement of the conversion of styrene and vinyl ester C=C bonds for the case of 1.5% CHP and 0.09% CoNap at 35°C, while Figure 5.5(b) is the reaction rate calculated from the data in Figure 5.5(a). From the conversion profile, one can see that at 35°C 100% conversion of vinyl ester was reached, which shows some discrepancy with previous work [Li et al, 1998] in which 92% of vinyl ester was obtained. There are several possible reasons. First, in the previous work C-H peak at 2942 cm⁻¹ was chosen as the internal standard to normalize the interested spectra area. However, this study found that the variation of this peak was too large to be considered as an internal standard. Instead, the styrene phenyl peak at 700 cm⁻¹ was used as the internal standard [Li et al.
Figure 5.5(a) FTIR results of styrene and vinyl ester C=C bonds conversion (55% VE, 1.5%CHP, 0.09%CoNap, w/o 2,4-P and BQ @ 35C)
Figure 5.5(b). FTIR results of reaction rate of styrene and vinyl ester C=C bonds (55% VE, 1.5%CHP, 0.09%CoNap, w/o 2,4-P and BQ @35°C)
1997]. Second, spectra subtraction may introduce some error, especially at higher conversions. In this study, we found that at 35°C the final conversion of vinyl ester C=C bonds reached 100%, or at least very close to 100% in consideration of experimental error for all the cases studied by FTIR. The reaction rates of styrene and vinyl ester C=C bonds as shown in Figure 5.5(b), however, are consistent with previous observations. Both vinyl ester and styrene C=C bonds started with a non-zero initial reaction rate. For vinyl ester C=C bonds the reaction rate kept increasing, while for styrene C=C we found a short decrease followed by an increase. This indicates that the reaction of vinyl ester C=C bonds was controlled by diffusion from the very beginning of the reaction because of their relatively large molecule size. The styrene C=C bonds underwent a kinetic-control stage at the beginning of the reaction which was represented by a decay in reaction rate. The reaction of styrene C=C bonds was also soon affected by the diffusion of monomer molecules and polymeric radicals which led to another maximum in the reaction rate [Huang and Lee, 1985]. This is the so-called Tromsdorff effect that is related to the variation in $k_p$ and $k_i$ which are the propagation and termination rate constants respectively in the free radical polymerization. The appearance of the second peak is indeed due to the high reaction rate of styrene C=C bonds as can be found from Figure 5.5(b). So if we decrease the styrene content in the resin, this peak would diminish. This is confirmed by Figure 5.6 in which the styrene content reduced to 33 wt %. The reaction with 33% styrene was faster than that with 45% styrene and only one peak occurred even at low promoter concentrations. The final total conversion, however,
Figure 5.6(a). Effect of CoNap concentration on isothermal reaction rate (67% VE, 1.5%CHP, w/o 2,4-P and BQ @35C)
Figure 5.6(b). Effect of CoNap concentration on isothermal conversion profile (67% VE, 1.5%CHP, w/o 2,4-P and BQ @ 35C)
remained almost the same. The small inflection in the reaction rate at low promoter concentration was probably due to the inhibition of the polymerization by dissolved trace oxygen. The 67% VE is so viscous that the oxygen trapped inside during the mixing of initiator and promoter with the resin is very difficult to get out. Figure 5.7(a) shows the reaction rate of styrene C=C bonds and vinyl ester C=C bonds vs. time measured by FTIR at 35°C for 67% VE. As we can see, different from that at high styrene content (Figure 5.5), the reaction of styrene stopped shortly after the vinyl ester C=C bonds were consumed. The peaks of the reaction rate for vinyl ester and styrene C=C bonds appeared almost at the same time instead of far apart as illustrated in Figure 5.5(b). All these experimental results support the speculation that the second peak in the isothermal cure is due to the homo-polymerization of styrene monomers. It is worth pointing out that from this result we might be able to say that the shoulder appearing at the low heating rate of 1°C/min for 55% VE resin probably can also be attributed to the styrene homo-polymerization. It is because low heating rate scanning may generate reaction rate profiles similar to the isothermal reaction.

The reaction of the vinyl ester resin is a co-polymerization between styrene and vinyl ester vinylene groups. The structure formation of the copolymer depends on the relative reaction rates of styrene vinyl to vinyl ester vinylene groups. Li et al. [1998] plotted the relative conversion of styrene C=C bonds vs. vinyl ester C=C bonds measured by FTIR at 35°C with three weight ratios of promoter to initiator, 1/3, 1/5, 1/10. They found that three curves merged nicely into a single master curve, which indicates that the
Figure 5.7(a). FTIR results of reaction rate of styrene and vinyl ester C=C bonds (67% VE, 1.5%CHP, 0.15% CoNap, w/o 2,4-P and BQ @35C)
Figure 5.7(b). Styrene \( \text{C=C} \) conversion vs. vinyl ester \( \text{C=C} \) conversion at different styrene content (w/o 2,4-P and BQ at 35°C)
promoter concentration does not change the reaction mechanism, therefore not affect the structure formation of the copolymer during polymerization. However, if the content of divinyl or monovinyl monomers changes, the structure of the formed polymer is different. Figure 5.7(b) shows that the conversion of styrene C=C bonds vs. vinyl ester C=C bonds curves with different monomer content don't seem to form a master curve. The two dashed lines shown in the figure represent two extreme cases: the upper one is under azeotropic condition and the lower one stands for the alternating co-polymerization. The actual reaction profile lies between these two extremes. As can be seen from this figure, in the beginning the curve is nearly linear and two lines for different styrene contents fall on the same line. The average number of styrene C=C bonds consumed for each vinyl ester C=C bond is about 1.5 for 55% VE, while for 67% VE it is about 1, which means the latter has a higher cross-linking density. At a vinyl ester conversion of about 35%, the two lines started to diverge. The styrene in the lower styrene content system, i.e. 67% VE, reacted more than that in the higher styrene content system, i.e. 55% VE. However, at the later stage after almost of the vinyl ester C=C bonds were consumed, styrene in both systems continued to react and reached almost the same final conversion. But apparently 67% VE had much less styrene homopolymerization than 55% VE.

Figure 5.8 shows the effect of promoter concentration on the scanning reaction rate profile with 1.5 wt.% of initiator. It was observed that without any promoter, the reaction did not start until at a temperature around 110°C under the current heating rate
Figure 5.8. Scanning reaction rate vs. temperature as a function of promoter concentration (55% VE, 1.5% CHP, w/o 2.4-P and BQ, 2C/min)
(2°C/min), where the reaction was apparently kicked off by the thermal initiation of cumene hydroperoxide. With the presence of a trace of promoter, e.g. 0.025%, one could observe the little movement of the reaction peak to a lower temperature. Further increasing the promoter concentration to 0.05% and 0.075%, the temperature where the reaction started became significantly lower, 58°C and 37°C respectively. This is consistent with the isothermal results that with a promoter concentration of 0.05%, no reaction could occur at 35°C, while with 0.075% promoter concentration, the reaction did occur at 35°C, although the final conversion was a little lower. The scanning reaction rate profiles all displayed a single peak at these low promoter concentrations. However, further increasing the promoter content from 0.075% to 0.1% and above, the reaction was induced right away at room temperatures and the reaction rate profile changed from one peak to two peaks. The second peak appeared at the temperature where the one peak at low promoter concentration originally took place, while the first peak emerged at a lower temperature as the concentration of the promoter increased. The single peaks we observed for 0.05% and 0.075% cases probably are the overlap of the two peaks. Obviously, the first peak is closely related to the room temperature initiation resulted from the decomposition of cumene hydroperoxide through redox mechanism participated by the cobalt promoter, since the peak position was very sensitive to the level of promoter. The second peak was most likely caused by the thermal initiation of the hydroperoxide.
When the content of promoter is not high enough, it cannot intrigue the redox initiation of cumene hydroperoxide at room temperatures. However, from Figure 5.8 we can see that its presence seems to have one of the following two effects: (1) The redox reaction still occurs but at a higher temperature; (2) it catalyzes the thermal initiation of hydroperoxide somehow. The fact that the position of the thermal initiation peak moved little with the further increase of promoter concentration from 0.1% to 0.75% implies that the catalytic effect of the promoter on the thermal initiation of the hydroperoxide was already saturated. Therefore further increase of the promoter concentration would not influence the thermal initiation any more.

Figure 5.9 plots the reaction rate vs. temperature for 67% VE as a function of promoter concentration. As can be seen, only one peak is observed which started from the very beginning of the reaction, while there was no peak but a plateau showing in the high temperature range where the thermal initiation supposed to occur. Considering the isothermal results which also showed one peak, one can reason that since the 67% VE contains more reactive vinyl ester C=C bonds and fewer less reactive styrene C=C bonds, most of the C=C bonds from both styrene and vinyl ester have been consumed in the reaction induced through the redox mechanism. Therefore, there are very few C=C bonds left for the reaction induced by thermal initiation. Hence, only a plateau appeared in the higher temperature region.
Figure 5.9. Effect of CoNap concentration on scanning reaction rate
(67% VE, 1.5% CHP, w/o 2,4-P and BQ @ 2C/min)
5.3.3. Effects of Initiator Concentration on Reaction Kinetics

Figures 5.10 and 5.11 show the effect of the initiator concentration on both the reaction rate and conversion profiles for a promoter concentration of 0.3% and 0.5% respectively at 35°C. From the figures one can see that when the initiator concentration was high enough, the final conversion, which is around 75%, was not a function of either promoter or initiator concentration. In the case of a higher promoter concentration, i.e. 0.5% in Figure 5.11(b), the concentration of the initiator hardly affected the time to reach the final conversion. However, at a lower promoter concentration, i.e. 0.3% in Figure 5.10(b), the time to reach the final conversion did become more sensitive to the change in initiator concentration. In these two cases, lowering the initiator concentration below a certain value, both the reaction rate and the final conversion significantly decreased. The reaction became very slow and stopped at very low final conversion. It can be concluded that like the promoter, there also exists a critical initiator concentration in order for the reaction to reach the maximum conversion at that temperature. Based on earlier discussion, we know that this conclusion is valid under the condition that the promoter concentration is above the critical level. Nevertheless, the reason for the existence of a critical value may be different for promoter and initiator. For promoters, a critical amount of promoter is needed because the activation energy of the redox decomposition of initiator should be lowered enough so that the reaction can proceed at room temperatures. The termination and trap of the free radicals during polymerization is the reason for the
Figure 5.10(a). Isothermal reaction rate profiles as a function of initiator concentration (55% VE, 0.3% CoNap, w/o 2,4-P and BQ @ 35°C)
Figure 5.10(b). Isothermal conversion profiles as a function of initiator concentration (55% VE, 0.3% CoNap, w/o 2,4-P and BQ @ 35C)
Figure 5.11(a). Isothermal reaction rate profiles as a function of initiator concentration (55% VE, 0.5% CoNap, w/o 2,4-P and BQ @ 35°C)
Figure 5.11(b). Isothermal reaction rate profiles as a function of initiator concentration (55% VE, 0.5% CoNap, w/o 2,4-P and BQ @ 35°C)
need of a critical amount of initiators that be maintained in the system so that they can incessantly generate free radicals to ensure the progress of the reaction.

The reaction rate vs. temperature as a function of initiator concentration is given in Figure 5.12. In all the cases, the promoter concentration was fixed at 0.5% weight percent, while the initiator concentration varied from 0% to 2.9%. It is found that without initiator, there was also a reaction starting at about 150°C. An experiment which used pure resin without promoter and initiator was carried out at the same heating rate. The comparison of these two cases is shown in Figure 5.13. It can be seen that there were reactions going on at high temperatures with or without promoter. Although the peaks for the two cases were not exactly at the same position, they were very close, which implies that they involved the same reaction mechanism. The thermal (self-initiated) polymerization of styrene at high temperature is well known [Billmeyer, 1971]. It is very likely that the reaction in this high temperature range is due to the thermal polymerization of the vinyl ester and styrene C=C bonds at elevated temperatures, since there is no curing agent present in the resin system. The initiation of the reaction is presumably due to thermal decomposition of the monomer to form radicals. Compared with Figure 5.8, one can see that the reaction rate of thermal polymerization was much smaller than that of polymerization in the presence of an initiator. The fact that the presence of promoter actually inhibited the reaction is mostly because of the redox reaction between an organic radical and the salt of the transition metal ion as shown in Equations (5.5) and (5.6).
Figure 5.12. Scanning reaction rate vs. temperature as a function of initiator concentration (55% VE, 0.5%CoNap, w/o 2,4-P and BQ @ 2°C/min)
Figure 5.13. Effect of CoNap on scanning reaction rate profiles (w/o 2,4-P and BQ @ 2C/min)
When a small amount of initiator, i.e. 0.1 ~ 0.2% weight percent, was added to the resin system with 0.5% cobalt promoter, a bell-shaped reaction rate profile appeared starting from the room temperature. In contrast to the promoter for which a critical concentration has to be reached to kick off the reaction at room temperatures, the concentration of the initiator is not important here. As long as there is initiator, there is reaction at room temperature. In all the cases presented in Figure 5.12, the concentration of the promoter is 0.5% weight percent, which is well above the critical value to intrigue the reaction as long as there is initiator present in the system. However, one can see that although a small amount of initiator can start the reaction at room temperature, the reaction rate was not high and the reaction stopped after a while even further increasing the temperature. This is because the free radicals generated by redox initiation underwent termination reaction or became trapped during the polymerization and the small amount of initiator had already been consumed during the redox cycle, which is consistent with the observation from the isothermal reaction. There was no initiator left for generating more free radicals through either redox initiation or thermal-initiated initiation mechanism. The remaining reactants could only undergo self-initiated thermal polymerization at higher temperatures. Nevertheless, the thermal polymerization could start at lower temperatures as the initiator concentration increased. For example, the kick-off temperature for the case of 0.1% initiator was around 140°C and for 0.2% was 100°C, which was much lower compared to 150°C in the case of no initiator. This seems to suggest that the formed products had a catalytic effect on the thermal polymerization.
Further increasing the initiator concentration, one can see that the reaction started to progress through the whole temperature range. The reaction rate profile displayed two peaks at lower temperatures and a small shoulder at high temperatures. Based on our earlier discussion, we know that the second peak around 100°C resulted from the thermal initiation of initiator. Therefore, the shoulder around 130°C can be attributed to the thermal polymerization, which is also supported by the fact that the position of the peak is at the temperature where the thermal polymerization occurred in the case of 0.2% of initiator. The reason that the thermal polymerization peaks became less and less is because there was more and more reaction proceeding at lower temperatures by redox or thermal initiation as the initiator concentration increased. Hence, there are fewer double bonds left for thermal polymerization. Also, because of the overlap between the thermal-initiation initiated polymerization and thermal polymerization, the thermal polymerization appears as a shoulder in the reaction rate profile. Further increasing the initiator concentration, the redox decomposition of initiator became much faster. More and more double bonds were reacted in the lower temperature range. Therefore, there were fewer or even no double bonds left for thermal-initiation initiated polymerization or thermal polymerization. Consequently, only two peaks are observed at higher initiator concentrations and the peak for thermal-initiation initiated polymerization became a shoulder. Figure 5.14 shows the effect of initiator concentration on the scanning reaction rate profile of 67% VE resin. Only one peak occurs at high initiator concentrations. The decrease of initiator concentration resulted in the appearance of two peaks and a shoulder.
Figure 5.14. Effect of CHP concentration of scanning reaction rate (67% VE, 0.5% CoNap, w/o 2,4-P and BQ @ 2C/min)
at higher temperatures with the same peak or shoulder position as in the case of 55% VE resin. Since the resin compositions were different, the fact that the peak positions are the same provides more support for our earlier discussion that the presence of these peaks must be closely related to the curing agents, i.e. the initiation mechanisms.

