INFLUENCE OF PROCESSING VARIABLES ON PROPERTIES OF
COMPOSITES MANUFACTURED BY
RESIN TRANSFER MOLDING AND
STRUCTURAL REACTION INJECTION MOLDING

A Thesis

Presented in Partial Fulfillment of the Requirements for
the Degree Master of Science in the
Graduate School of The Ohio State University

by


* * * * *

The Ohio State University

1991

Master's Examination Committee: Approved by

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To my parents
ACKNOWLEDGEMENTS

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  2. Polymer Composite manufacturing.
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CHAPTER I
INTRODUCTION

1.1 Introduction to composites

A composite material can be defined as a material that consists of two or more physically distinct materials, having a recognizable interface between them. However, because composites are usually used for their structural properties, the definition can be restricted to include only those materials that contain a reinforcing agent and a compatible matrix binder (i.e. a resin) [Lubin 1982, Reinhart 1987a]. Due to the desirability of lightweight materials for structural applications, fiber reinforced polymeric composites have become very popular. Excellent weight - to - performance ratios, cheap tooling, short mold manufacturing and tryout time, design flexibility, non - corrosive nature and the ability of replacing multiple metal components by a single more complex part (i. e. part consolidation) are some of the advantages offered by composite materials.

The first polymeric composite used in history was a binder for reeds in boat building in 5000 B. C. in the Middle East. But polymeric composites were not widely applied in human life until the 20th century. World war II promoted a need for materials with improved structural properties. In response, fiber-reinforced plastics (FRP) were developed
[Reinhart 1987a]. By the end of the war fiber-glass reinforced plastics were applied successfully for structural applications. Polymeric composites have rapidly become the most important material in many industries. They have entered civilian life as a material used in the manufacture of boats, cars, appliance housing, storage containers and many other items [Lubin 1982].

1.2 Conventional manufacturing processes for continuous fiber reinforced composites

A host of processes exist for the fabrication of continuous fiber reinforced composite components. The two most common are hand or machine lay-up and filament winding. In lay-up, material in the prepreg form is cut and laid up, layer by layer, to produce a laminate of desired thickness. In filament winding, a fiber bundle is impregnated with resin and wound on a mandrel to produce desired shape, such as pressure vessel, or helicopter rotor blade [Schwartz 1984].

The fiber placement process is followed by curing. Filament wound parts may be cured at high temperatures in open oven. Lay-ups are most commonly consolidated by applying heat and pressure in an autoclave. There are also special fabrication processes such as pultrusion, that combine fiber placement, consolidation and cure in one continuous operation [Reinhart 1987a].
1.3 Mass production of polymeric composites

Many early uses of composites were in the aerospace industry, where only a small number of parts are needed and performance rather than cost, ease and speed of manufacturing, tends to be of primary concern. Hence traditional processes such as lay-up are not a major drawback. However, when composites are to be used in high volume applications, such as automobile applications, the first challenge to be met is producing them rapidly and inexpensively.

Among various mass production techniques, resin transfer molding and structural reaction injection molding have been recognized as relatively new but very high potential processes to fulfill these needs.

1.3.1 Reaction injection molding

Reaction injection molding (RIM) is a polymer manufacturing process in which two or more ratio controlled monomer streams are metered and then impingement mixed under high pressure in a mixhead. The mixed materials flow into a mold where reaction is a diffusion controlled polymerization and gelation occurs in a very short period of time. This one step operation from monomer to finished product is shown schematically in Figure 1.1 [Lee et al. 1980]. The advantages of the RIM process include low energy requirements, low clamping pressure and temperature and flexibility in designing molds for complex parts [Scrivo 1986].
Figure 1.1  Schematic of RIM and its modifications (SRIM / RRIM) for the manufacture of composites [Lee et al. 1980]
1.3.2 Reinforced RIM and Structural RIM

The most popular resin system used in RIM is polyurethane. Polyurethanes have an inherent disadvantage due to their soft nature. Also, polyurethane's high coefficient of thermal expansion, its distortion due to creep, and an unsuitable high temperature modulus have limited the acceptance of RIM urethanes in applications requiring temperature insensitivity and high rigidity [Molnar 1988]. In order to enhance physical and mechanical properties, fillers or fibrous reinforcements are added to the resin and then the resin is cured. The reinforcements not only lower the plastic's coefficient of thermal expansion, but also provide the added benefits of increased modulus [Houston 1977].

Fillers, such as glass microspheres, flake glass, mica and calcium carbonate particles and fibrous reinforcements can be added to RIM parts in one of the two ways.

In reinforced RIM or RRIM, milled or chopped fiber reinforcement, usually glass fibers, are added into one or both monomer streams before they enter the mold. The fiber reinforcement which is trapped in the resin as it vitrifies is distributed randomly in the composite.

Addition of reinforcement into the streams for RRIM requires change in the design of processing equipment. Addition of reinforcement increases viscosity of monomer streams [Leidtke 1978]. The reinforcement is usually very abrasive and results in high wear rates of the injection equipment [Rupel 1989]. Clogging of orifices, fiber length attrition and fiber settling are some other problems. All these make the
use of standard RIM equipment quite unsuitable [Simkins 1979]. Some of the processing problems can be eliminated by using "L" shaped mixhead, wherein the fibers are added in the second chamber of mixhead [Molnar 1988]. However flow in the mold leads to excessive orientation of fibers in the direction of flow and this leads to directional physical properties and uneven shrinkage in the molded part [Macgreger & Parker 1979]. Another major drawback of RRIM process is that only short fibers or flakes can be used, whereas the best properties are achieved with long fibers [Macosko 1989].

A solution of these problems is to place the fibers in the mold and then inject reactive monomers into them. This process is known as structural RIM (SRIM).

Figure 1.2 displays schematic of SRIM process [Macosko 1983]. A fiber preform is placed into the empty mold cavity and the mold is then closed. Pressure is required to close the mold and compact fiber mats. The reactive monomer mixture is then injected into the mold. The part is then ejected from the mold [Macosko 1989].

Table 1.1 gives typical properties of SRIM composites for the four most commonly used resins [Macosko 1989]. SRIM composites have higher fiber content than RRIM, because there is no need to pump fibers into the mold. Fiber weight percent of 60 and higher are reported in literature. [Gonzalez & Macosko 1983, Slocum et al. 1986]. Because of higher fiber content and continuous long fibers, tensile strength and
Figure 1.2  Schematic diagram of the SRIM process [Macosko 1983]
<table>
<thead>
<tr>
<th>Property</th>
<th>Isocyanurate</th>
<th>Urethane</th>
<th>Acrylamate</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random glass mat (wt%) (3 mm thick part)</td>
<td>38</td>
<td>44.8</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.54</td>
<td>1.53</td>
<td>1.46</td>
<td>--</td>
</tr>
<tr>
<td>Void (vol %)</td>
<td>1.5</td>
<td>1.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$E_f$ (MPa at 25°C)</td>
<td>8,100</td>
<td>9,600</td>
<td>8,700</td>
<td>9,200</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>150</td>
<td>150</td>
<td>125</td>
<td>160</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>7.3</td>
<td>2.0</td>
<td>2.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Izod impact (J/m)</td>
<td>510</td>
<td>660</td>
<td>790</td>
<td>~ 800</td>
</tr>
<tr>
<td>Heat distortion temperature ($^\circ$C)</td>
<td>184</td>
<td>189</td>
<td>240</td>
<td>&gt; 200</td>
</tr>
<tr>
<td>Thermal expansion coefficient (m/m$^\circ$C)</td>
<td>~ 20</td>
<td>27</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>
flexural modulus of SRIM parts are much higher than those of RRIM parts.

Typical processing conditions for the four systems described in Table 1.1 are shown in Table 1.2 [Macosko 1989]. The viscosities are somewhat lower and gel times longer for SRIM resins than for typical RIM resins. This aids penetration of resin into the fiber mats [Macosko 1989]. Mold temperature and pressure are similar to RIM and hence conventional RIM equipment can be used quite satisfactorily [Ellerbe 1987]. To compress the fiber mats SRIM requires clamp pressure of about 1 MPa, about twice of that for RIM. Cycle times are of the order of 1-5 minutes. This combined with all the other advantages, make SRIM very attractive to the automotive industry [Nelson 1987].

1.3.3 Resin transfer molding

The schematic of a basic resin transfer molding (RTM) process is shown in Figure 1.3. In the RTM process a catalyzed resin is injected into a closed mold filled with dry fiber reinforcement. Once the resin has completely filled the mold, the injection process is stopped and the part is allowed to cure [Coulter & Gucer 1988]. In most RTM operations elevated temperatures are maintained throughout the process to reduce viscosity during filling and induce cure. When the part has gained sufficient strength, it is demolded and the process is repeated.

RTM process is similar to SRIM in principal. The key difference is that SRIM uses a RIM machine to fill the mold and the injection pressure is very high (of the order of 2.4 MPa). Here the chemical reaction is
<table>
<thead>
<tr>
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<th>Urethane</th>
<th>Acrylamate</th>
<th>Epoxy</th>
</tr>
</thead>
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<td><strong>Viscosity at $T_0$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A side (mPa.s)</td>
<td>130</td>
<td>175</td>
<td>250</td>
<td>100</td>
</tr>
<tr>
<td>B side (mPa.s)</td>
<td>45</td>
<td>50</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td><strong>Wt. ratio A / B</strong></td>
<td>2.24</td>
<td>1.18</td>
<td>2.0</td>
<td>3.6</td>
</tr>
<tr>
<td><strong>$T_0$ ($^\circ$C)</strong></td>
<td>25</td>
<td>25 - 40</td>
<td>25</td>
<td>60 - 70</td>
</tr>
<tr>
<td><strong>$T_m$ ($^\circ$C)</strong></td>
<td>95</td>
<td>50 - 70</td>
<td>100</td>
<td>120 - 130</td>
</tr>
<tr>
<td><strong>Mold pressure (MPa)</strong></td>
<td>1 - 5</td>
<td>--</td>
<td>0.2 - 0.4</td>
<td>--</td>
</tr>
<tr>
<td><strong>Gel time (s)</strong></td>
<td>8</td>
<td>3 - 60</td>
<td>10 - 20</td>
<td>25</td>
</tr>
<tr>
<td><strong>Demold time (s)</strong></td>
<td>45</td>
<td>30 - 300</td>
<td>50 - 70</td>
<td>75 - 300</td>
</tr>
</tbody>
</table>
Figure 2.3  Schematic diagram of the basic RTM process  
[Coulter & Guceri 1988]
activated by impingement mixing. Because of high injection pressures used in SRIM, steel molds held together by hydraulic press are used. RTM on the other hand uses heat activated resin systems and injection is under low pressure (of the order of 0.3 MPa). Hence molds are made of low cost material like epoxy and are often held together by manual clamps. Another key difference is in the filling time. In RTM, filling times may be longer than 15 minutes, whereas in SRIM they are a few seconds [Gonzalez - Romero & Macosko 1990]. Table 1.3 shows a comparison of RTM process to SRIM process for an isocyanurate resin [Macosko 1989].

RTM process offers many advantages over conventional fabrication techniques, such as:

- Lower parts, equipment and tooling cost
- Closed mold process with very small emission of solvents
- A wide range of possible resin types (polyester, vinyl ester, methacrylates, acrylamates and epoxy)
- A wide range of reinforcement types (glass, carbon and aramid) and forms (random, unidirectional, woven, knitted, 3-dimensional woven)
- Very large parts and complex geometry possible
- Ability to include encapsulated cores, ribs and inserts into the part
- Lower void contents (< 1%) in the part
- Tight tolerance
- Good surface quality on both sides
- Simple curing cycles
<table>
<thead>
<tr>
<th></th>
<th>RTM</th>
<th>SRIM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment cost</td>
<td>$ 30,000</td>
<td>$ 500,000</td>
</tr>
<tr>
<td>Flow rate (Kg / min)</td>
<td>2.3</td>
<td>55</td>
</tr>
<tr>
<td>Mixing</td>
<td>static mixers</td>
<td>impingement</td>
</tr>
<tr>
<td>Mold pressure (MPa)</td>
<td>0.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Void content (vol%)</td>
<td>0.1 - 0.5</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Mold materials</td>
<td>epoxy</td>
<td>steel</td>
</tr>
<tr>
<td>Mold temperature (°C)</td>
<td>25 - 40</td>
<td>95</td>
</tr>
<tr>
<td>Component viscosities (MPa.S)</td>
<td>100 - 550</td>
<td>&lt; 200</td>
</tr>
<tr>
<td>Cycle time (min)</td>
<td>10 - 60</td>
<td>2 - 6</td>
</tr>
</tbody>
</table>
• Controllable and predictable fiber content

Recent enhancement to the basic RTM process have made fabrication of advanced composite parts even more attractive. These modified manufacturing techniques include:

(a) Vacuum assisted resin injection

In order to facilitate resin flow, vacuum can be applied to the mold to extract air, and then resin is injected at very low pressure, often below atmospheric pressure [Reinhart 1987b]. The results are not always satisfactory because it is difficult to completely evacuate a large mold cavity with fiber reinforcement. The remaining air tends to be trapped in the mold near the end of mold filling. Also vacuum creates foaming problem during resin injection. The process may also result in resin clogged vacuum pumps. Because of all these problems the vacuum assisted resin injection (VARI) process has not become widely accepted [Coulter & Guceri 1988].