Several researchers have also reported multiple peaks observed in the scanning cure of unsaturated polyester resins and vinyl ester resins [Lem and Han, 1984; Avella et al. 1985; Salla et al. 1988; Cook et al, 1997]. However, the reaction mechanisms they proposed are not in agreement with each other. As mentioned earlier, Avella et al [1985] noticed the multiple peaks in the scanning DSC of Co²⁺/MEKP-initiated styrene/unsaturated polyester resins and suggested that the first peak was due to the copolymerization of the styrene and the polyester fumarate unsaturation, while the latter was caused by styrene homo-polymerization. On the other hand, Salla et al [1988] attributed the lower temperature peak to polymerization initiated by the redox mechanism and the second, higher temperature peak to the polymerization initiated by the uncatalyzed decomposition of initiator. A similar interpretation was also made by Lem and Han [1984] in studies on vinyl ester resins and polyester resins. All their statements have recently been challenged by Cook et al [1997] who claimed that their data were not consistent with the reaction scheme proposed by previous authors. Cook et al further argued that multiple exothermic peaks have also been reported in isothermal studies of the peroxide-initiated polymerization of styrene/MMA and in some photochemical homo-polymerizations, even though only one initiation system is present. Without any further
analysis, they therefore attributed the multiple peaks of the reaction rate to the complex variation in rate constants such as $k_p$ and $k_t$. The experimental results and analysis from our study have unified the above viewpoints in the sense that all these reasons are possible depending on the situation. In other words, they don't exclude each other. Based on our study of the effect of the promoter and initiator on both scanning and isothermal reaction kinetics using DSC and FTIR, the reaction mechanisms that may be involved in the actual SCRIMP process, which often covers a wide temperature range, can be summarized as follows. Multiple exothermic peaks occur in both isothermal and scanning cure of the vinyl ester resins, which may be attributed to the competition between the vinyl ester and styrene co-polymerization and the styrene homo-polymerization, or different initiation mechanisms. The initiation mechanisms that may be involved during the course of reaction of vinyl ester resins are: redox decomposition of initiator at low temperatures, thermal decomposition of initiator at middle temperatures and self-initiation of monomers at high temperatures which leads to the thermal polymerization. Depending on the rate of temperature change, the resin composition, the concentration of initiator and promoter, some of the mechanisms may dominate and others may not participate. Initiation mechanisms that dominate at certain temperatures could significantly speed up the reaction at that temperature, and therefore the reaction rate may show the maximum there. The FTIR results suggest that with a high initial molar ratio of styrene to vinyl ester C=C bonds, there is significant homo-polymerization of styrene or grafting reaction of styrene along vinyl ester chains at later stage, which leads to the second peak (or shoulder) on the isothermal reaction rate profiles. The second peak at
slow scanning rate may also be attributed to the same reason. There exist critical promoter concentrations in order to intrigue the reaction at room temperatures and to reach the maximum final conversion at that temperature. However, there is also an upper limit where the catalytic effect of the promoter becomes saturated. With the promoter concentration above the critical value, any amount of initiator can induce the polymerization at room temperatures, but the reaction rate and the final conversion may be low. There also exists a critical initiator concentration for the resin to reach the maximum final conversion at that temperature. The reason for the need of minimum promoter and initiator amount, however, is different.

5.3.4. Effects of Benzoquinone (BQ) Concentration on Reaction Kinetics

Inhibitors and retarders are of remarkable practical importance, especially in regulating the spontaneous processes of monomer polymerization in storage or of polymerizable compounds in the reaction mixtures. Retardation and inhibition are generally chemical processes in which retardation or complete suppression of the chain reaction of radical polymerization occurs. The general difference between inhibition and retardation is therefore only in the intensity of the effect. A low concentration of an inhibitor sometimes only acts as a retarder and sometimes we observe the inhibition effect of the compound on the polymerization of a specific type of monomer while it has only a retardation effect on other monomers. Figure 5.15 shows typical time-conversion curves for various inhibiting and retarding effects.
Figure 5.15. Typical time-conversion curves for various inhibiting and retarding effects.

1. Normal polymerization without inhibitor; 2. Typical retardation; 3. Ideal inhibition;
4. Non-ideal inhibition; and 5. Ideal inhibition followed by typical retardation.
The chemistry and technology of inhibition of unsaturated polyester (UP) resins have been reviewed by Novak [1988]. Quinones, hydroquinones, phenolics and some amines are effective polymerization inhibitors. Quinones and catechols used at levels generally less than 500ppm function as inhibitors by inactivating free radicals that are slowly generated at the unsaturated sites in the resin or monomer, and so preventing the initiation of crosslinking reactions that build molecular weight resulting in gelation. Styrene is normally inhibited with 25 ppm p-tertbutyl catechol to provide storage stability. Although extensive literature can be found for the inhibition of unsaturated polyester resins [Novak, 1988; Ramis and Salla, 1995], there is few work on the inhibition of vinyl ester resins initiated with redox system. In the present work, we have studied the influence of BQ as an inhibitor on the vinyl ester resin cure catalyzed by Co^{2+}/CHP. The inhibitors that had been added to the resin (proprietary to Dow Chemical) were not removed.

Figure 5.16 shows the effect of BQ on the isothermal cure of vinyl ester resin at 35°C. As can be seen, BQ is not an ideal inhibitor for the vinyl ester resin initiated by CHP/CoNap. Unlike in the case of UP resin where less than 500 ppm BQ often provides considerable induction time, there was no inhibition period observed for this vinyl ester resin even at very high BQ concentration, e.g. 2800 ppm. The BQ retarded the rate of polymerization at the beginning of the reaction, rather than controlled its onset. With the presence of BQ, the initial part of the reaction showed a clear trend of exponential decay, which became more profound with the increase of BQ concentration. However, once the
Figure S. 16(a). Effect of BQ on reaction rate profile
(55% VE, CHP/CoNap=5, 1.5%CHP, w/o 2,4-P @35C)
Figure 5.16(b). Effect of BQ on conversion profile
(55% VE, CHP/CoNap=5, 1.5%CHP, w/o 2,4-P @35C)
exponential decay period was over, the rest of the reaction showed a profile very similar to that without BQ. There is a jump in the reaction rate at the point where the exponential decay is over. The position, the height and the width of the peak changed a little bit, but the time to reach the final conversion remained almost the same even when the BQ concentration increased up to 1000 ppm. In other words, the presence of BQ only reduces the initial part of the reaction but not the overall reaction when its concentration is below a certain value. However, further increasing the BQ concentration to 1500 ppm, the overall reaction became slower and the curing time was extended. Up to this point, the presence of BQ still had no effect on the final conversion, which can be seen from Figure 5.16(b). Further increasing the BQ concentration to 2800 ppm, however, only the exponential decay occurred and the final conversion is only about 10%. The scanning of the isothermally cured sample, i.e. Figure 5.17, revealed that the remaining reaction was the thermal polymerization above 150°C. There was no polymerization induced by thermal initiation around 100°C. This apparently indicates that no initiator was left after the isothermal cure. All the initiators were consumed during the exponential decay period. This is obviously the reason why no reaction could be induced thereafter in the isothermal mode and only low conversion could be achieved.

In order to understand if the initial reaction exotherm is caused by C=C bonds reaction or by the reaction between the inhibitor and primary radicals, FTIR was again used to look into the details of the reaction. Figures 5.18(a) shows the reaction rate of vinyl ester and styrene C=C bonds measured by FTIR for a BQ concentration of 1500
Figure 5.17. Residual reaction rate @5C/min for sample cured at 35C (55% VE, CHP/CoNap=5, 1.5%CHP, 2800ppm BQ, w/o 2,4-P)
Figure 5.18(a). Reaction rate of vinyl ester and styrene C=C bonds measured by FTIR as a function of time (55% VE, CHP/CoNap=5, 1.5%CHP, 1500 ppm BQ, w/o 2,4-P @35°C)
Figure 5.18(b). Comparison of reaction rate measured by DSC and FTIR (55% VE, 1.5% CHP, 0.3% CoNap, 1500 ppm BQ, w/o 2,4-P @35°C)
ppm and Figure 5.18(b) shows the comparison of DSC and FTIR measurements. As can be seen from the figures, the initial reaction exotherm indeed resulted from the C=C bonds reaction. Compared to Figure 5.5 where no BQ was present, one can find the different reaction patterns for the two cases. With BQ the initial reaction rate for vinyl ester C=C bonds was zero, while without BQ it was higher than that of styrene C=C bonds as can be seen from Figure 5.5. However, for styrene C=C bonds, very different phenomenon was observed. With BQ, the styrene C=C bonds had an initial reaction rate in the same order as that without BQ, and so was the rest of the reaction for styrene C=C bonds. It seems that BQ is very effective to inhibit the reaction of vinyl ester C=C bonds, but not that of the styrene C=C bonds. Because of this reason, the two peaks for styrene and vinyl ester C=C bonds moved closer and the overall reaction showed only one peak. Figure 5.19 compares the conversion of styrene C=C bonds vs. that of vinyl ester with and without BQ. It can be seen that they don't form a master curve. At the same vinyl ester conversion, the styrene conversion with BQ was always higher than that without BQ. This indicates that the cross-linking density or network structure may have been changed because of the presence of BQ. For the resin with low styrene content, almost the same reaction profiles were observed (Figure 5.20).

In general, in a reaction system with the presence of inhibitor, the inhibitor and the reactive species in the reaction medium will compete for the primary radicals from the initiator. If the reaction rate between the inhibitor and the primary radicals is much faster than that between the monomers and the primary or propagating radicals, there is
Figure 5.19. Styrene C=C conversion vs. vinyl ester C=C conversion with and without BQ (w/o 2,4-P at 35°C)
Figure 5.20. Effect of BQ concentration on isothermal reaction rate (67% VE, 1.5%CHP, 0.3%CoNap, w/o 2,4-P @35°C)
complete inhibition up to a very low concentration of inhibitor, and the initiation and propagation of the polymerization are completely arrested. That is when we observe the induction or inhibition period. Our experimental results stated above apparently do not belong to this case. Instead, the following reaction mechanism may be proposed to explain the phenomena we observed. At the beginning of the reaction, because of the rate to generate free radical through the redox initiation mechanism is so fast that it can compete with the reaction between BQ and free radical. Therefore, some of the free radicals survive and the chain growth process can still continue even when there is still considerable amount of BQ in the resin system. However, because part of the radicals are terminated by BQ, the concentration of free radicals decreases and so does the reaction rate. That is why we saw the exponential decay of the initial reaction rate. The more the BQ was added, the longer the decay became. Once the BQ is consumed, the rest of initiators still can be decomposed to generate free radicals through the redox reaction with the promoter, and the rest of the reaction should be the same as that without BQ. However, if too much BQ is added, all of the initiator can be consumed before the BQ is depleted. Therefore, no further reaction can be observed.

Figure 5.21 shows the scanning reaction rate vs. temperature for different BQ concentrations. In all the experiments, the ratio of initiator and promoter remains at a constant of 3 and the initiator content is 1.5% by weight. Compared to Figures 5.8 and 5.12, the reaction rate profiles in Figure 5.21 are more complicated. There is no induction period in all the cases, even at high BQ concentration. The presence of BQ results in a
Figure 5.21(a). Effect of BQ concentration on scanning reaction rate profiles (55% VE, CHP/CoNap=3, 1.5%CHP, w/o 2,4-P at 2C/min)
Figure 5.21(b). Effect of BQ concentration on conversion profile (55% VE, CHP/CoNap=3, 1.5% CHP, w/o 2,4-P at 2C/min)
decrease in the initial reaction rates, which is demonstrated by a transition point before the first peak appears. In all the cases with the presence of BQ, the reaction rate profiles show three peaks in the temperature range studied. The first peak decreased with the increase of the BQ concentration, and so was the second peak. The third peak showed the opposite trend, that is, it increased with the increase of the BQ concentration. Although the relative strength of the peaks changed with the change of the BQ concentration, the peak positions remained nearly constant. In order to unravel the factors that determine the positions of these peaks, another set of experiments in which the initiator concentration was kept the same, i.e. 1.5%CHP, while the ratio of CHP and CoNap was changed to 15, were performed (Figure 5.22). It can be seen that only two peaks emerged. The position of the third peak remained the same. The first and the second peaks merged together, but they appeared around 80°C where the second peak originally positioned. As discussed earlier, the second peak is closely related to the thermal decomposition of initiators and the third peak is the thermal polymerization of the vinyl ester resin. The fact that their positions remained relatively constant at a constant initiator concentration might indicate that they were determined by the initial concentration of the initiator in the system. The position of the first peak, however, was closely related to the concentration of promoter. These observations are consistent with the mechanisms we proposed for these peaks.

Comparing Figure 5.12 and 5.21, one can find that although the main function of BQ is to consume the primary radicals generated by initiators, reducing the level of initiator is not equivalent to increasing the concentration of BQ, even only considering
Figure 5.22. Effect of BQ concentration on scanning reaction rate (55% VE, CHP/CoNap=15, 1.5%CHP, w/o 2,4-P @ 2C/min)
the reaction rate profiles after the transition point mentioned earlier. The shapes of the rate profiles are quite different. With BQ, the thermal polymerization at high temperatures became a distinct part of the overall reaction, which is not the case for low initiator concentrations without BQ. The effect of inhibitor on reaction kinetics can be very complicated. Some studies [Novak, 1988] have shown how the type and amount of inhibitor can modify the reactivity of the resin, the temperature of the mould, the color, the mechanical properties of the cured material and the degree of conversion. The study of the hydrolysis of cured polyester resins and research into styrene-fumaric acid copolymerization have shown that the length of the cross-linking styrene chains between polyester chains is a function of the inhibitor [Novak, 1984]. As mentioned earlier, our study also found that the cross-linking density or network structure may have been changed because of the presence of BQ.

5.3.5. Effect of 2,4-Pentandione (2,4-P) Concentration on Reaction Kinetics and Rheological Changes

The use of 2,4-Pentandione (2,4-P) in the cure of vinyl ester resin has three purposes: a) extend pot life; b) prolong gel times; and c) reduce or eliminate fiber prominence which is often known as "glints", "jackstraws", or "chicken tracking" due to the incompatibility between the fiber glass and the resins. It is reported [Dow Chemical, 1989] that 2,4-P can be incorporated into systems of MEKP, CHP and CoNap at a level of 0.05 to 0.30 to retard the gelling of DERAKANE resins. However, the gel time will not be delayed by addition of 2,4-P when a vinyl ester cure is catalyzed with BPO using
DMA as an accelerator. Also, in many polyester systems, 2,4-P may act as an accelerator. The study on the mechanism of 2,4-P on the reaction kinetics of vinyl ester resin has not been found in the literature. In this study, we focus on the effect of 2,4-P on the reaction kinetics and rheological changes of the DERAKENE 411-350 resin catalyzed with CHP using CoNap as a promoter.

5.3.5.1 Reaction Kinetics

Figures 5.23 and 5.24 show the effect of 2,4-P concentration on the reaction rate and conversion profiles of the commercial vinyl ester resin. From both figures, it can be clearly seen that 2,4-P is a very effective agent to reduce the reaction rate. In Figure 5.23, the promoter concentration is 0.5%. With 0.10% of 2,4-P, the time to reach the final conversion changed from about 100 minutes (for the case without 2,4-P) to 350 minutes and the time to reach 10% conversion was extended from 10 minutes to 25 minutes. But the final conversion stayed almost the same for all the concentrations of 2,4-P studied. However, if the concentration of the promoter is lower, e.g. 0.3% as shown in Figure 5.24, 2,4-P decreased the final conversion at a concentration of 0.1%. Therefore, the effect of 2,4-P is very much dependent on the levels of promoter used.

Although no literature has been found on the interaction between 2,4-P, CoNap and CHP, there are studies carried out on the catalyzed decomposition of hydroperoxides under the influence of transition metal chelates [Hiatt et al., 1968; Kochi, 1962; Barton and Horanska, 1972]. The first step in the catalyzed decomposition is the formation of a complex, consisting of hydroperoxide and the transition metal compounds [Richardson,
Figure 5.23(a). Effect of 2,4-P on reaction rate profile (55% VE, CHP/CoNap=3, 1.5%CHP, w/o BQ @35C)
Figure 5.23(b). Effect of 2,4-P on conversion profile
(55% VE, CHP/CoNap=3, 1.5%CHP, w/o BQ @35C)
Figure 5.24(a). Effect of 2,4-P on reaction rate profile (55% VE, CHP/CoNap=5, 1.5%CHP, w/o BQ @35C)
Figure 5.24(b). Effect of 2,4-P on conversion profile
(55% VE, CHP/CoNap=5, 1.5%CHP, w/o BQ @35C)
1965]. For this reason, the addition of complex forming substances to reaction systems in which simple salts of metals play the role of catalysts of hydroperoxide decomposition may significantly affect the course of hydroperoxide decomposition. Chelating agents can affect the catalytic activity by hindering or preventing the formation of a metal-hydroperoxide complex by blocking the sites of attack and by altering the redox potential of the metal atoms so that its catalytic activity is much impaired [Sheldon and Kochi. 1973]. Sheldon and Kochi found that the reactivity of metal ions is appreciably influenced by the existence of chelate and its type, i.e. a chelating agent may suppress, activate or have no effect on the reactions.