(b) High speed RTM

High speed RTM (HSRTM) process, shown in Figure 1.4, uses a three-dimensional preform with foam cores and attached inserts, which is placed in the mold. Following minimal hand arrangement of preform, mold is closed and resin is injected. Molding is carried out at high temperature to minimize cure time. Fiber contents range from 35% to 60% by weight. At high fiber weight fraction, mold is left open slightly during resin injection and then closed completely to promote rapid mold filling. Cycle
Figure 1.4  Schematic of high speed RTM [Reinhart 1987b]
times range from 1 minute for small parts to 8-12 minutes for complex structures [Reinhart 1987b].

(c) Thermal expansion RTM

Thermal expansion RTM (TERTM) process is shown schematically in Figure 1.5 [Coulter & Guceri 1988]. The process consists of four steps. First a rigid thermoelastic foam is formed to a desired shape. It is surrounded with a woven, knotted or braided fabric reinforcement and then the resultant unconsolidated structure is placed into a mold. Low viscosity thermoset resin is then injected into the mold and mold is heated. This causes foam core to expand, creating the flow of resin which fills the mold. Resin is then allowed to cure. TERTM has been used successfully for large scale production of lightweight hybrid foam core composite parts.

(d) Ultimately reinforced thermoset resin injection

A schematic diagram of the ultimately reinforced thermoset resin injection (URTRI) process is shown in Figure 1.6 [Coulter & Guceri 1988]. In this process, a syntactic foam core is first cast from high temperature epoxy embedded with hollow glass microspheres. Next, the core is wrapped with high modulus single component or hybrid reinforcement layers made up of graphite, kevlar, and/or glass fibers. The entire assembly is then placed in a mold and an advanced resin system made of epoxy, bismaleimide or quasi-prepolymer is injected. After subsequent curing, which takes between 5 and 10 minutes, the finished part is removed from the mold.
Figure 1.5  Schematic of thermal expansion RTM
[Coulter & Guceri 1988]

Figure 1.6  Schematic of ultimately reinforced thermoset resin injection process [Coulter & Guceri 1988]
1.4 Status of RTM / SRIM industry

Automotive molders currently produce composite components and, in several cases, large vehicle structures, using RTM / SRIM processes [Hartung 1979, Sayama et al. 1981]. This industry is attracted to RTM / SRIM's low energy requirements (1/4 of the energy necessary to produce a comparable steel part), and low clamping pressure (1/40 of those needed for production of similar compression molded composites and 1/100 of those needed for thermoplastics injection molding). Along with the backing of such a large and powerful industry has come the impetus to develop all aspects of RTM / SRIM technology [Damani 1989]. Automotive applications include bumper beams, hood, instrument panel support, quarter inner and outer panel, outer doors and roof. More applications are expected in the future because of imperatives of more aggressive styling, shorter development cycles, and more limited-edition models [Miller 1990]. Another reason for increased usage of RTM / SRIM process is due to restriction of styrene emissions, both in-plant and into the environment. Table 1.4 compares RTM process with open mold process such as hand lay-up [Miller 1990].

Until recently compression molding of sheet molding compound (SMC) was the only choice for large exterior panels because of surface finish, reproducibility and production speed. RTM has become a serious contender for such parts due to the advent of low profile resins, preform technology and the application of automotive quality control methods. Cycle times for class A parts are 10-25 minutes for RTM and 1-2 minutes for SMC. However for production volume under 20,000 vehicles / year,
<table>
<thead>
<tr>
<th></th>
<th>RTM</th>
<th>Open mold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical annual volume</td>
<td>250-10,000</td>
<td>up to 750</td>
</tr>
<tr>
<td>Equipment costs</td>
<td>$ 10-25 K</td>
<td>$ 4-8 K</td>
</tr>
<tr>
<td>Core and inserts capabilities</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Quality control</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Styrene emissions</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Two finished surfaces</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>
the cycle time disadvantage is more than offset by 50-75% savings in tooling costs, 50% shorter tooling lead time, and lower equipment costs.

Another advantage of RTM over SMC is the ability to encapsulate foam cores and other types of structural inserts and produce complex parts in a single molding operation. With SMC, on the other hand, the part must be made in two pieces (an outer skin and a reinforcing inner piece), requiring a separate mold for each part and assembled by adhesive bonding.

SRIM is a faster process than RTM. SRIM use in automotive industry is limited to non-appearance parts. RTM on the other hand can be used for class A parts. Table 1.5 compares SMC, RTM and SRIM processes for automotive parts [Miller 1990].

In addition to automotive industry, RTM / SRIM processes are becoming popular in aerospace and defence related industries as an alternative to hand lay-up of prepreg and autoclave to cut costs, improve dimensional stability, and avoid time-consuming and potentially dangerous situations [Wilder 1989].

1.5 Research issues in RTM / SRIM and scope of study

Although RTM and SRIM are already being used in industry for small quantity productions, the processes have not been thoroughly analyzed. Relatively little useful technical information appears to be available from which appropriate choice of process and material variables can be made [Hayward & Harris 1990]. Selection is often carried out
<table>
<thead>
<tr>
<th></th>
<th>RTM</th>
<th>SRIM</th>
<th>SMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class A</td>
<td>G-E</td>
<td>P-F</td>
<td>E</td>
</tr>
<tr>
<td>Complex shapes</td>
<td>G-E</td>
<td>G-E</td>
<td>F-G</td>
</tr>
<tr>
<td>Ribs, bosses</td>
<td>F</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Cores, inserts</td>
<td>E</td>
<td>E</td>
<td>NA</td>
</tr>
<tr>
<td>Selective reinforcement</td>
<td>E</td>
<td>E</td>
<td>P-F</td>
</tr>
<tr>
<td>Annual volume range</td>
<td>to 15K</td>
<td>to 20K</td>
<td>over 75K</td>
</tr>
<tr>
<td>Relative tool cost</td>
<td>1.0</td>
<td>1.0-1.2</td>
<td>3-6</td>
</tr>
<tr>
<td>Tool lead time</td>
<td>12-20</td>
<td>12-20</td>
<td>40-50</td>
</tr>
<tr>
<td>(weeks)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle time (minutes)</td>
<td>10-25</td>
<td>10-20</td>
<td>1-2</td>
</tr>
</tbody>
</table>

E = excellent; G = good; F = fair; P = poor
based on experience or on similar processes such as conventional reaction injection molding. Hence, there is a considerable potential for improving these processes through a greater technical understanding.