In our reaction system, 2,4-P also functions as a chelating agent. Based on the studies reviewed above, the possible interaction between 2,4-P, CoNap and CHP may be explained as follows. As shown in Figure 5.25, vacant orbitals on cobalt ions can accommodate electron pairs on the oxygen atoms of 2,4-P, and thus form complex. The formed complex or chelate may have decreased, enhanced or no catalytic effect on the decomposition of hydroperoxides, depending on whether the structure of the complex still allows interaction with hydroperoxide. On the other hand, because of the formation of Co$^{2+}$ chelates, the concentration of free Co$^{2+}$ decreases, which would lead to a decrease in catalytic activity of the cobalt ions in the decomposition of hydroperoxides.

Comparing Figures 5.4 and 5.23, it can be found that both a slight decrease in promoter concentration and a slight increase in 2,4-P concentration resulted in significant decrease in reaction rate. In other words, the reaction rate is very sensitive to the level of
Figure 5.25 Schematic of cobalt ions and 2,4-Pentanedione
both promoter and 2,4-P. However, the shape of the reaction rate profile is different. when comparing low promoter concentrations with high 2,4-P concentrations. First of all, with 2,4-P, the exponential decay is more profound. Secondly, the second peak is lower than the first peak at high 2,4-P concentrations, while the situation is vice versa for low promoter concentrations where the second peak is even higher than the first peak. These experimental observations indicate that the role of 2,4-P is not simply reducing the concentration of free cobalt ions.

Using FTIR, we studied how the styrene C=C bonds and vinyl ester C=C bonds react differently in the cases with and without 2,4-P. Figure 5.26 shows the comparison of the reaction rate of VE and styrene C=C bonds with and without 2,4-P. It can be seen that the presence of 0.03% 2,4-P reduced the reaction rate of both VE and styrene C=C bonds significantly. The reaction rate for both styrene and vinyl ester C=C bonds decreased initially, reached a minimum point and then increased again. However, in the case of no 2,4-P, the reaction rate for vinyl ester C=C bonds reached an initial value and then kept increasing, while that for styrene showed a similar trend as in the case with 2.4-P. In addition, the distance between two peaks increased in the presence of 2,4-P. Further comparing Figure 5.26 with Figure 5.5(b), it can be seen that the reaction rate of styrene did not vary much as reducing promoter or adding 2,4-P, but that of vinyl ester C=C bonds did change a lot. In other words, the effect of 2,4-P on vinyl ester C=C bonds is different from that on styrene C=C bonds. This may affect the polymer structure formation. Figure 5.27 plots styrene C=C bonds conversion vs. vinyl ester C=C bonds conversion for these two cases. It can be seen that they don’t form a single master curve.
Figure 5.26. Comparison of reaction rate of VE and styrene C=C bonds with and without 2,4-P (55% VE, 1.5% CHP, 0.3% CoNap @ 35°C)
Figure 5.27. Styrene C=C conversion vs. vinyl ester C=C conversion at 35°C with and without 2,4-P (w/o BQ @ 35°C)
The deviation became larger at higher conversions. Therefore, the function of 2.4-P is not simply forming a complex with cobalt ions to reduce the concentration of free cobalt ions. It also changed the reaction mechanisms in some unknown way.

Figure 5.28 shows the scanning reaction rate profiles as a function of 2.4-P concentration. It can be seen that in all the cases the reaction rate showed two peaks. As we discussed earlier, the first peak is associated with the redox decomposition of the initiator, which decreased with the increase of 2,4-P concentration. The second peak, which is due to the thermal initiation of the initiator, increased as the 2,4-P level increased. The reaction in the whole temperature range changed from redox-decomposition dominated initiation reaction to thermal-initiation dominated initiation reaction. These changes are expected in consideration of the fact that 2,4-P formed a complex with the cobalt ions and reduced the promoter concentration. At low 2,4-P concentrations, all the reaction started at room temperatures. The reaction rate decreased as the 2,4-P concentration increased. At a high 2,4-P concentration such as 0.3%, no reaction was observed until 42°C. Further increasing 2,4-P concentration to 0.5%, both the reaction onset temperature and peak position changed little. It seems that the effect of 2,4-P has saturated. It can be explained by the fact that 2,4-P has almost scavenged all the free cobalt ions, therefore further increase in the 2,4-P concentration has little effect. Nevertheless, with the increase of temperature, the reaction rate still showed two peaks. It is interesting to note that at low 2,4-P concentrations (i.e. < 0.06%) the first peak reduced its peak height very dramatically with the increase of 2,4-P concentration, but its position
Figure 5.28. Effect of 2,4-P concentration on scanning reaction rate profile (55% VE, CHP/CoNap=3, 1.5%CHP, w/o BQ @ 2C/min)
hardly moved. At high 2,4-P concentrations, however, the first peak moved to the higher
temperature and its peak height increased with the decrease of 2,4-P concentration. This
phenomenon is different from what we observed as the promoter concentration changed
(Figure 5.8). This further indicates that the presence of 2,4-P has complicated influences
on the curing kinetics. The reaction of forming 2,4-P chelates is an equilibrium reaction
which may favor the dissociation of the complex to release the cobalt ions at high
temperatures, so that the free cobalt ions can again participate in the redox decomposition
of hydroperoxide. On the other hand, the chelate may also have a catalytic effect on the
decomposition of hydroperoxide at higher temperatures. We could not draw a conclusion
from our current experimental results. Further investigation by means of UV or ESR may
help to elucidate the detailed mechanism of retardation caused by 2,4-P.

It is worthwhile to summarize the difference in the mechanisms that 2,4-P and BQ
influence the reaction of vinyl ester resins catalyzed by CHP/CoNap. BQ reduces the
reaction rate by consuming the free radicals generated through whatever mechanisms.
2,4-P decreases the reaction rate by chelating the promoter ions and therefore reducing
the rate to generate free radicals. Too much BQ would deplete all the free radicals and
hence result in little reaction even at elevated temperatures (below thermal
polymerization temperature). 2,4-P, on the other hand, does not interact with free radicals
but promoters. It would still allow the redox or thermal decomposition of the initiator at
elevated temperatures. even if its concentration is high. Figure C.1 in appendix C is an
example to show the different mechanisms of 2,4-P and BQ in the reaction.
5.3.5.2 Rheological Changes

During the free radical chain-growth co-polymerization of vinyl ester and styrene monomers, the cross-linking reaction causes resin gelation through network formation. The resin is usually a viscous liquid before the reaction, but as the reaction progresses, it becomes more viscous. This increase in viscosity is caused by the formation of macromolecules. The reacting system finally forms a macro-network because of the cross-linkings on the multi-unsaturation points of the vinyl ester molecules, which leads to an infinite viscosity.

Understanding of viscosity changes during curing is very important for process control in mold filling of the SCRIMP process. Mold filling analyses which have been presented in Chapters 3 and 4 used non-reactive fluids as the model materials whose viscosity does not change with time. In real production, however, the viscosity increases due to the chemical reaction of the resin may result in incomplete mold filling, especially in making large parts which is often the case for SCRIMP application. It is a critical step to select the right type and amount of curing agents such as initiator, promoter, inhibitor and retarder in order to adjust the gel time of the resin according to the size of the part and processing conditions. In practice, 2,4-P is normally used as a main tool to adjust the gel time. In this study, we investigated how 2,4-P influences the gel time and gel conversion of the vinyl ester resin. Since we also observed the retardation effect of BQ on the reaction kinetics, its effect on the viscosity change will also be presented for the purpose of comparison.
Figure 5.29 plots the viscosity vs. shear rate for the pure DERAKANE 411-350 resin without any curing agent at 23.2°C. It can be seen that the viscosity of the resin is dependent on shear rate at low shear rates. But at high shear rates, the viscosity is nearly a constant. Since the viscosity of unthixed resin is independent of shear rate [Juska and Puckett, 1997], this resin may contain some thixotropes. During reactive processing, shear has major implications on the structure formation as well as the rheogical changes of unsaturated polyester resins [Muzumdar and Lee, 1996]. For example, Muzumdar and Lee [1996] found that increasing the shear rate delays the onset of the viscosity rise. Therefore, this study first checked the effect of the shear rate on the viscosity change of the vinyl ester resin during reaction, which is shown in Figure 5.30(a). The same phenomenon was observed, i.e. the viscosity rise was again shear-rate dependent, but less sensitive compared to the unsaturated polyester resin (Figure 5.30(b)). According to Muzumdar and Lee [1996], the reason that the viscosity rise is shear-rate dependent is because the shear rate affects the chance for the adjacent microgels to be linked together by a chemical bond to form a secondary polymer. Since for vinyl esters the unsaturation is limited to two sites at the end of each molecule and the equivalent molecular weight/(mole C=C) is often larger than that of unsaturated polyesters, microgel phenomenon may not be as profound as in the unsaturated polyester case. Therefore, the viscosity rise is less shear-rate dependent. In order to correlate with DSC results, a shear rate of 0.1s⁻¹ was used in all steady shear experiments. Gel time was assumed to occur when the viscosity reached 2500 Pa.s, or the reduced viscosity (=viscosity/initial viscosity) reached 5000.
Figure 5.29. Effect of shear rate on viscosity change of vinyl ester resin (55% VE, w/o any curing agent, @ 23.2°C)
Figure 5.30(a). Effect of shear rate on viscosity change during reaction (55% VE, 1.5%CHP, 0.5% CoNap, 0.05%24-P, w/o BQ @35C)
Figure 5.30(b). Effect of shear rate on the viscosity profile for UP resin at 80°C [Muzumdar and Lee, 1996]
Figure 5.31 illustrates the effect of varying 2,4-P concentration on the viscosity rise of 55% VE resin at 35°C. According to the gelation criteria (i.e. 2500 Pa.s viscosity), the gel time and gel conversion as a function of 2,4-P concentration are plotted in Figure 5.32. It is found that the gel conversion varied very slightly, i.e. from 9.6% to 11.7% as the 2.4-P concentration changed from 0% to 0.1%. Since the change is little, we can not rule out the possible experimental error. The gel time, on the other hand, increased significantly from 10 minutes to 35 minutes as the 2,4-P concentration changed from 0% to 0.1%. Therefore, 2.4-P is a very effective gel time retarder.

As we discussed earlier, the presence of BQ also retards the initial reaction, but not the overall reaction if the concentration of BQ is within a certain range. Therefore BQ may also be a good tool to adjust the gel time and yet keep the cycle time short. Figures 5.33(a) and 5.33(b) show the viscosity rise and reaction kinetics of the vinyl ester resin as a function of BQ concentration at 35°C. Figure 5.34 summarizes the corresponding gel time and gel conversion. It can be clearly seen that BQ at low concentrations hardly influenced the gel time. At higher concentrations, it prolonged the gel time, but not as effectively as 2.4-P.

Although the control of gelation is very important in mold filling, the cycle time and final conversion which may change with the gel time are two parameters that also deserve much attention, since they are closely related to the productivity of the process and the properties of the final products. Table 5.2 compares the effect of 2,4-P and BQ on peak time (related to cycle time), final conversion and gel time. It can be seen that within
Figure 5.31(a). Viscosity change vs. time as a function of 2,4-P concentration (55% VE, CHP/CoNap=3, 1.5% CHP, w/o 2,4-P @ 35C, 0.1 s⁻¹)
Figure 5.31(b). Enlarged view of 5.31(a) at low viscosity
Figure 5.32. Gel time and conversion as a function of 2,4-P concentration (55% VE, CHP/CoNap=3, 1.5% CHP, w/o BQ @ 35°C, 0.1s⁻¹)
Figure 5.33(a). Viscosity change vs. time as a function of BQ concentration (55% VE, 1.5% CHP, 0.5% CoNap, w/o 2,4-P @ 35°C, 0.1s⁻¹)
Figure 5.33(b). Reaction rate and conversion vs. time as a function of BQ concentration (55% VE, 1.5% CHP, 0.5% CoNap, w/o 2,4-P @35C)
Figure 5.34. Gel time and conversion as a function of BQ concentration (55% VE, 1.5% CHP, 0.5% CoNap, w/o 2,4-P at 35C)
Table 5.2 Effect of 2,4-P and BQ on peak time, final conversion and gel time

<table>
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<th>Concentration (wt %)</th>
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<tbody>
<tr>
<td></td>
<td>2,4-P</td>
<td>BQ</td>
<td>2,4-P</td>
<td>BQ</td>
</tr>
<tr>
<td>Peak time (min)</td>
<td>25</td>
<td>32</td>
<td>N/A</td>
<td>48</td>
</tr>
<tr>
<td>Final conversion</td>
<td>0.78</td>
<td>0.75</td>
<td>N/A</td>
<td>0.73</td>
</tr>
<tr>
<td>Gel time (min)</td>
<td>10.7</td>
<td>16.1</td>
<td>N/A</td>
<td>25.1</td>
</tr>
</tbody>
</table>

the concentration range studied, the presence of 2,4-P only slightly decreased the final conversion but dramatically increased the peak time and the time to reach the final conversion. BQ, on the other hand, almost did not change the final conversion as well as the peak time. It did not increase the gel time very effectively either. Therefore, from the viewpoint of adjusting gelation time for better process control, 2,4-P is a better choice than BQ. The disadvantage is that the cycle time may also be significantly longer.
5.4 SCRIMP Molding and Curing Simulation

5.4.1 Molding Experiment

Two groove based SCRIMP mold curing experiments were conducted at room temperature with 1.5 weight percent of CHP and 1/5 Co²⁺/CHP. The experimental set-up is shown in Figure 5.35. The upper 'mold' was a layer of thin plastic film, i.e. a vacuum bag, while the lower 'mold' was a 1.0 cm thick composite plate (a molded SMC plate). Under the vacuum bag was a 7.62 cm thick foam core with precut grooves, which served as runners to bring the vinyl ester resin into the mold. The reinforcement materials, glass fiber mats (QM6408), were placed between the composite mold and the foam core. The resin was first stored in a container, then pulled into the mold via the grooves under the vacuum force. The groove size and the thickness of the fiber preform are two important design variables. In this study, two different cases were investigated to show these effects on the temperature profiles inside the mold during curing of the vinyl ester resin.

In case 1, the groove size was 0.3175 cm x 0.3175 cm, and the groove spacing was 2.54 cm. Three layers of glass fiber mats were used as the fiber preform. Three thermocouples, which are shown in Figure 5.35, were placed at the surface of each layer of the fiber mat to follow the temperature change in the thickness direction during curing. The fourth thermocouple, T₄, was placed at the same thickness as T₂ but in the middle of two grooves to investigate the effect of groove on the temperature distribution. Case 2
Figure 5.35. Experimental set-up for SCRIMP mold curing
involved a larger groove size, 0.635 cm x 0.635 cm, larger groove spacing, i.e. 3.81 cm, and five layers of glass fiber mats. Here, the three thermocouples were placed at the surface of fiber layers 1, 3, and 5 from top.

The experimental result, i.e. Figure 5.36, showed that the curing reaction occurred in the very beginning of molding, and the temperature inside the mold increased because of reaction exotherm. After a certain time (about 1 hour), most of the reaction has completed and the temperature started to decrease. Comparing these two cases, one can find that the temperature in case 2 of larger groove size and thicker fiber mats reached as high as 90°C, while that in case 1 was about 70°C. The temperature difference from location to location in case 2 was also larger than that in case 1. It can be seen that the highest temperature $T_5$ was always in the resin rich area, i.e. grooves. Although $T_2$ and $T_4$ are at the same thickness, $T_2$ was higher than $T_4$ due to the effect of grooves.

5.4.2 Cure Simulation

Figure 5.37 shows the schematic of the cure simulation. Cure simulation necessitates the establishment of a kinetic model for the resin material and heat transfer model for the whole system. With appropriate numerical methods, the cure profile can then be obtained by solving these two models.

5.4.2.1 Kinetic Model

For a very complicated reaction system like vinyl ester resins cured under redox type initiation, a phenomenological modeling approach may be used to generate a kinetic
Figure 5.36. Measured temperature distribution in SCRIMP
Figure 5.37. Schematic of cure simulation
model that can describe the major behavior of the reaction system and is yet simple enough to be used in cure simulation. Li et al [1998] employed this approach to set up a kinetic model for the vinyl ester resin with the consideration of redox reaction between the promoter and initiator. This kinetic model was used in this study without further incorporation of the effects of retarder and inhibitor because their reaction mechanisms still have not been fully understood and the reaction kinetics are too complicated.

For a redox type of initiation, the initiator can be decomposed rapidly by the promoter at low temperatures as shown in Equations 5.2 and 5.3. For cobalt promoters, these equations can be specifically written as Equations 5.7 and 5.8:

\[
\begin{align*}
\text{ROOH} + \text{Co}^{2+} & \xrightarrow{k_d1} \text{RO}^* + \text{OH}^- + \text{Co}^{3+} \\
\text{ROOH} + \text{Co}^{3+} & \xrightarrow{k_d2} \text{ROO}^* + \text{H}^+ + \text{Co}^{2+}
\end{align*}
\]

Where ROOH is the initiator, Co\(^{2+}\) is the promoter and ROO\(^*\) and RO\(^*\) are free radicals. Hiatt et al [1968] showed that, for the redox type of initiation, the decomposition rate of initiator is proportional to the initiator concentration and the square root of the promoter concentration, i.e.

\[
\frac{dI_i}{dt} = -k_d I_p^{1/2} I_i
\]

Where \(I_i\) is the initiator concentration, \(k_d\) is the decomposition rate constant of the initiator, and \(I_p\) is the promoter concentration. Single decomposition rate constant \(k_d\)
replaces $k_{d1}$ and $k_{d2}$ because of the similarity of these two equations. $I_p$ is assumed constant due to the regeneration function shown in Equation 5.8.

The actual reaction mechanism of styrene-vinyl ester system may be complicated. Like styrene-unsaturated polyester resin system [Huang and Lee, 1985], it can be assumed that the reaction follows the typical free radical co-polymerization, which is expressed as follows:

**Initiation:**

\[
ROO^\cdot(RO^\cdot) + M_1 \xrightarrow{k_{i1}} M_1^\cdot
\]

\[
ROO^\cdot(RO^\cdot) + M_2 \xrightarrow{k_{i2}} M_2^\cdot
\]

**Propagation:**

\[
M_1^\cdot + M_1 \xrightarrow{k_{p11}} M_1^\cdot
\]

\[
M_1^\cdot + M_2 \xrightarrow{k_{p12}} M_2^\cdot
\]

\[
M_2^\cdot + M_1 \xrightarrow{k_{p21}} M_1^\cdot
\]

\[
M_2^\cdot + M_2 \xrightarrow{k_{p22}} M_2^\cdot
\]

**Termination:**

\[
M_n^\cdot + M_m^\cdot \xrightarrow{k_t} P_{n+m}
\]

Where $M_1$ represents the styrene vinyl group; $M_2$ represents vinyl ester vinylene group; $M_1^\cdot$ is a radical ended with styrene; $M_2^\cdot$ is a radical ended with vinyl ester; $P$ is a dead polymer chain; $k_p$'s, $k_t$ are rate constants of propagation and termination respectively. It can be assumed that the reactivity of all vinylene groups on vinyl ester chains is
independent of the length of polymer chain during polymerization and \( k_{p11}, k_{p12}, k_{p21} \) and \( k_{p22} \) can be replaced by \( k_p \) and \( k_{p2} \) where \( k_p \) stands for the propagation reaction rate constant of a styrene vinyl group to a growing polymeric radical, while \( k_{p2} \) denotes that of a vinylene unit in a vinyl ester chain to a growing polymeric radical [Huang and Lee. 1990]. Therefore, the propagation reaction rates of styrene vinyl, vinyl ester vinylene groups and the total reaction rate can be written as

\[
\text{Styrene vinyl: } \frac{dM_1}{dt} = -k_{p11}M_1^*M_1 - k_{p21}M_2^*M_1 = -k_pM^*M_1 \tag{5.17}
\]

\[
\text{Vinyl ester vinylene: } \frac{dM_2}{dt} = -k_{p12}M_1^*M_2 - k_{p22}M_2^*M_2 = -k_pM^*M_2 \tag{5.18}
\]

\[
\text{Overall reaction rate: } R_p = \frac{d(M_1 + M_2)}{dt} = \frac{dM}{dt} = -k_pM^*M_1 - k_{p2}M^*M_2 \tag{5.19}
\]

where

\[
M^* = M_1^* + M_2^*, \quad M = M_1 + M_2, \quad k_p = \frac{k_{p11}M_1^* + k_{p21}M_2^*}{M^*}, \quad k_{p2} = \frac{k_{p12}M_1^* + k_{p22}M_2^*}{M^*}
\]

Equation 5.19 can also be rewritten as

\[
\frac{d\alpha}{dt} = \frac{M_{10}}{M_{10} + M_{20}} \frac{d\alpha_1}{dt} + \frac{M_{20}}{M_{10} + M_{20}} \frac{d\alpha_2}{dt} \tag{5.20}
\]

where

\[
\alpha = \left[ (M_{10} + M_{20})V_0 - (M_1 + M_2)V \right] \left[ (M_{10} + M_{20})V_0 \right]
\]
\[ \alpha_1 = \frac{(M_{10}V_0 - M_1V)}{(M_{10}V_0)} \]

\[ \alpha_2 = \frac{(M_{20}V_0 - M_2V)}{(M_{20}V_0)} \]

Where \( V \) is the system volume, \( \alpha_1 \) is the styrene conversion and \( \alpha_2 \) is the vinyl ester vinylene conversion.

For cross-linked reaction systems, the reaction kinetics would be affected by chain diffusion. Therefore, the apparent propagation rate resistance, \( 1/k_{p1} \) and \( 1/k_{p2} \), for styrene vinyl and vinyl ester vinylene groups, and the apparent termination rate resistance, \( 1/k_t \), can be all expressed as a combination of two terms: a kinetic resistance and a diffusion resistance [Huang and Lee, 1985], i.e.

\[
\frac{1}{k_{p1}} = \frac{1}{k_{p01}} + \frac{A_{1}M^{*}}{D_{M_1}} 
\]

(5.21)

\[
\frac{1}{k_{p2}} = \frac{1}{k_{p02}} + \frac{A_{2}M^{*}}{D_{M_2}} 
\]

(5.22)

\[
\frac{1}{k_t} = \frac{1}{k_{t0}} + \frac{A_{t}M^{*}}{D_{t}} 
\]

(5.23)

Based on the Bueche's free volume theory, the diffusion coefficient, \( D_t \), can be expressed as a function of the free volume fraction \( V_f \):

\[
D_{M_1} = A_{M_1} \exp(-B_{M_1} / V_f) 
\]

(5.24)

\[
D_{M_2} = A_{M_2} \exp(-B_{M_2} / V_f) 
\]

(5.25)
\[ D_i = A_p \exp(-B_i / V_f) \] (5.26)

So Equations 5.21-23 can be written as:

\[
\frac{1}{k_{p1}} = \frac{1}{k_{p01}} + M^* A_{M_i} \exp\left(\frac{B_{M_i}}{V_f}\right) \] (5.27)

\[
\frac{1}{k_{p2}} = \frac{1}{k_{p02}} + M^* A_{M_i} \exp\left(\frac{B_{M_i}}{V_f}\right) \] (5.28)

\[
\frac{1}{k_i} = \frac{1}{k_{i0}} + M^* A_i \exp\left(\frac{B_i}{V_f}\right) \] (5.29)

Neglecting the volume contraction effect of the system, \( V_f \) is given as [Soh and Sundberg, 1982; Bueche, 1962]:

\[ V_f = [V_{f_p} + \lambda \beta_p (T - T_{gp})] \alpha + [V_{f_m} + \beta_M (T - T_{gm})](1 - \alpha) \]

\[ \lambda = 1.0 \quad \text{for} \quad T \geq T_{gp} \]

\[ \lambda = 0.3 \quad \text{for} \quad T < T_{gp} \]

Applying the quasi-steady-state assumption of free radicals leads to the following equation:

\[ M^* = \left( \frac{f_k d I_n I_p^{1/2}}{k_i} \right)^{1/2} \] (5.30)

With some manipulation of above equations, the final form of the kinetic model is listed as follows [Li et al, 1998]:

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Styrene vinyls:

\[
\frac{d\alpha_1}{dt} = \frac{1 - \alpha_1}{1 + \left(\frac{\alpha_2}{\pi_3}\right)^2 + \frac{\alpha_2}{\pi_3} + \pi_4}
\] (5.31)

Vinyl ester vinylenes:

\[
\frac{d\alpha_2}{dt} = \frac{1 - \alpha_2}{1 + \left(\frac{\alpha_2}{\pi_3}\right)^2 + \frac{\alpha_2}{\pi_3} + \pi_4}
\] (5.32)

Where

\[
\pi_1 = \frac{f k_d \overline{I_p} I_p^{1/2} k_{p01}^2 \exp(\int_0^\infty - k_d I_p^{1/2} dt)}{k_{t0}}
\] (5.33)

(kinetic effect on propagation and termination of styrene)

\[
\pi_1' = \frac{f k_d \overline{I_p} I_p^{1/2} k_{p02}^2 \exp(\int_0^\infty - k_d I_p^{1/2} dt)}{k_{t0}}
\] (5.34)

(kinetic effect on propagation and termination of vinyl ester)

\[
\pi_2 = \pi_2' = \frac{A_1}{F} \exp( B_1 / V_c)
\] (5.35)

(diffusion effect on termination)

\[
\pi_3 = \frac{1}{2} f \overline{I_0} k_{p01} F k_d I_p^{1/2} \exp(\int_0^\infty - k_d I_p^{1/2} dt)
\] (5.36)

(kinetic effect on propagation of styrene)
\[ \pi_3' = \frac{1}{2} f I_{01} k_{p_{02}} F k_d l_p^{1.2} \exp(\int_{t_1}^{t} -k_d l_p^{1.2} dt) \]  
(5.37)  
(kinetic effect on propagation of vinyl ester)

\[ \pi_4 = A_{M_1} \exp(B_{M_1}/V_f) \]  
(5.38)  
(diffusion effect on styrene propagation)

\[ \pi_4' = A_{M_2} \exp(B_{M_2}/V_f) \]  
(5.39)  
(diffusion effect on vinyl ester propagation)

F is a parameter defined as [Huang and Lee, 1985]:

\[ F = \frac{k_d A_1 \exp(B_1/V_f)}{(1-\alpha) \exp(k_d l_p^{1.2} (t - t_z)) - 1} \]  
(5.40)

Li et al [1998] used this kinetic model to fit the DSC and FTIR data to get the model parameters for DERAKANE 411-350 resin with CoNap as promoter and CHP as initiator but without 2,4-P and additional inhibitor. The parameters are shown in Table 5.3.

5.4.2.2 Heat Transfer Model

In SCRIMP, resin curing occurs at room temperature. Hence, the only heat source is the reaction exotherm of the reactive, room-temperature curable resins. The foam core and the composite mold used in this study are both low thermal-conductivity materials.
\[
\begin{align*}
kd\left(\frac{1}{(s \cdot \text{mol/l})^{1/2}}\right) &= 1.89 \times 10^6 \exp(-49246.54/RT) \\
T_{sp} &= 373.33 \text{K} \\
T_{pm} &= 216.07 \text{K} \\
\beta_p &= 0.00027 \\
\beta_m &= 0.00056 \\
\lambda &= 1 \\
\epsilon &= 0 \\
B_t &= 5.32 \\
A_t / F(s) &= \exp\left(a + b \cdot \ln\left(1 / V_f\right) + c \cdot \left(\ln\left(1 / V_f\right)\right)^2\right) \\
\end{align*}
\]

where

\[
\begin{align*}
a &= -14434.26 + 84.70 \cdot T - 0.13 \cdot T^2 \\
b &= 9100.31 - 53.08 \cdot T + 0.079 \cdot T^2 \\
c &= -1427.32 + 8.17 \cdot T - 0.012 \cdot T^2 \\
\end{align*}
\]


<table>
<thead>
<tr>
<th>Styrene Vinyl</th>
<th>Vinyl Ester Vinylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f(\omega)k_d k_{p01}^2 / k_{i0}$</td>
<td>$f(\omega)k_d k_{p02}^2 / k_{i0}$</td>
</tr>
<tr>
<td>$= 7731.17 \exp\left(-\frac{74317.55}{RT}\right)$</td>
<td>$= 700.58 \exp\left(-\frac{55227.68}{RT}\right)$</td>
</tr>
<tr>
<td>$\frac{1}{2} f(\omega)k_{p01} F = 8.92 \times 10^{-30} \exp\left(\frac{181129.74}{RT}\right)$</td>
<td>$\frac{1}{2} f(\omega)k_{p02} F = 1.43 \times 10^{-47} \exp\left(\frac{280224.18}{RT}\right)$</td>
</tr>
<tr>
<td>$B_{M1} = 0.36$</td>
<td>$B_{M2} = 0.45$</td>
</tr>
<tr>
<td>$A_{M1} = 4.63 \times 10^7 \exp\left(-\frac{56314.878}{RT}\right)$</td>
<td>$A_{M2} = 1.00 \times 10^7 \exp\left(-\frac{56787.30}{RT}\right)$</td>
</tr>
</tbody>
</table>

Table 5.3. Numerical Values of Kinetic Parameters for Styrene-Vinyl Ester Reactions [Li et al, 1998]
Therefore, the reaction heat would accumulate in the mold and a high internal temperature can be reached, which would in turn accelerate the reaction and produce more heat. Figure 5.36 shows that the highest temperature was reached in the resin rich area, i.e. grooves. In the thickness direction, the lowest temperature was observed at the rigid mold surface. Non-isothermal temperature distribution may result in a non-uniform curing pattern. In other words, the material near the bottom surface tends to react later than that at other locations. This may affect physical properties, such as surface quality, of the cured parts.

In practical SCRIMP molding, it often takes a long time, minutes to hours, to fill the mold. To prevent premature gelling, excess amount of retarders and inhibitors are often added to the resin. Consequently, resin reaction may be neglected in the filling stage. Although no external retarder or inhibitor was used in this study, a very small mold that only needs several seconds to fill was chosen. Therefore, it is reasonable to assume that no significant reaction would occur during mold filling. In the curing stage, which starts after the mold has been filled, only the cure reaction and heat transfer need to be considered. Heat transfer occurs in the grooves, the fiber preform, the foam core and the mold wall. Since these areas have different thermal properties, separate governing equations are needed to describe the heat transfer in each area. Because of the very low thermal conductivity of the foam core (i.e. 0.002 J/m-s-°C), it can be treated as a perfect insulator during curing. Because the grooves in the foam core are repetitive, it is not necessary to simulate the whole part. Only a portion of it (i.e. Figure 5.38) needs to be
Figure 5.38 Coordinate and geometry used in cure simulation

simulated. The basic equations of heat transfer and the boundary and initial conditions are written as follows:

Rigid Mold:

\[
\rho_m C_{pm} \frac{\partial T_m}{\partial t} = k_m \left( \frac{\partial^2 T_m}{\partial x^2} + \frac{\partial^2 T_m}{\partial y^2} \right) \tag{5.41}
\]

I. C. \quad T_m = T_{air} \quad \text{at } t=0
B. C.

\[ \frac{\partial T_m}{\partial x} = 0 \quad \text{at } x = 0 \]

\[ \frac{\partial T_m}{\partial x} = 0 \quad \text{at } x = L_1 \]

\[ T_m = T_f \quad \text{at } y_m = 0 \]

\[ -k_m \frac{\partial T_m}{\partial y} = h(T_m - T_{\text{air}}) \quad \text{at } y_m = L_3 \]

**Fiber Preform:**

\[ \rho C_p \frac{\partial T_f}{\partial t} = k \left( \frac{\partial^2 T_f}{\partial x^2} + \frac{\partial^2 T_f}{\partial y^2} \right) + H_{R_f} \frac{\partial \alpha}{\partial t} \quad (5.42) \]

I. C. \( T_f = T_{\text{air}} \) \quad \text{at } t=0

B. C.

\[ \frac{\partial T_f}{\partial x} = 0 \quad \text{at } x = 0 \]

\[ \frac{\partial T_f}{\partial x} = 0 \quad \text{at } x = L_1 \]

\[ -k_f \frac{\partial T_f}{\partial y} = -k_m \frac{\partial T_m}{\partial y} \quad \text{at } y_f = H \]

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\[ T_f = T_r \quad \text{at } y_f = 0 \text{ and } 0 \leq x \leq L_2 \]

\[-k \frac{\partial T_r}{\partial y} = 0 \quad \text{at } y_r = 0 \text{ and } x > L_2 \]

**Groove:**

\[ \rho_r C_{pr} \frac{\partial T_r}{\partial t} = k_r \left( \frac{\partial^2 T_r}{\partial x^2} + \frac{\partial^2 T_r}{\partial y^2} \right) + H_{Rr} \frac{\partial \alpha}{\partial t} \quad (5.43) \]

**I. C.**

\[ T_r = T_{air} \quad \text{at } t=0 \]

**B. C.**

\[ \frac{\partial T_r}{\partial x} = 0 \quad \text{at } x = 0 \]

\[-k_r \frac{\partial T_r}{\partial x} = 0 \quad \text{at } x = L_2 \]

\[-k_r \frac{\partial T_r}{\partial y} = -k_f \frac{\partial T_f}{\partial y} \quad \text{at } y_r = 2L_2 \]

\[-k_r \frac{\partial T_r}{\partial y} = 0 \quad \text{at } y_r = 0 \]

Where \( \rho \) is density, \( C_p \) heat capacity and \( k \) thermal conductivity. \( h \) are the heat transfer coefficients between the mold and air. Subscripts \( m \), \( f \) and \( r \) refer to mold, fiber preform.
and groove respectively. \( L_1 \) is half of the groove spacing, \( L_2 \) half of the groove width, \( L_3 \) the thickness of the mold (3 mm) and \( H \) the thickness of the fiber preform. The thermal properties of composites were estimated from the properties of each component by assuming [Lee, 1981]:

\[
\frac{1}{\rho} = \sum \frac{\omega_i}{\rho_i}, \quad C_p = \sum \omega_i C_{p_i}, \quad \frac{1}{k} = \sum \frac{\omega_i}{k_i}
\]

where \( \omega_i \) is the weight fraction of resin. The data used in this study are summarized in Table 5.4.