The composite manufacturing processes may be divided into two steps: mold filling and curing of the resin [Gonzalez - Romero & Macosko 1990]. The flow and cure of the resin has a dominant effect on the final microstructure, and, consequently, on the performance of composite parts. In most of the traditional polymeric composite manufacturing processes, such as, prepreg layup and SMC molding, fibers and resin are premixed for a prolonged time period. This provides intimate contact between the fibers and the resin, leading to good interface bonding and wetting. Thus an understanding of the resultant resin flow during processing is primarily needed to determine small scale fiber relocation and volume fraction variations. In RTM / SRIM, the reinforcements used are initially in an unimpregnated form, and it is the complete impregnation of these networks that is the ultimate goal of the process. Here wetting and mold filling occur simultaneously during resin injection process [Robertson 1988]. The reinforcement has very little time to interact with injected resin and this often leads to poor resin - fiber interface. As a result control of these competitive flows, i.e. mold filling and fiber wetting is an important issue in RTM / SRIM. Current problems in resin injection include incomplete fill, poor fiber wetting, mat distortion, and mold leakage.

Cure of thermoset resins utilizes heat to cause the reaction. The polymerization reaction being exothermic generates heat, which may
affect temperature uniformity of the composite. Controlling the curing step is essential in reducing the cycle time as well as preventing degradation of the material [Gonzalez - Romero & Macosko 1990]. In addition to the matrix curing, the interface reaction between fiber sizing and resin is also critical in RTM / SRIM. This is because resin solidification (i.e. gelation or vitrification) occurs in seconds (SRIM) or minutes (RTM). Hence the resin - fiber interface has to built up in such a short "wet time". Current problems in curing include non uniform cure in the part, low ultimate conversion, poor resin - fiber bonding and residual stresses.

It is well known that the ultimate mechanical properties of a fiber reinforced polymeric composites are determined to a large extent by the quality (adhesion) and quantity (wetting) of interfacial contact [Drazal & Rich 1982, Garton & Daly 1985, Chang & Jang 1990]. Hence it is very important to understand and manipulate the competitive flows (mold filling and fiber wetting) occurring during resin injection and the competitive reactions (matrix curing and resin - sizing reaction) occurring during the curing step. In order to reduce or eliminate some of the above mentioned problems, many processing variables, such as injection rate (or pressure), mold temperature (and fiber temperature), clamping force, mold cavity evacuation, are manipulated on a trial - and - error basis [Johnson et al. 1986]. The interaction of these variables with the governing phenomena and process issues are shown in Figure 1.7. In addition there are some important material variables. These include reinforcements (type of fiber reinforcement, orientation, surface treatment, ply stacking sequence,
Figure 1.7 Interactions among manipulated variables, controlled variables, governing phenomena, and process issues.
volume fraction), resin characteristics (type of resin, viscosity, gel time) and thermal characteristics of mold.

Studies of RTM / SRIM mold filling, flow visualization, fiber mat permeability measurement, and flow and curing simulation, have been reported elsewhere [Young et al. 1991, Lin 1991, Molnar 1988, Trevino 1990]. In this study a systematic investigation of the influence of important operating variables on final product quality was conducted. The process variables studied include resin injection pressure, and mold / fiber mat temperature. To avoid too much complexity, this study was aimed at non-aerospace type processes and materials. Hence focus was on glass fiber reinforcements and fiber weight fraction was low. Two different types of glass fiber reinforcements were used: random and unidirectional fiber mats. Resins chosen were commonly used commercial RTM / SRIM resins, polyurethane and polyurethane-unsaturated polyester hybrid resins. The influence of these variables on resin-fiber wetting and bonding was also studied. Tensile tests were conducted to study quality of composite samples prepared under varied conditions. Scanning electron microscopic analysis of composite fracture surfaces was carried out to investigate the degree of resin wetting and adhesion on individual fibers. In order to investigate the environmental effects on composite properties, water boil tests were carried out. Presented in this work are pertinent literature review, experimental procedure, results and discussion, and conclusions and recommendations on resin-fiber wetting and bonding in RTM / SRIM.
CHAPTER II
LITERATURE REVIEW

2.1 Resin injection step

In the resin injection step the resin flows through the fiber packed mold until it is completely filled. In general the incoming resin, fiber reinforcements and mold walls are at different temperatures. Hence, heat transfer takes place during the filling stage. Most suitable chemical systems for these kind of processes are thermosetting resins with low initial viscosity [Gonzalez & Macosko 1990]. If the reaction is so fast that the mold filling is not complete due to premature gelation, a phenomenon called "short shot" would occur.

2.2 Modelling of the filling step

Since the mold cavity in RTM / SRIM is filled with many fibers, it can be treated as a porous media. Figure 2.1 depicts the general configuration that is used in modelling the RTM / SRIM process as a flow through porous media [Coulter & Gucer 1988]. In the area of traditional composite manufacturing, many workers have utilized the porous medium flow approach to analyze the flow of resin during autoclave type processes [Loos & Springer 1983, Gutowski 1985, Gutowski & Cai 1988, 26
Figure 2.1 The general configuration for modelling RTM / SRIM mold filling process [Coulter & Guceri 1988]
Dave 1990]. The pores act like many tiny capillary tubes. Thus the fluid moves like a plug into the mold and there is no fountain flow. Several models are available in literature. The most common and simple one is based on D'Arcy's law [Michaels et al. 1982].

D'Arcy's law states that the volumetric flow rate \( Q \) through a constant area specimen is proportional to the cross-sectional area \( A \), pressure difference over the specimen \( \Delta P \) and inversely proportional to the length in a stream wise direction of the specimen \( L \) and the viscosity \( \mu \):

\[
Q = \left( \frac{KA}{\mu} \right) \left( \frac{\Delta P}{L} \right)
\]

...............(2.1)

\[
\frac{Q}{A} = \frac{Q}{WH} = V = \left( \frac{K}{\mu} \right) \left( \frac{\Delta P}{L} \right)
\]

...............(2.2)

\( V \) is average superficial velocity. The constant \( K \) with dimensions \([L^2]\) is termed the permeability. Permeability is a property of the porous material which characterizes how easily the fluid may flow through the material with an applied pressure gradient [Collins 1961].