**5.4.2.3. Numerical Method**

The heat transfer model is a set of parabolic partial differential equations (PDEs) that have two space coordinates, which can be solved by using the implicit alternating-direction method [Carnahan, 1969]. The basic principle of this method is to employ two difference equations which are used in turn over successive time-steps each of duration \( \Delta t/2 \). The first equation is implicit only in the x-direction and the second is implicit only in the y-direction. If \( v_{i,j}^* \) is an intermediate value at the end of the first time-step, we have

\[
\frac{v_{i,j}^* - v_{i,j,n}}{\Delta t/2} = \delta_x^2 v_{i,j}^* + \delta_y^2 v_{i,j,n}
\] (5.44)
<table>
<thead>
<tr>
<th></th>
<th>( \rho ) (g/cc)</th>
<th>( C_p ) (J/g.-°C)</th>
<th>( k ) (J/m-s.-°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>1.04</td>
<td>1.5</td>
<td>0.17</td>
</tr>
<tr>
<td>Glass fiber</td>
<td>2.56</td>
<td>0.67</td>
<td>0.75</td>
</tr>
<tr>
<td>Steel mold</td>
<td>7.82</td>
<td>0.49</td>
<td>50.9</td>
</tr>
<tr>
<td>Aluminum mold</td>
<td>2.72</td>
<td>0.87</td>
<td>202.4</td>
</tr>
<tr>
<td>Composite mold</td>
<td>1.85</td>
<td>1.12</td>
<td>0.37</td>
</tr>
<tr>
<td>( H_{Rf} ) (J/g)</td>
<td></td>
<td>364.0</td>
<td></td>
</tr>
<tr>
<td>( H_{Rf} ) (J/g)</td>
<td></td>
<td>182.0</td>
<td></td>
</tr>
<tr>
<td>( h ) (J/m²-K)</td>
<td></td>
<td>5.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4. Thermal properties used in simulation
followed by

\[
\frac{v_{i,j,n+1} - v_{i,j}^*}{\Delta t/2} = \delta_x^2 v_{i,j}^* + \delta_y^2 v_{i,j,n+1}
\]  

(5.45)

Where the operator \( \delta_x^2 \) and \( \delta_y^2 \) are defined by

\[
\delta_x^2 u_{i,j} = \frac{u_{i-1,j} - 2u_{i,j} + u_{i+1,j}}{(\Delta x)^2}, \quad \delta_y^2 u_{i,j} = \frac{u_{i,j-1} - 2u_{i,j} + u_{i,j+1}}{(\Delta y)^2}
\]

Written out in full and rearranged, with \( \Delta x = \Delta y \) for simplicity, Equations 5.44 and 5.45 become

\[
-v_{i-1,j}^* + 2\left(\frac{1}{\lambda} + 1\right)v_{i,j}^* - v_{i+1,j}^* = v_{i,j-1,n} + 2\left(\frac{1}{\lambda} - 1\right)v_{i,j,n} + v_{i,j+1,n}
\]  

(5.46)

\[
-v_{i,j-1,n+1} + 2\left(\frac{1}{\lambda} + 1\right)v_{i,j,n+1} - v_{i,j,n+1} = v_{i-1,j}^* + 2\left(\frac{1}{\lambda} - 1\right)v_{i,j}^* + v_{i+1,j}^*
\]  

(5.47)

where \( \lambda = \frac{\Delta t}{(\Delta x)^2} \). According to Equations 5.46 and 5.47, a system of equations with a tridiagonal coefficient matrix are obtained, which can be readily solved by a Gaussian elimination method [Carnahan, 1969].
5.4.2.4. Results and Discussion

Figure 5.39 shows the comparison of the simulated temperature distribution and the experimental results. As can be seen, the prediction fits the experimental results reasonably well for both cases. This indicates that the cure simulation, which integrates the heat transfer analysis and the kinetic model, was able to successfully predict the temperature profiles during curing in SCRIMP molding process.

As mentioned earlier, curing in SCRIMP normally starts at room temperature and the only heat source is the reaction exotherm of the resin. Ideally, the reaction exotherm should be stored in the curing composite such that a higher temperature can be reached during curing, which would in turn accelerate the reaction, produce more heat and drive the curing reaction to completion. However, this ideal situation can not always be achieved because of the heat dissipation into the mold and heat loss to the surroundings. In winter when the room temperature is low, such heat loss may result in a very long curing time. By adopting computer simulation, the effect of various processing variables such as ambient temperatures, tooling materials and groove design on SCRIMP curing can be probed.

Figures 5.40(a) and 5.40(b) show the temperature ($T_2$) and conversion profiles respectively for composite mold, steel mold and aluminum mold at room temperatures of 35°C, 25°C and 15°C. At the same room temperature, a higher temperature is achieved in the curing part with the composite mold than with the aluminum or steel mold, and so is...
Figure 5.39. Comparison of experimental and simulated temperature profiles in SCRIMP Curing
Figure 5.40(a). Effect of tooling materials and ambient temperature on temperature profiles in SCRIMP curing.
Figure 5.40(b). Effect of tooling materials and ambient temperature on conversion profiles in SCRIMP curing.
the final conversion. Although the thermal conductivity of aluminum is 3 times larger than that of steel, higher temperature is achieved with the aluminum mold, which can be attributed to the smaller thermal mass of aluminum. For the same mold material, the final conversion depends on ambient temperature. The higher the room temperature, the higher the final conversion. For this vinyl ester resin, the gelation occurs at the conversion of 10%. If we assume that demolding can be proceeded when 70% conversion is achieved, Figure 5.40 leads to Figure 5.41, which reveals the relationship between the gel time and the demold time at various room temperatures for composite, steel and aluminum molds. It can be seen that at the same room temperature, the demold time is shorter for the composite mold than for the steel mold and aluminum mold, and the difference becomes larger at lower room temperatures. It is possible that at lower temperature (i.e. <15°C), the reaction system can never reach 70% conversion, which means the part will never be strong enough to be demolded. This possibility is larger for the steel mold than for the composite mold at the same low room temperature. The gel time is affected by room temperature, but is not sensitive to mold materials.

One idea to increase the temperature inside the curing part is to place an insulating material outside the mold. In the simulation, we can assume \( h = 0 \) to mimic the insulation effect. The simulation shows that a higher temperature can be reached with mold insulation, which leads to a higher reaction rate and higher final conversion. Table 5.5 summarizes the effect of insulation on demold time and gel time.
Figure 5.41. Demold time and gel time as a function of room temperature with different mold materials

- composite
- steel
- aluminum
Through several examples stated above, it has been demonstrated that the cure simulation developed in this study can be used as a design and analysis tool. It needs to point out that we defined the time to reach 70% conversion as the demold time (i.e. the time for the composite to reach the green strength). 70% conversion was chosen arbitrarily. The demold time would change if this conversion criteria changes. For example, if the demold conversion is greater than 70%, the difference in the demold time with different tool types would be larger at lower room temperatures. On the other hand, if the demold conversion is less than 70%, the difference will be smaller.
5.5. Conclusions

Free radical cross-linking polymerization at low temperatures is different from that at high temperatures due to the different curing agents used. In this study, the cure of vinyl ester resins at low temperatures has been investigated using FTIR, RDA and DSC under both scanning and isothermal conditions. The reaction kinetics and mechanism were probed by studying the effect of systematically varying the concentration of curing agents on the reaction rate and conversion profiles of the total reaction or individual reaction of vinyl ester and styrene C=\(\text{C}\) bonds. It was found that the reaction mechanisms that may be involved with a low temperature curing resin are complex. Multiple exothermic peaks may occur in both isothermal and scanning cure of vinyl ester resins, which may be attributed to the competition between the vinyl ester and styrene co-polymerization and the styrene homo-polymerization, the variation in \(k_p\) and \(k_t\), or different initiation mechanisms. The initiation mechanisms that may be involved during the course of reaction of vinyl ester resins are: redox decomposition of initiator at low temperatures, thermal decomposition of initiator at middle temperatures and self-initiation of monomers at high temperatures that leads to the thermal polymerization. Depending on the rate of temperature change, the resin composition, the concentration of initiator and promoter, some of these mechanisms may dominate and others may not participate. Initiation mechanisms that dominate at certain temperatures could significantly speed up the reaction at that temperature, and therefore the reaction rate may show the maximum there. The FTIR results suggest that with a high initial molar ratio of
styrene to vinyl ester C=C bonds, there is significant homo-polymerization of styrene or grafting reaction of styrene along vinyl ester chains at later stage, which leads to the second peak (or shoulder) on the isothermal reaction rate profiles. The second peak at slow scanning rate may also be attributed to the same reason. There exist critical promoter concentrations in order to intrigue the reaction at room temperatures and to reach the maximum final conversion at that temperature. However, there is also an upper limit where the catalytic effect of the promoter becomes saturated. When the promoter concentration is above a critical value, any amount of initiator can induce the polymerization at room temperatures, but the reaction rate and the final conversion may be low. There also exists a critical initiator concentration for the resin to reach the maximum final conversion at that temperature. The reason for the need of minimum promoter and initiator amount, however, is different. With the presence of 1,4-Benzoquinone (BQ), the initial part of the reaction shows a clear trend of exponential decay, which becomes more profound with the increase of BQ concentration. However, once the exponential decay period is over, the rest of the reaction shows a very similar profile compared to that without BQ. 2,4-Pentandione (2,4-P) functions as a retarder by forming complex with the transition metal ions to reduce the effective concentration of promoter. It also changes the reaction mechanisms. The cure behavior of the vinyl ester resin in SCRIMP processes was successfully simulated by a cure model which integrates the reaction kinetics and heat transfer analysis.
6.1. Introduction

The network formation process in free radical chain growth crosslinking polymerizations is quite different from that in step growth crosslinking polymerizations [Flory, 1953]. Many researchers [Galina, 1980; Ito et al. 1975] have found that the measured gel conversions of multifunctional monomers in chain growth polymerizations were much higher than the predicted values. Three possible non-ideal network formation mechanisms have been proposed to explain these deviations. They are (i) ring formation or cyclization due to intramolecular reaction, (ii) reduced reactivity of pendant vinyl groups, and (iii) molecular shielding effect on the reaction of pendant vinyl groups due to microgel formation [Dusek, 1982].
The vinyl-divinyl systems are of great importance for elucidation of the process and structure of the network formation. Some aspects of the copolymerization of MMA/EGDMA have been investigated since 1945 [Walling, 1945]. Experimental investigations of free radical crosslinking polymerizations have illustrated that the characteristics of the reaction and the structure of the resulting network depend on the concentration of the crosslinking agent. Dusek and Spevacek [1980] proposed that the microgel particles would dominate the copolymerization process of MMA-EGDMA systems with high content of divinyl components. Chiu [1994] observed the formation of bimodal polymer size distribution as a function of the concentration of the crosslinking agent by using Dynamic Light Scattering (DLS) technique. The comparison of the experimental gel conversions measured by RDA and theoretical gel conversions calculated from Flory-Stockmayer theory showed increasing difference as the concentration of crosslinking agent increases. Based on the experimental data, it was proposed that primary polymers, i.e., microgels, form at the very beginning of the reaction, and the inter-molecular reaction between primary polymers causes the formation of larger polymer clusters when the reaction proceeds further.

Percolation models are able to generate information which cannot be obtained by traditional models, such as cyclization fraction, polymer size distribution, crosslinking density and reactivity ratio of primary double bonds to pendant ones. In this study, a percolation model is developed to simulate MMA/EGDMA copolymerization.
6.2. Description of the Percolation Model

A 3-D percolation model is developed to simulate the copolymerization of MMA and EGDMA. Unlike the previous work [Chiu et al., 1995b], we start with a cubic lattice of point-like monomer molecules. Normally, by computer simulation, one can model a small region of matter in full atomistic detail. e.g. for a simple fluid it often is sufficient to simulate a small box containing of the order of $10^3$ atoms which interact with each other with chemically realistic forces. These methods work because simple fluids are homogeneous on a scale of $10\,\text{Å}$. However, for long flexible polymers the situation is very different: a simple chain exhibits structure from the scale of a single chemical bond ($\approx 1\,\text{Å}$) to the persistence length ($\approx 100\,\text{Å}$). The treatment of the polymers in full chemical detail necessitates the use of large simulation boxes with linear dimensions of hundred $\text{Å}$ or larger, containing many millions of atoms. Obviously, chemically realistic models are prohibitively difficult because they would require enormous computer time. An alternative way to simulate the network formation on lattice is to simply omit the very fast motions on very small length scales, thus sacrificing some chemical details.

Some researchers [Brown and Peppas, 1992; Chiu and Lee, 1995b] tried to use multiple sites to approximate molecular structure of the monomers. However, these representations of monomers are still very unrealistic and without justification. In the case of copolymerization, inaccurate representation of the monomer size and conformation would artificially change the relative mobility and reactivity of the
monomers. Therefore, in this simulation, it is assumed that each monomer molecule and free radical occupies one site of the lattice with six nearest neighbor sites as shown in Figure 6.1(a). Due to the lack of chemical structure information, the comparison between simulation and experimental data either is necessarily of a qualitative nature or material parameters can be absorbed in constants normalizing coordinate scales.

Periodical boundaries (or folding boundaries) are applied to mimic the behavior of an infinitely large system so that molecules experience no diminution in their capacity to react on account of their locations. Molecules at an edge of the lattice can form a bond with molecules on the opposite side of the edge. In this way, molecules that grow out of one side of the lattice can enter again from the other side of the lattice. For example, monomer 1 in Figure 6.1(b) can react with monomer 2 according to the periodical boundary condition.

In this simulation, the same reactivity is assumed for MMA and EGDMA functional groups [Landin et al. 1988]. The lattice size is 30x30x30 with $2 \times 10^4$ monomers and 52 initiators. The free radical is generated from the initiator molecules according to the first order exponential decomposition mechanism and initiator molecules decay into two radicals per initiator. The computation focuses on the free radical sites as its basis. In every time step, the neighbors of the free radicals are checked and then the probabilities
Figure 6.1. Conformation of monomers: a) each free radical can have up to six nearest neighbors. b) each monomer occupies one lattice site (3x3x3 lattice).

(○: MMA, ●: EGDMA, *: free radical)
of each event (propagation, cyclization, and termination) are set. The setting depends on the number and status of the nearest neighbors of the inspected radical. The neighbors are defined as those that can react with active radicals, i.e. other active radicals and unreacted functional groups. In the case of \( n \) \((0 \leq n \leq 6)\) neighbors, if \( m \) neighbors of them are active radicals, then the probability of propagation or cyclization is

\[
\frac{(n-m)k_{po}}{mk_{io}+(n-m)k_{po}}
\]

and the probability of termination is

\[
\frac{mk_{io}}{mk_{io}+(n-m)k_{po}}
\]

Since \( k_{io} \) is much larger than \( k_{po} \), the termination is the most possible thing to occur when there is an active radical as one of the neighbors. By generating random numbers we can then decide which event may take place and which neighbor this radical will form a bond to.