In using D'Arcy' law for modelling, there is a problem determining the proper viscosity. Typically the mold and fiber reinforcements are at considerably higher temperature than incoming resin. Hence near the gate, resin flow will cool down the mat but far away the resin will be close to mold temperature. Hence it may be necessary to consider heat transfer during mold filling. Also viscosity will change due to chemical reaction. Variations of viscosity has to be taken into account, if there are
significant viscosity changes in the flow domain due to chemical reaction and / or the temperature variations. Also it should be noted that D'Arcy’s law assumes Newtonian behavior.

2.3 Experimental verification of D'Arcy’s law and fiber wetting

There have been a number of experimental investigations in which the flow behavior in fibrous porous media has been studied. Gonzalez (1983) observed that for the flow of water through a chopped strand fiber glass mat, D'Arcy’s law was obeyed. This result was obtained in liquid filled mats (i.e. saturated media). Adams and co-workers also found that D'Arcy’s law was obeyed in experiments carried out in an unsaturated porous media [Adams & Rebenfeld 1987, Adams et al. 1986]. Fracchia [1990] reports the same for experiments in a saturated porous media. Williams et al. [1974] observed conformity with D'Arcy’s law in both saturated and unsaturated media. An interesting observation in the study by Williams et al. was that the permeability was about three times lower for flow into unsaturated media than into saturated media. The reason for this is that the pressure to push liquid into a dry mat may be greater due to air bubbles trapped in between the fibers.

However, these results contrast with those reported by Molnar et al. [1989], Trevino et al. [1990] and Martin and Son [1986] who have observed flow behavior in both unsaturated and saturated porous media that deviates significantly from D'Arcy’s law.
These deviations may have occurred because flow in fibrous porous media differs from the idealized case of flow in homogeneous porous media for which D'Arcy's law is derived. The RTM / SRIM preform materials are heterogeneous in the sense that the network of fiber bundles that make up the global porous media are themselves porous. Each fiber bundle consists of a number of fibers. Hence two types of flow occur simultaneously in these materials. One is mold filling which involves distribution of resin throughout the entire cavity (the macro flow) and the other is wetting which involves penetration of resin into the fiber bundles (the micro flow). The macro flow is around the fiber bundles, whereas the micro flow is around the fibers in the bundles [Damani & Lee 1990]. This phenomenon is shown schematically in Figure 2.2. During the injection of resin into the mold, resin must quickly fill the mold and wet all the individual fibers before much reaction occurs. If the fibers are not completely wet with resin, the strength of composite part will be reduced [Macosko 1989, Drazal & Rich 1982, Chang & Jang 1990]. Poor wetting produces voids at the interface. Such voids cause stress concentrations and degrade composite performance [Zisman 1963]. In the absence of chemical bonding at the interface, interfacial properties are governed by the stick - slip behavior between the fiber and the matrix. This stick - slip behavior can be significantly affected by the extent of wetting the fiber undergoes.

Wetting is governed, primarily by the differences in surface tensions of the fiber and the resin. If the surface tension of the resin is lower than that of the reinforcement, wetting will occur [Elmendrop 1990]. The
Figure 2.2 Schematic displaying micro flow in a bundle and macro flow around a bundle [Damani & Lee 1990]
driving force for the resin impregnation process is capillary force [Macosko 1989]. A schematic of capillary effect is shown in Figure 2.3. If one assumes that the space between the parallel fiber bundles are cylindrical channels, the suction pressure developed due to capillary action is given by:

$$\Delta P_s = \left( \frac{2 \gamma}{R} \right) \cos \theta$$

.............(2.3)

Where $\gamma$ is the resin surface tension, $\theta$ is the resin - fiber contact angle, and $R$ is the effective radius of the channels. $R$ is usually of the order of fiber radius. It can be seen from equation 2.3 that a smaller contact angle yields a higher value of suction pressure, thereby improving wetting. Thus the ideal flow front, due to capillary effect, would be semi-circular, resulting in a contact angle of $0^\circ$. It is important to examine the wetting characteristics of a given resin to ensure that it will be effective in providing favorable contact angle.

2.4 Studies on micro flow

A complete analysis of resin flow through the unwetted fiber mats needs to consider not only the macro scale mold filling, but also the micro scale fiber wetting. The studies at micro level are aimed at investigating the motion of the advancing free surface around the fibers. Larson and Higdon [1986, 1987] characterized the porous media as tube banks and solved a viscous flow through the tube banks. Couland et al. [1988] used the same model with different sizes of cylinders in the flow field. Some researchers used a network model to solve two phase flow in porous
\[ \Delta P_s = \frac{2 \gamma}{R} \cos \theta \]

Figure 2.3 Capillary effect for different contact angles [Damani 1989]
media [Koplik & Lasseter 1984, Blumenfeld 1987]. By this method, the fingering effects and air entrapment during fluid flow can be studied. However, large amount of computation time is a major drawback of this model.

In RTM and SRIM, very little resin flow study has been carried out on the micro scale. The interaction of competitive micro and macro flows during resin injection was studied by Young [1991]. He found that during the resin injection process, the maximum inlet pressure was not obtained at the end of mold filling. After the mold filling process, if the resin injection was continued, the inlet pressure continued to rise and reached a steady state value after a period of time as shown in Figure 2.4. RTM / SRIM mold filling is an unsaturated flow process, regions of the preform close to the flow front may have apparent permeabilities equal to the unsaturated value, while in regions of the preform far behind the flow front the apparent permeabilities may be equal to the saturated value. As the advancing flow front encounters a fiber bundle, it may flow around it, entrapping a pocket of air as it does so. After the front surrounds and bypasses a fiber bundle, the fiber bundle is slowly impregnated with fluid. Thus at the end of mold filling, impregnation process is not complete and pressure continues to rise until the micro flow is complete. Figure 2.5 shows the pressure drop for flow through dry and wet fiber reinforcements [Young 1991]. The differences implied the interaction between the micro flow and the macro flow during mold filling.
Figure 2.4  A typical pressure curve in RTM / SRIM mold filling  
[Young 1991]

Figure 2.5  Inlet pressure vs. superficial velocity for 6 layers of 
Certain Teed - U750 (porosity = 73%)  [Young 1991]
Flow visualization studied by Molnar [1988] showed that evacuating mold cavity improved impregnation of fibers. For both evacuated and non-evacuated cavity, at low flow rate, flow in the fiber bundles (the micro flow) led flow between the fiber bundles (the macro flow) and the opposite results were obtained at a higher flow rate. Thus lower flow rate favored the micro flow.

Fracture surface analysis of composite samples by scanning electron microscopy [Damani 1989] showed that the fiber region in the direction of flow was much better impregnated than that antipodal to the flow. During resin injection, a combination of micro and macro flows may lead to some air being trapped at the bundle end away from the flow. This in turn, would lead to poor interphasial behavior at the side of the bundle away from the direction of flow.

2.5 Matrix curing and interface bonding

Although some reaction takes place during mold filling, most of the reaction occurs during the curing step [Gonzalez & Macosko 1990]. Temperature exotherm controls demolding time and may cause thermal degradation of the material. Controlling the curing step is essential in reducing cycle time as well as preventing degradation of the material.

In polymeric composite manufacturing, in addition to matrix curing, physical / chemical bonding between the resin and the fiber sizing also takes place. Thus there are two competitive reactions occurring during processing and the resin and fibers must be bonded quickly and securely
before the matrix resin solidifies. As pointed out earlier, solidification occurs in seconds in SRIM and in minutes in RTM. Because of the short "wet time", good interface bonding may have to rely on chemical interactions instead of physical interactions usually occurring in thermoplastic composites. Fiber sizings are used to improve the chemical and physical behavior at the interface. Because sizing chemicals are in the form of a thin solid coating on the fiber surface, they have to be compatible with the matrix resin in order for the resin molecules to penetrate in and chemical reaction to occur. It has been pointed out that as the resin is cast around the fiber, the initial interface between the resin and the fiber sizing will gradually change into an interphase in compatible systems (Figure 2.6, Drazal et al. 1983). The simultaneous diffusion and reaction of resin and sizing components across the interface is believed to lead to the formation of an interpenetrating polymer network (IPN). This diffusion governed process has to be completed within the "wet time" to ensure a good interface bonding. Better sizing compatibility, highly reactive functional groups in sizing chemicals and resins may all enhance such a process.

The most desirable interface is not the one that provides the strongest chemical bonding. Too strong an interphase will tend to drive a crack normal to the fiber [Drazal & Rich 1988]. The composite could be regarded to behave as a homogeneous material and crack propagation would be unstable. Poor bonding at the interphase would mean crack propagation along the interphase. Essentially, good adhesion results in
Figure 2.6  Schematic of formation of interphase from initial interface in compatible systems

[Drazal et al. 1983]
high shear strength but low fracture toughness and vice versa. Thus, the ideal interphase would have to lie between these two extremes.

2.6 Sizing and its functions

Sizings are an essential factor in fiber reinforced composite technology. They are critical in composite manufacturing and can have both negative and positive effects on composite properties. Historically, the primary function of sizing was meant to be an aid in improving the processing and to protect reinforcement from damage during processing. However, increasingly, it is being used as a tool in improving the chemical and physical behavior at the interface for different applications [Damani 1989].

Sizing is carried out on glass fibers for a variety of reasons. These include enhancing and catalyzing chemical interactions between the inorganic glass fiber and organic matrix resin, flexibilizing the brittle virgin fiber for processing, protecting it from abrasion, covering up surface imperfections and improving overall strength of bundles to ease processing. Modifications are often made to satisfy specific needs.

The sizing for commercial glass fibers consists of a film former, silane coupling agents, lubricants and additives such as anti - statics, defoamers and surface tension reducers [Plueddemann 1974]. The anti - statics work toward reducing charges that may develop due to friction between filaments in a strand. Lubricants prevent abrasion during handling and processing. Surface tension reducers improve wetting during mold filling. The silane coupling agent, as the name suggests, is
believed to provide linkage between the fiber surface and the resin. On one side it links itself to the inorganic glass fiber and on its other end, it has chemical groups that can react with the organic matrix resin. The bonding with the fiber is also due to van der Waal's forces and hydrogen bonding with the hydroxyl (-OH) groups [Plueddemann 1974]. Due to covalent bonding with the polymer in the matrix an entangled network is formed at the resin - fiber interface. This resists hydrolysis and leads to increased stability at the interface under unfavorable conditions [Hoh et al. 1986].

Currently, in most glass fiber reinforcements used in commercial RTM and SRIM, the sizing consists of an unsaturated polyester resin and polyvinyl acetate [Drum & Ulicny 1988]. If the matrix resin is an unsaturated polyester or polyvinyl ester, good compatibility can be expected at the resin - fiber interface. If the matrix resin is very different from the polyester, for example polyurethane or epoxy, interfacial strength may be rather ineffective.

The end groups on the silane coupling agent used in glass fiber sizing are often modified for use with different matrix systems. Examples are the use of an epoxy / polyether combination for use with epoxy resins, a fumarate / muconate combination for use with polyesters and acetate (or acrylate) / polyester (or polyether) combination for use with polyvinyl esters [Drumm & Ulicny 1989].

An important aspect in determining composite properties is the level of surface treatment. The effect of sizing concentration at the interface
on mechanical properties has been analyzed using a variety of mechanical tests [Norita et al. 1986]. Using different levels of surface treatment, it was concluded that increasing surface treatment improves all mechanical properties except those controlled by fibers.

2.7 Analyzing the interface

2.7.1 Spectroscopic analysis

The first step in analyzing the interface is to characterize chemical interactions at the interface, and to examine the chemical nature and reactivity of the sizing and resin matrix. Spectroscopic methods are very popular for kinetic and compositional analysis of the interface. Some of the spectroscopic analyses are suitable for analyzing surface chemistry, which is useful in evaluating fiber surfaces for reactivity and structural changes before and after specified treatments.

(a) Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is one of the most popular methods for chemical analysis. Although interfacial reactions were postulated long back, detection of these bonds was possible only due to the development of FTIR. With FTIR, it is possible to study the structure of adsorbed coupling agents on fibers and to obtain information on molecular structure and bonding at the interface [Ishida & Koenig 1978].

Matrix - sizing interaction was studied by Damani [1989] using FTIR. FTIR scans of polyurethane - unsaturated polyester hybrid resin
and commercial glass fiber sizing were run to quantify the consumption of polyesters and related components during curing. The enlarged portion of the spectra obtained with polyurethane and sizing is shown in Figure 2.7. The peak of importance is 982 cm$^{-1}$ and it can be seen that even after 22 minutes significant amounts of polyester remain in the system (resin gel time was less than 22 minutes). This shows that there is minimal interaction between the polyurethane resin and the sizing.

The IPN formed between an epoxy resin and a silane coupling agent has been studied using FTIR by Hoh et al. [1986]. FTIR spectroscopy with single reflection has been used to study kinetics of hydrolysis and condensation of high concentration aminosilanes [Ishida & Suzuki 1986]. It provides information about the changes in molecular structure of the aminosilane in water solution.