Translational diffusion of monomers, radicals and polymers are incorporated in this model. It is assumed that monomers, free radicals, and the sol fraction of polymers can diffuse with the constraints being that all bonds must be preserved and movement must occur from an occupied site to a vacant one, but not necessarily the neighboring one. Owing to the high monomer diffusivity compared to that of the polymer, the diffusion of monomers is assumed free of restriction while that of the polymers is
simulated as if polymers can penetrate through monomers. At each time step, all monomers are first drawn out of the lattice such that there is more space for polymers to diffuse. Random numbers are then generated for all polymers, polymeric radicals and free radicals to determine their next movements. For a free radical, if the selected site is not occupied, then this free radical moves to that site. However, for a polymer chain, new sites that are assigned to the polymer segments have to be unoccupied; otherwise, the polymer cannot move. Therefore, it is much more difficult for polymer and polymeric radicals to have translational diffusion. The translational mobility of a polymer or polymeric radical decreases greatly as its size increases. The segmental diffusion of polymers is not included in this model in order to keep the computation simple. This assumption should not affect much the translational diffusion of polymers. It, however, may reduce the extent of intra-molecular reaction. Finally, diffusion of monomers is simulated by redistributing monomers back on the lattice randomly. In addition, cyclization or intra-molecular reaction is also included here. Gelation is assumed to occur when there is a polymer extending from one end of the lattice to the opposite end. This is equivalent to Flory's statement [1953] that an indefinitely 'macro' structure, i.e., an infinite network, extends throughout the volume of the polymerized material. A summary flow chart of this simulation algorithm is shown in Figure 6.2.
6.3. Results and Discussion

Before applying this percolation model to MMA/EGDMA chain growth copolymerization, we wrote a code based on the same idea stated above for a much more well studied step growth co-polymerization of bi-functional and tri-functional (i.e. A3+B2) monomers. As shown in Table 6.1, the simulated gel point agrees with the theoretical gel conversions remarkably well at stoichiometric functional group ratio; however, there is some deviation when the ratio is not equal to 1. The above simulation results show that this percolation model is valid for step growth polymerization systems.

The free radical concentration in the system controls the average length of chains, the reaction rate and the gel conversion. In order to approach experimental conditions, the decomposition rate should be much lower than the propagation rate. By adjusting the decay constant, $k_d$, we can vary the relative rates of initiation and propagation. As Table 6.2 shows, for a given lattice size and initiator concentration, decreasing the initiation rate decreases the gel conversions. The decay constant of $5 \times 10^{-4}$ (computation time)$^{-1}$ gives gel conversions close to experimental data. Four different systems were simulated: MMA with 0, 5, 20, and 100 wt.% of EGDAM. Table 6.2 lists the simulated gel conversions and the extent of intramolecular reactions i.e. $\alpha_{\text{intra}}$, at gel point for each system. Here $\alpha_{\text{intra}}$ is defined as the conversion of the pendent double bonds which react with the polymeric radicals on the same polymer chain. Although a comparison of the experimental gel conversions and the results of simulation reveals some discrepancy, the simulations do show a better agreement.
Begin

Input: Lattice size, $K_d$, fraction of free volume, monovinyl/divinyl mole ratio, initiator/monomer mole ratio, $K_p/K_t$

Random Number
Distributing monomers

Random Number
$[I]=[I_0] \exp(-K_dt)$

For all the radicals $i = 1, n_{free}$

Check neighbors (free radical, unreacted double bond)

Determine the movement of the free radical

Update the System: length, cluster number, status of double bond

Calculate monomer conversion, polymer size, etc. and check gel point

Maximum step reached?

Yes
Stop

No

Preset conversion reached?

Yes

No

Any active radical left?

Yes

No

Determine the amount of decomposed initiator and distributing generated free radicals on the lattice

Random Number

Distribute monomers

Random Number

Determine the amount of decomposed initiator and distributing generated free radicals on the lattice

237
\[ r_{AB} = \frac{N_A}{N_B} \]

<table>
<thead>
<tr>
<th>( r_{AB} )</th>
<th>( \alpha_{\text{simulation}} )</th>
<th>( \alpha_{\text{theoretical}} )</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.706</td>
<td>0.707</td>
<td>0.22</td>
</tr>
<tr>
<td>0.796</td>
<td>0.785</td>
<td>0.793</td>
<td>0.92</td>
</tr>
</tbody>
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Table 6.1. Simulated gel conversion versus theoretical values for a step growth polymerization \((A_3 + B_2)\)

than the Flory-Stockmayer theory. The percolation model also provides us the information on the extent of cyclization. From the simulation, we know that the gel conversion decreases with the increase of the crosslinker concentration, but the extent of the intra-molecular reaction increases significantly. For 100% EGDMA, 27% of the reaction is intra-molecular reaction at gel point while for 5 wt.% of EGDMA, only 0.8% of the reaction is intra-molecular reaction. Since every reaction of a pendant double bond with a polymeric radical on the same polymer chain forms a loop, the actual conversion of double bonds for loop formation would be much higher than \( \alpha_{\text{intra}} \). This shows that the intra-molecular reaction is a very important part of free radical polymerizations, especially at higher crosslinker concentrations.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Experiment(^a)</th>
<th>(\alpha_{\text{theo}})</th>
<th>(k_d=0.0005)</th>
<th>(k_d=0.005)</th>
<th>(k_d=0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\alpha_{\text{exp}})</td>
<td>gel time</td>
<td>(\alpha_{\text{total}})</td>
<td>(\alpha_{\text{intra}})</td>
<td>(\alpha_{\text{total}})</td>
</tr>
<tr>
<td>MMA-5wt% EGDMA</td>
<td>12.8%</td>
<td>55 min</td>
<td>13.3%</td>
<td>12.9%</td>
<td>0.1%</td>
</tr>
<tr>
<td>MMA-20wt% EGDMA</td>
<td>6.9%</td>
<td>28 min</td>
<td>3.3%</td>
<td>9.0%</td>
<td>0.3%</td>
</tr>
<tr>
<td>100% EGDMA</td>
<td>2.6%</td>
<td>47 min</td>
<td>0.7%</td>
<td>5.2%</td>
<td>1.4%</td>
</tr>
</tbody>
</table>

\(^a\) use RDA to measure \(G'\) and \(G''\) crossover point as gel point, quench the sample, then use DSC to measure the residual exotherm to determine the gel conversion

\(^b\) based on Flory-Stockmayer theory

\(^c\) based on percolation model

Table 6.2. Comparison of experimental, theoretical and simulated gel conversions.
Figure 6.3 shows the simulated isothermal reaction rate profiles for systems with different amount of crosslinking agents. The kinetic controlled reaction region is observed for systems with 0 and 5 wt.% of EGDMA, but not for systems with 20 and 100 wt.% of EGDMA. Increasing the crosslinker concentration from 0 to 5 wt.%, the reaction rate peak moves to left and the maximum reaction rate increases a little bit. Further increasing the crosslinker concentration to 20wt.% and 100wt.%, the peaks move to right again and the maximum reaction rate decreases. In view of the many simplifications made in this percolation model, the simulation shows right reaction trend compared to the experimental results [Chiu, 1994].

Figure 6.4 shows the polymer size distribution of the simulated systems. For the systems with 5, 20 and 100 wt.% of EGDMA, although the single polymer size distribution is found at the beginning of the reaction, bimodal polymer size distributions are found at higher conversions. The actual polymer size can not be predicted, but the simulated polymer size ratio between the two polymer groups is very close to that measured by DLS. i.e., a ratio of two to four [Chiu, 1994]. Polymer sizes increase as the conversion increases, especially of larger polymer clusters. For the system with 20 and 100 wt.% of EGDMA, the intensity of the larger polymer clusters becomes higher than that of primary polymers when gelation occurs. But this is not found for system with 5 wt.% of EGDMA.
Figure 6.3. Simulated isothermal reaction rate profile for copolymerization of MMA and 0, 5, 20, and 100 wt % EGDMA.
Figure 6.3 continued

![Graph showing reaction rate over computation time step for 20% and 100% EGDMA solutions. The x-axis represents computation time step, ranging from 0 to 1750, and the y-axis represents reaction rate (time step-1), ranging from 0 to 0.0007. Two curves are shown: one for 20% EGDMA (dotted line) and one for 100% EGDMA (solid line). The reaction rate peaks at different time steps for each solution.]
Figure 6.4. Simulated polymer size distribution of copolymerization of MMA and 
(a) 5 wt%, (b) 20 wt%, and (c) 100 wt% of EGDMA.

to be continued on next page
Figure 6.4 continued...
6.4. Conclusions

The formation of heterogeneous structure through intra-molecular reaction is an important feature of the free radical cross-linking co-polymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). Such structure formation affects not only the curing behavior but also the rheological changes of the resin. In this study, a 3-D percolation model is developed to simulate this mono-vinyl and di-vinyl co-polymerization system. The percolation model takes into account spatial correlations, and therefore can provide information about the intra-molecular reaction which often occurs in free radical polymerizations. The simulation results agree well with the experimental observations qualitatively.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. Mold Filling in SCRIMP

Mold Filling is a critical step in determining the overall success of the SCRIMP process. In this stage, the reactive resin flows into the fiber preform to fill the mold. At the same time, the viscosity of the resin increases because of the reaction. This increase may result in incomplete mold filling since the reacting system finally forms a macro-network that leads to an infinite viscosity. Therefore, it is very important to design the resin distribution systems and predict the mold filling time so that appropriate amount of curing agents such as promoter, initiator, retarder and inhibitor can be added in the resin formulation. Two types of SCRIMP processes have been studied: SCRIMP based on a high-permeable medium and SCRIMP based on grooves.

Mold filling in SCRIMP based on a high-permeable medium is complicated because of the considerable difference in the permeabilities of the fiber reinforcement, the peel ply and the high permeable medium. Permeabilities of major processing
materials, i.e. a stitched fiber reinforcement, a high-permeable medium and a peel ply, were measured under different molding conditions. Flow visualization of SCRIMP mold filling was also carried out. It was found that the high-permeable medium played an important role in determining the mold filling time. A peel ply laid between the high-permeable medium and the fiber preform can not only help demolding but also speed up mold filling. A 3D CV/FEM model was applied to simulate the mold filling process, which elucidates the influences of the flow properties of the high-permeable medium, the fiber preform and the peel ply on the mold filling time. The simulation results indicate that mold filling time is a strong function of the permeability of the high-permeable medium, but is not sensitive to the permeability of the fiber preform. Based on the experimental observations and the 3D CV/FEM simulation, a simplified leakage flow model was also developed to simulate the three-dimensional SCRIMP mold filling. In this model, the resin is assumed to flow into the mold cavity through the high-permeable medium only. The fiber preform is impregnated by the resin leaked from the high-permeable medium. The leakage flow model greatly reduces the computation time and yet provides a reasonable estimation of the mold filling time in SCRIMP based on a high-permeable medium.

Mold filling in SCRIMP based on grooves is much faster than that in SCRIMP based on a high-permeable medium. Mold filling experiments showed that the resin always filled the grooves first and then infused from the grooves to the fiber preform. The mold filling time was controlled by the flows in the grooves, in the thickness direction to
the fiber preform and into the spacing between the grooves. For thin composite parts with large groove spacing, the flow between the groove spacing dominated the mold filling time. For thick composite parts, flow through the thickness direction dominated the filling time. The leakage flow model was able to simulate the mold filling process in SCRRiMP based on grooves. Compared with CV/FEM, the leakage flow model greatly reduced the computation time and yet provided simulation results that were in good agreement with the experimental observation.

For mold filling in simple geometry, the leakage flow model was able to simulate the mold filling pattern and filling time with computation time much shorter than the conventional CV/FEM method. However, for mold filling in non-planar, large-scale mold geometry, the leakage flow model proposed in this study may still not fulfill the simulation in a reasonably short time. Figure 7.1 shows the schematic of a bridge deck floor with hundreds or thousands of macro-grooves and micro-grooves cut on the core. A further simplified approach such as cascade model is needed to handle this case. The basic idea is to group one or more grooves to form an element. The filling rate to this element can be pre-calculated as a function of feed pressure and the fraction filled using the present leakage flow model. This information can be stored in the computer. When the program runs, the filling rate can be looked up and interpolated for the particular fraction filled at a particular feed pressure. With this approach, the computation time may be expected to be shortened substantially.
Figure 7.1 Schematic of making a bridge deck floor using SCRIMP
7.2. Low Temperature Reactions

Compared to high temperature free radical cross-linking polymerizations, different curing agents are used for low temperature reactions. This difference would certainly change the reaction kinetics and mechanism of the resin that determine the final conversion, cycle time, chemorheological changes, micro-structure formation and resulting properties of the final products. The information of the heat of reaction and the rate of heat generation as a function of time and temperature is also necessary for quantifying the heat transfer in the molding process. The reaction induced rheological changes would affect the flow pattern in the mixing and mold filling steps. Therefore, thorough investigation of the reaction kinetics and mechanism of low temperature free radical cross-linking polymerization is critical for better understanding and controlling the manufacturing process and the quality of the final products.

The cure of vinyl ester resins at low temperatures has been investigated in this study. The reaction kinetics and mechanism were probed by studying the effect of systematically varying the concentration of curing agents on the reaction rate and conversion profiles of the total reaction or individual reaction of vinyl ester C=C bonds and styrene C=C bonds by using FTIR and DSC under both scanning and isothermal conditions. It was found that the reaction mechanisms that may be involved with a low temperature curing resin are complex. Multiple exothermic peaks were found in both isothermal and scanning cure of vinyl ester resins, which may be attributed to the competition between the vinyl ester and styrene co-polymerization and the styrene homo-
polymerization, the variation in $k_p$ and $k_i$, or different initiation mechanisms. It was revealed that the initiation mechanisms that may be involved during the course of reaction of vinyl ester resins are: redox decomposition of initiator at low temperatures, thermal decomposition of initiator at middle temperatures and self-initiation of monomers that leads to the thermal polymerization at high temperatures. Depending on the rate of temperature change, the resin composition, the concentration of initiator and promoter, some of these mechanisms may dominate and others may not participate. Initiation mechanisms that dominate at certain temperatures could significantly speed up the reaction at that temperature, and therefore the reaction rate may show the maximum there. The FTIR results suggest that with a high initial molar ratio of styrene to vinyl ester C=C bonds, there was significant homo-polymerization of styrene or grafting reaction of styrene along vinyl ester chains at later stage, which led to the second peak (or shoulder) on the isothermal reaction rate profiles. The second peak at slow scanning rate may also be attributed to the same reason.

It was also found that in order to intrigue the reaction at room temperatures and reach the maximum final conversion at that temperature, the promoter concentration must be above a critical level. Too much promoter, however, did not favor the reaction. With the promoter concentration above a critical value, any amount of initiator can induce the polymerization at room temperatures, but the reaction rate and the final conversion may be low. There also exists a critical initiator concentration for the resin to reach the maximum final conversion at that temperature. With the presence of 1,4-Benzoquinone
(BQ), the initial part of the reaction shows a clear trend of exponential decay, which becomes more profound with the increase of BQ concentration. However, once the exponential decay period is over, the rest of the reaction shows a very similar profile compared to that without BQ. 2,4-Pentandione (2.4-P) functions as a retarder by forming complex with the transition metal ions to reduce the effective concentration of promoter. The presence of either BQ or 2,4-P would change the rates of the competing reactions and therefore the network structure. 2.4-P is more effective than BQ in extending the gel time, but the cycle time is also significantly prolonged.

Although DSC and FTIR measurements have shed light on the reaction kinetics and mechanisms, other analytical instruments may provide more direct evidence. The promoters used in low temperature polymerization are transition metal ions. They have excited state levels that have absorption bands in the region 200-700 nm, the ultraviolet (UV) region. So do the organic substances with the presence of double bonds such as 2,4-P. Therefore, UV Spectroscopy may be able to provide insight into the interaction between the cobalt promoter and the 2,4-P retarder. Appendix B shows the absorption spectra of the individual components and the mixture in the UV region obtained at 20°C. As can be seen, with 2,4-P adding to the promoter solution, new peaks emerged and the intensity of the absorption band changed. Figure B.1 was obtained without fine tuning the concentration of the components so that better quality spectrum could be produced. By studying the effect of varying the level of 2,4-P and temperature on the spectra change, some questions may be answered. For example, how does the temperature influence the
2.4-P and promoter complex? Will the complex be dissociated and release free cobalt ions at high temperatures?

The interaction of cobalt ions with 2.4-P, the effect of BQ and the mechanisms associated with exothermal peaks during scanning may also be revealed by means of the ESR spectra. ESR can be used to follow the radical concentration profile during reaction, which may provide a better understanding of the reaction mechanism. Some questions may get direction answer from ESR measurements. For example, is the exponential decay in the reaction rate due to the consumption of the free radicals? How does the concentration of free radical change with the change of BQ concentration?

In order to better understand the interaction between promoter, initiator and retarder, it is probably a good idea to first carry out their reaction in a non-reactive solvent such as benzene. The undecomposed cumene hydroperoxide can be determined iodometrically [Barton and Horanska, 1972] so that the initiator's decomposition rate can be calculated. By carrying out the reaction at various concentrations of promoter, initiator and retarder, we can get the kinetic equation for the reaction. Coupled with UV and ESR spectra, the reaction mechanism may be understood.