(b) Internal reflection spectroscopy

Internal reflection spectroscopy (IRS) has been used in conjunction with infrared spectroscopy to analyze thin surface layers in contact with the IRS element [Garton & Daly 1985]. In this technique an interface is created on the IRS element and information regarding its chemical composition and consumption of species is obtained. In this case, an aramid surface coating was obtained by dip coating the element using a solution of aramid fiber in sulfuric acid. A carbon fiber coating was simulated by coating the element with a solution of polyacrylonitrile. The epoxy layer was placed on top of these layers, thereby effectively simulating the resin-fiber interface in such systems.
Figure 2.7 FTIR spectra of polyurethane resin + commercial glass fiber sizing reacted at 80°C [Damani 1989]
(c) Solid state carbon13 nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is a rapid and sensitive analytical technique in the study of resin - fiber interface. Drum and Ulicny [1989] used NMR to study bulk coating on several commercially available glass fiber reinforcements. FTIR and NMR were used to identify the major components of the coatings. All of the coatings analyzed could be sorted into three classes of coatings which matched the matrix types recommended by the glass manufacturer. Hoh et al. [1986] used NMR to study the silane coupling agent / epoxy resin interface. It was concluded that Si - O - Si bonds are important in determining the rigidity or mobility of the interface. The entrapment of epoxy chains in the silane network leads to the formation of a pseudo - IPN.

(d) Other spectroscopic techniques

Diffuse reflection spectroscopy (DRIFT) relies on the measurement of reflected light from powdered sample radiated with light. DRIFT can be used to study the surfaces and interfaces of organic and inorganic materials [Makenzie 1984]. Laser Raman spectroscopy is a popular technique for the analysis of carbon fibers. It is frequently used to evaluate the lattice structure of carbon materials. It enables measurements of small particles or areas of interest down to 1 μm. It gives information of the lateral and depth distributions of the composition and structure of materials [Ishitani et al. 1986]. X - ray photoelectron spectroscopy (XPS) has been used to provide atomic and molecular information about the fiber surface [Drazal et al. 1982]. Secondary ion
mass spectroscopy (SIMS) has a high degree of sensitivity. It has been used for surface analysis of sizing agents and the study of surface oxidation reactions [Ishitani et al. 1986]. All these techniques are useful in determining the nature and functionality of the fiber surface. This information, in turn, helps in providing information regarding likely interactions, both, at the interface and during the formation of the interphase.

2.7.2 Mechanical analysis

Mechanical analysis serves two purposes: one is to test the changes in ultimate properties due to changes at the interface and the other is to test the interphase itself. Although there are a number of models of adhesion in literature, none are effective in relating the degree of fiber-matrix adhesion to composite mechanical properties or in predicting the level of fiber sizing or treatment required to obtain optimum properties. Majority of techniques available to characterize fiber-matrix adhesion can be grouped into either single fiber or composite methods.

2.7.2.1 Single fiber methods

(a) Fiber pull-out test

In the fiber pull-out experiment, a fiber is embedded in a matrix or disk of known geometry. The free end of the fiber is gripped and a steadily increasing force is applied in order to pull the fiber out of the matrix. The embedded fiber can be pulled out of the matrix as long as its length is below a critical length \( L_c \). Otherwise the fiber will break during
pull-out. The relation between the critical length and the interfacial shear stress is given by:

\[
\frac{L_c}{d} = \frac{\sigma_{fu}}{4\tau_i}
\]

\[
\text{.........(2.4)}
\]

Where, \(L_c\) is the critical length, \(d\) is diameter of fiber, \(\sigma_{fu}\) is the ultimate strength of the fiber and \(\tau_i\) is the interfacial shear strength. A schematic of the test and typical results are shown in Figure 2.8 [Piggot & Chua 1985]. The initial slope of the graph (M) gives interfacial shear stress:

\[
\tau_i = \frac{M}{\pi d^2}
\]

\[
\text{.........(2.5)}
\]

and the maximum force for fiber breakage (\(F_{\text{max}}\)) gives ultimate fiber strength

\[
\sigma_{fu} = \frac{F_{\text{max}}}{\pi d^2}
\]

\[
\text{.........(2.6)}
\]

In principal, this is a direct measurement method, but the success rate is poor. Special gripping technique have to be used to avoid fiber breakage, since the fracture strength of thin fiber is very low. Moreover only one data point is obtained in an experiment, making the process tedious and time consuming [Franco et al. 1991].

Recent development to overcome some of the difficulties have resulted in a method in which a fiber is pulled out of small droplets of resin attached to it. However, in this case, at the juncture of the fiber and the matrix a normal tensile stress exists, which is not encountered in actual
Figure 2.8  (i) Schematic of fiber pull out test, (ii) various methods of clamping fiber and (iii) typical results [Chua & Piggot 1985]
composite [Franco et al. 1991]. This tensile stress will tend to reduce the interfacial shear strength.

(b) Single fiber fragmentation test

This test uses a fiber totally encapsulated in a matrix coupon, to which tensile load is applied. The stress is transferred to the fiber through the interphase. As shown in Figure 2.9, the fiber axial stress rises from the ends until the fiber fracture strength $\sigma_f$ is reached. The fiber will then fracture at a position where fiber stress is maximum, depending on the fiber defect location and distribution and probability. Continued application of tensile stress to the specimen will result in repetition of fragmentation process until the remaining fiber fragment lengths can no longer build up enough tensile stress to cause any further failure with increasing strain [Drazal et al. 1982]. This final fragment length is known as critical length $L_C$. Experiments yield a distribution of critical lengths. The interfacial shear strength is obtained by force balance as:

$$\tau = \frac{\sigma_f}{2} \left( \frac{d}{L_C} \right)$$

...............(2.7)

Where $\tau$ is the interfacial shear strength, $\sigma_f$ is the fiber fracture strength at the critical length $L_C$ and $d$ is the fiber diameter. Due to the non-uniform fragmentation of the fibers, a statistical analysis of the data is required. Drazal et al. [1982] used a two parameter Weibull distribution:

$$\tau = \frac{\sigma_f}{2\beta} \Gamma \left( 1 - \frac{1}{\alpha} \right)$$

...............(2.8)
Figure 2.9  
(i) Schematic of single fiber fragmentation test and (ii) typical results [Damani 1989]
where $\alpha$ and $\beta$ are the Weibull shape and scale factors and $\Gamma$ is the gamma function [Cohen 1978].

This method assumes that the matrix surrounding the fiber behaves as a perfectly plastic material. The shear stresses at the interface are considered to be constant along the short fiber critical length. Thus the technique yields an average value of the interfacial shear strength.

The advantage of this technique is that a large number of data points are obtained from each test coupon. Also in the case of transparent matrix, induced optical anisotropy on the matrix surrounding the fiber allows photoelastic observations to be made. Limitation of transparent matrix has been overcome in the case of carbon fiber reinforced samples due to recent development in acoustic emission [Drazal et al. 1983].