It can be seen that the vinyl ester resin systems used in our study are too complex to be used to fully elucidate the basic reaction mechanisms and kinetics of low temperature reactions. The commercial nature of the resin makes it impossible to know the detailed composition of the resin. The competing nature of the copolymerization reaction further complicates the issue by presenting additional possibilities when
interpreting experimental observations. Since there are so few fundamental studies on low temperature polymerizations, it is better to start with a well-defined homopolymerization system such as methyl methacrylate (MMA) or ethylene glycol dimethacrylate (EGDMA). This would certainly make data interpretation easier. Furthermore, there are more literature data for high temperature reactions that can be used to compare with those obtained at low temperatures to help understand the reaction mechanisms.

7.3. Cure Simulation

Many resin systems, such as vinyl esters, produce a large exotherm during cure, causing high temperatures in the center of the part. In thick-section components, significant thermal gradients induce spatial variations in the degree of cure as well as related material response. However, many resin systems including the vinyl ester resins are sensitive to changes in the amount and type of initiator, promoter, inhibitor and other additives. Using cure simulation, it is possible to design and optimize the cure process. Cure simulation requires an accurate kinetics model for the resin that is further based on the thorough understanding of the reaction mechanisms. The reaction mechanisms of retarder and inhibitor in the cure of vinyl ester resins have not yet been fully understood and the reaction kinetics are too complicated. Therefore, in this study a kinetic model based on a phenomenological modeling approach and only considers the redox reaction between the promoter and initiator was used. The cure behavior of the vinyl ester resin in SCRFIM processes was successfully simulated by a cure model, which therefore can be
used to assist in the design of the cure cycle, selection of tooling material and ambient temperatures.

The kinetic model used in this cure simulation has not yet included the effect of retarder, which should be considered as a future work since 2,4-P has been widely used to adjust the gel time in practice.

In the mold filling analysis carried out in this study, we neglected the rheological changes induced by reaction. In this cure simulation, we neglected the reaction that may have occurred during mold filling. In real case, curing and mold filling may not always be de-coupled. So it is also a future work that non-isothermal mold filling be carried out. This future work, however, necessitates the accurate modeling of network formation during free-radical cross-linking polymerization.

7.4. Modeling of Network Formation

The network formation process in free radical chain growth cross-linking polymerizations is quite different from that in step growth cross-linking polymerizations. The formation of heterogeneous structure through intra-molecular reaction is an important feature of the free radical cross-linking co-polymerization of mono-vinyl and divinyl system, such as the vinyl ester resins used in this study. Such structure formation affects the rheological changes of the resin. There are several mathematical models that can explain the network formation, such as kinetic models, statistical models and computer simulation models in n-dimensional spaces — the percolation model. In this study, a 3-D percolation model is developed to simulate a "model" mono-vinyl and di-
vinyl co-polymerization system, i.e. methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). Since the percolation model takes into account spatial correlations, it can provide information about the intra-molecular reaction which often occurs in free radical polymerizations. The simulation results agree well with the experimental observations qualitatively.

Changing the on-lattice model to off-lattice model would make the percolation model more realistic because the number of neighboring sites will increase. Also giving the monomers more chemical structure information would make the comparison between simulation and experimental data more of quantitative nature and the comparison between different systems possible. Maybe only then, a comprehensive model that combines mean field theory and the percolation model can be developed to describe the viscosity rise in the inhomogeneous free radical cross-linking polymerization.
REFERENCES


Dow Chemical. Fabricating Tips. DERAKENE epoxy vinyl ester resins (1994)


Flory, P.J. Principles of Polymer Chemistry; Cornell University Press: Ithaca (1953)


Huh, C., *PhD Dissertation*, University of Minnesota, Minneapolis, MN (1969)


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Landin, D.T. *PhD Dissertation*, University of Minnesota, Minneapolis, MN (1985)


Li, S., Master Thesis, The Ohio State University (1997)


Lin, R., PhD Dissertation, The Ohio State University (1991)


Macosko, C.W. and Miller, D.R., Macromolecules 9, 199 (1976)


Marten, F.L. and Hamielec, A.E., ACS Symp. Ser. 104, 43 (1979)


Miller, D.R., Macosko, C.W., Macromolecules 13, 1063 (1980)


Mortimer, C.T. Reaction Heats and Bond Strengths; Pergamon: London (1962)

Muskat, I.E., U.S. Patent 2,495,640 (1950)

Mussatti, F.G., PhD Dissertation, University of Minnesota (1975)

Ni, J. *PhD Dissertation*. The Ohio State University (1996)


*Plastics Tech.* March 1995

Puckett P.M. (Dow Chemical Company), personal communication


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APPENDIX A

CHEMORHEOLOGY OF POLY(URETHANE/ISOCYANURATE) FORMATION

ABSTRACT

Poly(urethane/isocyanurate) is a major resin used in the structural reaction injection molding (SRIM) process. In this study, the kinetics and viscosity changes of a poly(urethane/isocyanurate) resin were investigated by the adiabatic temperature/viscosity rise method and differential scanning calorimetry. The effect of the catalyst concentration and the volume ratio of isocyanate to polyol was investigated. It is found that isocyanate trimerization depends on the diffusion effect resulted from the urethane formation. A kinetic model including the diffusion effect is developed, which is able to predict the experimental results. The reaction induced viscosity rise depends on the concentration and the molecular weight of the formed polymer. The measured adiabatic viscosity rise correlates well with the calculated molecular weight growth using the recursive method.
INTRODUCTION

Analysis of the structural reaction injection molding (SRIM) process necessitates a thorough understanding of the reaction kinetics and rheological changes of the reacting resin. A knowledge of the reaction rate, degree of cure and the reaction exotherm of the resin system as a function of thermal history is essential for predicting the structural and physical property changes of the reacting resin. Understanding the reaction induced rheological changes is critical to the selection of proper processing conditions.

Kinetic measurements during the reactive processing of thermoset resins is inherently difficult. Resin solidification due to chemical crosslinking obviates most solution techniques. Since the SRIM process is very fast and highly exothermic, a simple way to follow the overall resin conversion is to monitor the heat generation under the adiabatic condition. Several researchers have used this idea together with linear or non-linear regression methods to predict the kinetic parameters (1, 2). Because the thermal conductivity of polymers is extremely low, an insulated disposable cup can serve as a suitable adiabatic reactor. Fast responding thermocouples can be used to follow the adiabatic temperature rise.

In the SRIM process, the reaction system starts at a low viscosity. The resin fills the mold in a very short period of time (i.e. seconds) and once the mold is filled, the resin cures quickly to reach the ultimate strength. During the process, mold filling must be finished before the resin viscosity reaches too high a value. Therefore, the prediction of
the viscosity rise and the determination of the gel point are very important for process control. The rheological changes of reactive polymers are mainly measured by shear flow methods. A Brookfield viscometer or similar devices (3) can be used in the adiabatic reactor to measure the viscosity rise. Since the measuring probe can be disposable and the viscometer is portable, these viscometers are quite appropriate for measuring viscosity changes in fast cure processes. However, due to its empiricism, the measured results are often less accurate than those from the conventional rheometers.

Poly(urethane/isocyanurate) is a major resin used in the SRIM process. This resin is recommended for applications with high flow resistance (e.g. due to the presence of a fiber preform in the mold cavity) and large surface area because of its low viscosity, long gel time and rapid cure characteristics. A commercial poly(urethane/isocyanurate) system was studied in this work. Both the adiabatic temperature/viscosity rise method and differential scanning calorimetry (DSC) were used to investigate the kinetics and viscosity changes of the resin during curing.

EXPERIMENTAL

Materials

The resin system used for this study consists of two components. SPECTRIM MM364-A isocyanate (a specialty isocyanate based on methylene diphenyl diisocyanate) and MM364-B polyol from Dow Chemical. The functionality of the isocyanate is 2.43
and of the polyol is 2. Triethylenediamine (DABCO+ 33LV. Air Products and
Chemicals) was used as a catalyst.

Instrumentation and Procedure

The experimental set-up for the adiabatic temperature/viscosity rise measurement is shown in Figure A.1. The set-up consisted of a 400ml polypropylene cup covered by insulation, a mixer, two J type thermocouples, a Brookfield viscometer with a disposable spindle and a data acquisition system (DianaChart, PC Acquisition).

For the measurement of adiabatic temperature rise, the procedure consisted of thoroughly mixing a certain volume ratio of isocyanate and polyol for about 8 seconds, and then injecting the catalyst. After catalyst injection, the system was mixed for additional 5 seconds. The experiments conducted included various volume ratios of isocyanate to polyol and different catalyst levels, from 0.2-2.0 wt% of polyol. The total volume of the resins used in each run was 170 ml.

The procedure for measuring the adiabatic viscosity rise is virtually the same as for measuring the adiabatic temperature rise, with the exception of using double the amount of isocyanate, polyol and catalyst. After complete mixing, the mixer was removed and replaced by a Brookfield digital viscometer (Model DV-I+, Version 2.0). A disposable spindle consisting of a glass rod glued to the inside of a small cylindrical glass container was used as the measuring device. This spindle design provides a low thermal mass with low thermal conductivity, which is important for adiabatic measurements. The
Figure A.1 Experimental setup for adiabatic measurements
spindle's large surface area allows for the measurement of low viscosity resins. Each spindle was individually calibrated with a set of silicone oils with viscosity ranging from 10 to 1000 cP. The experiments were conducted at a speed of 50 rpm and both temperature and viscosity data were recorded as a function of time by the data acquisition system.

The reaction exotherm for both the poly(urethane/isocyanurate) reaction and the pure isocyanate trimerization was also measured by a differential scanning calorimeter (Thermal Analyst Instruments, DSC 9210). After the reactants were quickly mixed, 5-10 mg of the mixture was placed in an aluminum DSC pan. In the isothermal runs, the DSC was set at a prescribed temperature and the isothermal run was continued until no further reaction exotherm. Samples were then reheated from room temperature to 250°C in the scanning mode with a heating rate of 2°C/min to detect the residual reactivity left in the isothermally reacted samples. The total heat of reaction during cure was calculated from the areas under both isothermal and residual scanning DSC curves. DSC cure was also carried out in the scanning mode from room temperature to 250°C at heating rates varied from 2 to 20°C /min. The total heat of reaction was also calculated from the area under the scanning curve.
RESULTS AND DISCUSSION

Reaction Kinetics

The poly(urethane/isocyanurate) resin combines two types of isocyanate reactions: the formation of urethanes and the isocyanate trimerization. A urethane reaction mechanism was proposed by Steinle et al. (4):

\[ [\text{NCO}^-] + \text{catalyst} \xleftrightarrow{\text{K}_1} \text{complex-1} \xrightarrow{\text{K}_2} \text{Urethane} + \text{catalysts} \]

The reaction mechanism results in a hyperbolic kinetic model as shown by equation (A.1), where \( C_C \), \( C_{OH} \), \( C_I \) and \( C_U \) are concentrations of catalyst, hydroxyl, isocyanate and urethane respectively; \( K_{C1} \) and \( K_{C2} \) are reaction rate constants; \( E_c \) is the activation energy; \( T_r \) is the reference temperature (373K); and \( R \) is the gas constant.

\[
- \frac{dC_{OH}}{dt} = \frac{dC_U}{dt} = \frac{K_{C1}C_CC_{OH}C_I}{1 + K_{C2}C_{OH}} \exp\left[-\left(\frac{E_c}{R}\right)\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] = r_U
\]  

(A.1)

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The mechanism of the base-catalyzed trimerization of isocyanates is complex and may differ from one catalyst type to another. Results of kinetic studies with anionic bases on model systems indicate that sequential addition of three isocyanate groups to the catalyst is followed by displacement of isocyanurate with a fourth isocyanate (5):

\[
\begin{align*}
[NCO^-] + \text{catalyst} & \xrightleftharpoons{K_1}{K_{11}} \text{complex-1} \\
\text{complex-1} + [NCO^-] & \xrightleftharpoons{K_2}{K_{11}} \text{complex-2} \\
\text{complex-2} + [NCO^-] & \xrightleftharpoons{K_{21}} \text{complex-3} \\
\text{complex-3} + [NCO^-] & \xrightleftharpoons{K_{211}} \text{complex-1 + isocyanurate} \\
\text{complex-3} & \xrightleftharpoons{K_3} \text{catalyst + isocyanurate}
\end{align*}
\]

Assuming pseudo steady state conditions and \( K_1 > K_{11}, K_2 >> K_1, K_{211} >> K_3 \) and \( K_2 = K_{21} = K_{211} \). Vespoli and Alberino used this mechanism to derive the rate equation described by equation (A.2)(6):

\[
\begin{align*}
-\frac{1}{3} \frac{dC_1}{dt} &= \frac{dC_T}{dt} = \frac{K_{A1} \exp\left[-E_{A1}/R(1/T - 1/T_r)\right]C_1^2C_c}{K_{A42} \exp\left[-E_{A42}/R(1/T - 1/T_r)\right]C_1 + 1} = r_T
\end{align*}
\]
where $C_T$ is the concentration of the trimer; $K_{A1}$ and $K_{A42}$ are rate constants; $E_{A1}$ and $E_{A42}$ are activation energies and:

$$\frac{K_3 K_1}{K_{11} - K_3} = K_{A1} \exp(-\frac{E_{A1}}{R} (\frac{1}{T} - \frac{1}{T_0})) \quad (A.3)$$

$$\frac{K_2}{K_{11} - K_3} = K_{A42} \exp(-\frac{E_{A42}}{R} (\frac{1}{T} - \frac{1}{T_0})) \quad (A.4)$$

Combining the urethane and trimerization kinetics, an overall rate equation can be written for the consumption of isocyanate:

$$- \frac{dC_I}{dt} = r_U + 3 r_T \quad (A.5)$$

In order to determine the kinetic constants, a simplified energy balance must also be solved to yield the predicted adiabatic temperature rise. The adiabatic energy balance can be described as follows:

$$\rho C_p \frac{dT}{dt} = \Delta H_{RT} \frac{dC_T}{dt} - \Delta H_{RU} \frac{dC_{OH}}{dt} \quad (A.6)$$
\( \rho \) is the density. \( C_p \) is the specific heat, and \( \Delta H_{\text{RT}} \) and \( \Delta H_{\text{RU}} \) are the heat of reaction for trimerization and urethane formation respectively. Equations (A.1), (A.2), (A.5) and (A.6) constitute the adiabatic kinetic model.

**Effect of Catalyst Concentration**

Figure A.2 shows the adiabatic temperature rise generated for various catalyst concentrations with a constant volume ratio of isocyanate to polyol to be 2.4:1. The shape of the temperature profiles reflects a mixing induced urethane formation at low temperatures followed by a rapid heat induced trimerization. It can be seen from the figure that the urethane reaction proceeded until a temperature of about 80°C, at which the trimerization started. Trimerization caused an instantaneous temperature rise of the system resulted from the rapid consumption of isocyanate. The trimerization began at nearly the same temperature for all the cases with different catalyst concentration. After the maximum temperature was reached, the temperature was found to remain at that level for an extended time (several minutes) so the system can be considered adiabatic.

A non-linear curve fitting technique was used to determine the kinetic constants: 1) guessing a set of parameters. 2) solving equations (A.1), (A.5) and (A.6) simultaneously for temperature. 3) comparing the predicted temperature with the
Figure A.2 Adiabatic temperature rise a function of catalyst concentration. (Volume ratio of isocyanate to polyol 2.4:1)
experimental data. 4) using a direct pattern search to pick a new set of parameters based on the cost and 5) repeating the second through fourth steps until the desired cost is achieved. A FORTRAN program utilizing IMSL subroutines was written to conduct this numeric scheme.

The temperature rise curve for a catalyst concentration of 1.2% by weight of the polyol component was used to determine the model parameters. The resulting model parameters are given in Table A.1 and the model prediction of the adiabatic temperature rises is shown in Figure A.2. The prediction is excellent for higher catalyst concentrations, but is somewhat off for catalyst concentration of 0.4 wt%. As can be seen from Figure A.2, the experimental data of the final temperature for catalyst concentration of 0.4 wt% is much lower than those for higher catalyst concentrations. A possible reason for this is that the reaction exotherm for either polyurethane reaction or trimerization, or both, changes with catalyst concentration when the catalyst concentration is below a certain value. DSC results prove our surmise. Figure A.3 shows the isothermal DSC exotherm curves for trimerization at 45°C. The induction period encountered in this catalyzed trimerization allows us to use DSC at high catalyst concentrations without introducing much error. Figure A.4 shows the trimerization exotherm vs. the catalyst concentration obtained from both isothermal DSC and scanning DSC measurements. As we can see, for different temperatures and different scanning rates, the trimerization exotherm is a function of catalyst concentration at lower catalyst concentrations. It
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Various Catalyst Concentrations (Volume Ratio=2.4:1)</th>
<th>Various Volume Ratios (Catalyst Concentration = 0.0031 g/ml)</th>
</tr>
</thead>
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<tr>
<td>$K_{c1}$</td>
<td>2144.32 (ml²/g mol s)</td>
<td>4085.2 (ml²/g mol s)</td>
</tr>
<tr>
<td>$K_{c2}$</td>
<td>4.198 (ml/mol)</td>
<td>10.0 (ml/mol)</td>
</tr>
<tr>
<td>$E_c$</td>
<td>51.612 (cal/mol)</td>
<td>1.30E-11 (cal/mol)</td>
</tr>
<tr>
<td>$K_{A1}$</td>
<td>2645.8 (ml²/g mol s)</td>
<td>1516.67 (ml²/g mol s)</td>
</tr>
<tr>
<td>$K_{A2}$</td>
<td>115.76 (ml/mol)</td>
<td>0.00718 (ml/mol)</td>
</tr>
<tr>
<td>$E_{A1}$</td>
<td>38689.8 (cal/mol)</td>
<td>21774.9 (cal/mol)</td>
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<tr>
<td>$E_{A2}$</td>
<td>39435.33 (cal/mol)</td>
<td>60278.2 (cal/mol)</td>
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<tr>
<td>$\Delta H_f$</td>
<td>43474.95 (cal/mol)</td>
<td>59007.8 (cal/mol)</td>
</tr>
<tr>
<td>$\Delta H_c$</td>
<td>19470.19 (cal/mol)</td>
<td>13322.4 (cal/mol)</td>
</tr>
<tr>
<td>$A$</td>
<td>3608.84 (ml²/g mol s)</td>
<td></td>
</tr>
<tr>
<td>$E_n$</td>
<td>15874.7 (cal/mol)</td>
<td></td>
</tr>
<tr>
<td>$c^*$</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

Table A.1 Kinetic Model Parameters.
Figure A.3 Isothermal DSC exotherm curves of trimerization at 45°C with various catalyst concentrations.
Figure A.4 Trimerization exotherm as a function of catalyst concentration
reaches a constant value at a catalyst concentration of $1 \times 10^{-3}$ g/ml. The reason for this phenomenon is still not clear and further investigation of the trimerization mechanism is needed.

Effect of Volume Ratio

Figure A.5 shows the adiabatic temperature rise vs. time generated for different volume ratios of isocyanate to polyol varying from 2.4:1 to 7.5:1 at a constant catalyst concentration of $3.1 \times 10^{-3}$ g/ml. It can be seen from the figure that the two-step nature of the reaction is obvious for all the ratios, but the kick-off temperature at which the trimerization becomes significant changes with the volume ratio. For a volume ratio of 2.4:1, this temperature is about 80°C and for 7.5:1 it is around 55°C. The higher the volume ratio of isocyanate to polyol, the lower the kick-off temperature. This effect is most likely related to the diffusion effect resulting from the polyurethane formation. In this two-step reaction, the urethane would form first in the excess amount of isocyanate. After the urethane reaction is complete, the system is a mixture of urethane oligomers in isocyanate monomer. When the volume ratio of isocyanate to polyol is lower, more urethane would form in the system and the molecular weight of the formed urethane would be higher. The remaining reactants (mostly isocyanate) in such a system should have a lower diffusivity and, consequently, the reaction rate of trimerization is slowed down. The significant reaction of trimerization could only be observed at higher temperatures.
Figure A.5 Adiabatic temperature rise as a function of volume ratio.
(Catalyst concentration 0.0031 g/ml)
DSC results support this explanation. Figure A.6 shows the isothermal exotherm curves for different volume ratios of isocyanate to polyol at a constant catalyst concentration of $2 \times 10^{-4}$ g/ml. For a catalyzed step-growth polymerization such as polyurethane, the reaction started immediately after mixing. The initial part of the reaction could not be measured by DSC because sample preparation and sample loading took certain amount of time. With the very low catalyst concentration used, we were able to catch a portion of the polyurethane reaction and the complete trimerization curve. As can be seen from Figure A.6(a), at a temperature of 35°C, there is no trimerization peak for the ratio of 2.4:1, while a big peak appears for the ratio of 7.5:1. Increasing the cure temperature to 50°C, i.e. Figure A.6(b), the trimerization peak also appears for the ratio of 2.4:1, while the peaks for the other two ratios become much larger. So we have clearly seen the urethane induced diffusion effect in the trimerization.

When we tried to model the adiabatic temperature rise as a function of volume ratio using equations (A.1)-(A.4), no single set of parameters can be found to correlate the entire data range. Vespoli and Alberino (6) and Viola and Schmeal (7) also experienced similar difficulty describing the behavior of their systems at large isocyanate indices. This is because that the kinetic equations (A.1) and (A.2) do not account for the diffusion effect.

The diffusion effect can be incorporated into the reaction kinetics by modifying the rate constants. The overall reaction rate constant can be written as follows (8):

\[ k_{overall} = k_{A} + k_{B} + k_{C} \]
Figure A.6 Isothermal DSC results for system with different volume ratio.
(Catalyst concentration 0.0002 g/ml)
Figure A.6 continued

b) Isothermal @ 50°C
\[ K_t = \frac{A_i \exp(-E_a / RT)}{1 + (a'/D) \exp(-E_a / RT)} \]  

(A.7)

where \( D \) is the diffusivity, and \( a' \) includes the vibrational frequency and a geometric factor. The diffusivity \( D \) is related to the free volume, glass transition temperature and the conversion of the reaction system in the following way (9-11):

\[ D \propto \exp\left(-\frac{b'}{V_f}\right) \]  

(A.8)

\[ V_f = V_{f_g} + \beta(T - T_g) \]  

(A.9)

\[ T_g = f_i(\alpha) + T_{g0} \]  

(A.10)

Where \( V_f \) is the free-volume fraction of the system at temperature \( T \); \( V_{f_g} \) is the free-volume fraction of the system at its glass transition temperature \( T_g \); \( f_i(\alpha) \) is a function correlating \( T_g \) and conversion; \( b' \) is a constant; \( \beta \) is the thermal expansion factor. The relationship between the glass transition temperature and conversion usually must be determined experimentally, which is very difficult for a fast adiabatic reaction with two reactions going on simultaneously. Therefore, a simplified approach was proposed in our
model. Since the diffusivity is related to the viscosity of the system, a form similar to the one used for viscosity can be adopted for diffusivity. In other words, we can express diffusivity as a function of temperature and molecular weight, i.e.

\[ D = A_0 \exp\left(\frac{-E_0}{R} \left( \frac{1}{T} - \frac{1}{T_R} \right) \left( \frac{M_{W0}}{M_W} \right)^c \right) \]  

(A.11)

Here, \( M_{W0} \) is the initial weight average molecular weight of the reaction system, and \( M_W \) is the weight average molecular weight of the formed polyurethane. \( M_W \) can be calculated using the recursive method. The details of the recursive method will be discussed later. Since most of the polyurethane reaction occurs in the early stage of reaction, we assume that only the trimerization is affected by diffusion limitation. The trimerization is described by equation (A.2) which contains two rate constants described by equations (A.3) and (A.4) respectively. Since the rate constant described by equation (A.3) is more related to the rate-controlling step (i.e. the first step in trimerization reaction), for the sake of simplification, we assume that only this rate constant is modified using equation (A.7) to account for the diffusion effect. Equation (A.2) thus becomes:
\[
\frac{1}{3} \frac{dC_1}{dt} = \frac{dC_T}{dt} = \frac{K_a C_1^2 C_c}{K_{A_{42}} \exp\left[-E_{A_{42}} / (R(1/T - 1/Tr))\right] C_1 + 1} = \tau_T \tag{A.12}
\]

where

\[
\frac{1}{K_a} = \frac{1}{K_{A_1} \exp\left(-E_{A_1} / (R(1/T - 1/Tr))\right)} + \frac{1}{A \exp\left(-E_0 / (R(1/T - 1/Tr))\right)} \left(\frac{M_{W_0}}{M_W}\right)^c \tag{A.13}
\]

and \(A = A_0 / a'.\)

The non-linear curve fitting technique was again applied to determine the model parameters. The temperature rise curve for the volume ratio of 2.4:1 was used for the model parameter analysis. The resulting model parameters are given in Table A.1 and the model prediction of the adiabatic temperature rise is shown in Figure A.5. The model fits all data quite well.

As can be seen from Table A.1, the values of many parameters change a lot from equation (A.2) to equation (A.12). One of the reasons is that the reactivity of the resin changes with time. Since the experiments studying the effect of catalyst concentration were done about six months before those studying the effect of volume ratio, the resin reactivity has changed. Consequently, some of the model parameters such as the heat of
reaction changed. Another reason is that during non-linear curve fitting, the choice of the best parameters is based on the cost. In order to get the best fit, the values of the parameters may not always bear their physical meaning, especially when there are many parameters in the model.

**Viscosity Modeling**

The adiabatic viscosity rise of the poly(urethane/isocyanurate) resin was also measured. Using the previously described kinetic model, the viscosity vs. time data (Figure A.7) obtained from experiments with a constant volume ratio of 2.4:1 and different catalyst concentrations were transformed to viscosity vs. conversion. The data formed nearly a master curve in Figure A.8, thus making Castro-Macosko type model (12) applicable. The model is written as:

\[
\eta = \eta_0 \left( \frac{\alpha_g}{\alpha_g - \alpha} \right)^{f_2(\alpha, T)}
\]  

(A.14)

where

\[
\eta_0 = \eta_x \exp \left( \frac{E_n}{RT} \right)
\]  

(A.15)

Here, \(\alpha\) is isocyanate conversion and \(\alpha_g\) is the gel conversion.

Using the model in this form, a non-linear regression was conducted. The viscosity profile can be fit by assuming that the function \(f_2\) is a second order polynomial:
Figure A.7 Adiabatic viscosity rise vs. time as a function of catalyst concentration
Figure A.8 Adiabatic viscosity vs. isocyanate conversion as a function of catalyst concentration
\[ T(t) = a + b \alpha + c \alpha^2 \]  \hspace{1cm} (A.16)

The resulting parameters are shown in Table A.2. The comparison of the model and the experimental viscosity rise is displayed in Figure A.7. This model, however, cannot be used to predict the viscosity changes when the volume ratio of the reactants varies. Figure A.9 shows the viscosity vs. conversion curves for different volume ratios at a constant catalyst concentration. These curves do not form a master curve. This is because
Figure A.9 Adiabatic viscosity vs. isocyanate conversion as a function of volume ratio
that the conversion in equation (A.14) is the total conversion of isocyanate consumed in both urethane reaction and trimerization. A change of catalyst concentration does not change the relative significance of the two reactions. Therefore, all viscosity rise data can be expressed as a function of temperature and isocyanate conversion. But a change of volume ratio changes the relative significance of the two reactions, which means the isocyanate conversion is no longer a good parameter for viscosity modeling.

It is the development of three dimensional molecular structure that determines the viscosity rise and the gelation in a reacting system. Knowing the reaction kinetics, the corresponding molecular weight growth can be calculated using appropriate theories. Thus, the viscosity changes during polymerization can be expressed as a function of molecular weight and an Arrhenius temperature dependence (13). The weight average molecular weight is used here, i.e.

\[
\eta = K \exp \left( \frac{E_A}{RT} \right) \left[ \frac{M_W}{(M_W)_0} \right]^{f_3(T,M_W)}
\]  

(A.17)

There are several theories capable of predicting the network structure and molecular weight profile during a stepwise network polymerization. One of them is the recursive method (14). It is based on the recursive nature of the branching process and elementary probability laws. For an ideal stepwise network polymerization, the recursive
method can be used to derive a number of simple relations for the molecular weight averages. Several urethane network polymerizations have been studied by using the recursive method and found to obey the ideal network assumption (15,16). Based on the principle of recursive method, the following equations can be derived for the molecular weight averages of the poly(urethane/isocyanurate) system:

\[ M_W = \omega_{\text{polyol}}E(W_{\text{polyol}}) + \omega_{\text{isocyanate}}E(W_{\text{isocyanate}}) \]  \hspace{1cm} (A.18)

\[ E(W_{\text{polyol}}) = f_{\text{polyol}}E(W_{\text{OH}}^{\text{out}}) + M_{\text{polyol}} \]  \hspace{1cm} (A.19)

\[ E(W_{\text{OH}}^{\text{out}}) = \alpha_{\text{OH}}E(W_{\text{NCO}}^{\text{in}}) \]  \hspace{1cm} (A.20)

\[ E(W_{\text{NCO}}^{\text{in}}) = M_{\text{isocyanate}} + (f_{\text{isocyanate}} - 1)E(W_{\text{NCO}}^{\text{out}}) \]  \hspace{1cm} (A.21)

\[ E(W_{\text{NCO}}^{\text{out}}) = \alpha_{\text{U}}E(W_{\text{OH}}^{\text{in}}) + \alpha_{\text{I}}[M_{\text{trimer}} + 2E(W_{\text{NCO}}^{\text{out}})] \]  \hspace{1cm} (A.22)

\[ E(W_{\text{OH}}^{\text{in}}) = M_{\text{polyol}} + (f_{\text{polyol}} - 1)E(W_{\text{OH}}^{\text{out}}) \]  \hspace{1cm} (A.23)

\[ E(W_{\text{isocyanate}}) = M_{\text{isocyanate}} + f_{\text{isocyanate}}E(W_{\text{NCO}}^{\text{out}}) \]  \hspace{1cm} (A.24)

From equations (A.20) to (A.23), the expressions of \( E(W_{\text{NCO}}^{\text{out}}) \) and \( E(W_{\text{OH}}^{\text{out}}) \) can be derived:

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Combining equations (A.25) and (A.26) with (A.19), (A.24) and then (A.18), the weight average molecular weight $M_W$ can be calculated according to equation (A.27).

$$M_W = \omega_{\text{polyol}} E(W_{\text{polyol}}) + \omega_{\text{isocyanate}} E(W_{\text{isocyanate}})$$  \hspace{1cm} (A.27)

In the above equations, $W$ refers to the weight attached to a randomly selected group; $E(W^{\text{in}})$ and $E(W^{\text{out}})$ are the expectation weights looking in and out of that randomly selected group respectively; $f$ is the functionality of isocyanate or polyol; $M$ is the molecular weight of the structure units; $\omega$ is the weight fraction of polyol or isocyanate; $\alpha_{\text{OH}}$ is the conversion of OH group; $\alpha_U$ and $\alpha_I$ are the conversions of isocyanate to polyurethane and isocyanurate respectively.

Combining the expression for the molecular weight and the adiabatic kinetic model, we can calculate the profile of the weight average molecular weight during reaction. The predicted molecular weight profiles for catalyst concentrations of 1.1 wt% and 0.44 wt% with a volume ratio of 2.4 are plotted in Figure A.10. For different volume
Figure A.10 Comparison of viscosity and molecular weight profiles as a function of catalyst concentration
Figure A.11 Comparison of viscosity and molecular weight profiles as a function of volume ratio
ratios. The viscosity and molecular weight profiles are shown in Figure A.11. At the gel point, both the viscosity and the weight average molecular weight approach infinity. So using the recursive method, we are able to predict the gel time. The predicted gel time for the catalyst concentration of 1.1 wt% is 68 seconds and for 0.44 wt% is 168 seconds. These values are very close to the measured gel time of 70 seconds and 172 seconds respectively. For different volume ratios, the difference between the measured and predicted gel time is also within 10 seconds. These results show that the recursive method works well for our reaction system and imply that there are no significant side reactions or nonidealities in the network formation of poly(urethane/isocyanurate).

CONCLUSIONS

The information on reaction kinetics and viscosity changes during resin cure is essential for controlling the molding process. The experimental data showed that both the catalyst concentration and the volume ratio of isocyanate to polyol have great effect on the reaction rate and rheological behavior of the poly(urethane/isocyanurate) resin. Increasing the catalyst concentration increases the reaction rate and decreases the gel time, while increasing the volume ratio of isocyanate to polyol decreases the reaction rate and increases the gel time. Trimerization depends on the diffusion effect resulting from the urethane formation. Viscosity rise for different catalyst concentrations at a constant volume ratio can be described as a function of temperature and conversion only.
Viscosity rise for different volume ratios at a constant catalyst concentration, however, needs to be described as a function of temperature and molecular weight.

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REFERENCES

**APPENDIX B. UV Absorption Spectra**

Figure B.1. Absorption spectra of the individual components and the mixture in the solution of methanol at 20°C
Figure C.1. Comparison of the effect of 2,4-P and BQ on reaction kinetics (55% VE, w/o promoter, scan @ 2C/min)