(c) Other single fiber methods

Another technique to determine interlaminar shear strength is shown in Figure 2.10. In (i) test piece is a rectangular prism matrix in which fiber is buried, and a compressive load is applied to it in the direction of fiber axis. The difference between the fiber and the matrix causes shear stress on the end face of the fiber. The interfacial shear strength is measured by the compressive load value at which the fiber peels off from the matrix when the load is increased and is given by:

$$\tau = 2.5\sigma_c$$

...............(2.9)
Figure 2.10  Single fiber specimens (i) rectangular, (ii) curved neck, (iii) trapezoidal [Yosomiya et al. 1989]
where $\sigma_c$ is the compressive stress applied to the test piece [Yosomiya et al. 1989].

In the case of (ii), when a compressive load is applied to the end face of the test specimen, the difference in Poisson's ratio value between the matrix and the fiber causes tensile stress in the interface between them. Interfacial tensile strength can be obtained by the load at which the fiber peels off from the matrix when the compressive load is increased and is given by:

$$\sigma_a = \frac{\sigma_s (\nu_m - \nu_f) E_f}{(1 + \nu_m) E_f + (1 - \nu_f - 2\nu_f^2) E_m}$$  \hspace{1cm} (2.10)$$

where $\sigma_s$ is the stress at the minimum cross-section of the test specimen, $\nu$ is Poisson’s ratio, $E$ is vertical elastic modulus, and the suffix $f$ and $m$ represent the fiber and the matrix respectively.

In the model (iii), when the compressive load is applied to the end face of the test piece, the interfacial shear stress $\tau_c$ induced at the minimum cross section between the fiber and the resin is given by:

$$\tau_c = -\frac{P}{nX_0^2T} \frac{E_f}{E_r} \frac{d_f}{4}$$  \hspace{1cm} (2.11)$$

where $P$ is the compressive load, $n$ the gradient of the test piece, $E_f$ and $E_r$ the elastic module of the fiber and the resin, respectively, and $d_f$ is the diameter of the fiber [Yosomiya et al. 1989].
Figure 2.11 shows the method of measuring the interfacial strength by the use of three fibers [Jarvela et al. 1983]. In this method, the fiber to be tested is adhered to two supporting fibers, with the matrix at right angles to the fibers. The interfacial shear strength is determined by the load at which the fiber to be tested is pulled out when a tensile load is applied to the fiber. The average interfacial shear strength is determined by the use of the maximum load $F_{\text{max}}$ for pulling out the fiber:

$$\tau_m = \frac{F_{\text{max}}}{\pi dD}$$

............(2.12)

2.7.2.2 Composite methods

It would be desirable to characterize fiber - matrix adhesion in an actual high fiber volume fraction composite in which the material has been subjected to processing and / or environmental conditions encountered in manufacturing and fabrication or service. Following methods can be used for this purpose.

(a) Microdebonding test

Mandell and co-workers proposed a method known as microdebonding test to characterize interfacial shear strength [Franco et al. 1991]. In this technique single fibers perpendicular to a cut and polished surface of a regular high fiber volume fraction composite are compressively loaded to produce debonding and / or fiber slippage. Individual fibers are selected on a polished cross section. A probe approximately 75% of the fiber diameter is placed on the fiber end and
Figure 2.11 Schematic of the three-fiber method used to determine fiber-resin bond strength [Jarvela et al. 1983]
load on the probe is slowly increased until debonding of fiber from the matrix is detected. A simplified finite element model is used to reduce the data. The model includes the fiber, surrounding matrix and average composite properties beyond the matrix. The advantage this technique offers is that it can be used to test samples obtained from manufactured composites. It allows determination of the interface strength due to fatigue, environmental exposure or possible monitoring interface properties of parts in service.

The Dow Chemical Co. has recently developed a microdebonding indentation system known as Interfacial Testing System (ITS), which allows automated positioning of fibers, loading probe and measurement of interfacial shear strength [Caldwell & Cortez 1988]. A diamond tipped stylus is used to push fibers from the surrounding matrix in microtomed samples.

Inspite of many advantages this technique offers, there are several technical concerns, such as effects of local fiber arrangement and fiber spacing, effects of thermal and elastic residual stresses, effects of flatness and smoothness of polished surface, probe realignment and positioning accuracy after each observation and accuracy in measurement of fiber diameter.

(b) Thermoacoustic method

Thermal expansion coefficients of fibers and resin are different. Above the glass transition temperature, the thermal expansion coefficient
of the polymer matrix can be higher than that of fibers by a few orders of magnitude. Hence localized heating can induce debonding at the interface. Localized heating can be coupled with acoustic emission events to detect interfacial debonding [Franco et al. 1991]. For a given temperature, thermally induced displacement of fiber and matrix will depend on interface strength. Therefore a relationship exists between the interface strength and temperature for debonding. A laser beam is focused on a small area to minimize the size of heat damaged zone. The debonding is monitored using acoustic emission techniques.

(c) Short beam shear test

The short beam shear test can be used for evaluating interlaminar shear strength in composite containing high loading of continuous unidirectional fibers. This test is much like a three point bending test except that the sample has a small span to enhance interlaminar shear failure (Figure 2.12, Strong 1989). This test assumes that since there is compression on the top of the sample and tension on the bottom, a mid-plane at which shear occurs must be present. This shear at the mid-plane is the shear strength. This test does not measure interfacial bond strength but rather provides relative bond strengths in a given system for different bonding level.

(d) Transverse tensile test

This is a simple tensile test in which the composite sample is such that the fibers are oriented in a direction perpendicular to the applied force (Figure 2.13, Strong 1989). The test provides an indirect measure of the
Figure 2.12  Short beam shear test [Strong 1989]

Figure 2.13  Transverse tensile test [Strong 1989]
bond strength. Using untreated fibers, Elkin et al. [1969] found that an increase in fiber content tends to lower the transverse strength. Their results indicated that the transverse tensile strength is a sensitive one for assessing the quality of interphasic bonding.

The major difficulty with this test arises because of the large differences in moduli of the matrix and the fibers which may focus failure in the interfacial region but not exactly at the interface.

(e) Dynamical mechanical analysis

Dynamical mechanical analysis has been used to characterize interfacial adhesion through energy loss measurement [Chua 1987]. The quality of adhesion can be characterized by the loss tangent, $\tan \delta_{Tg}$ of the composite. The loss tangent is the measure of the fraction of energy dissipated as heat during oscillation. The peak in $\tan \delta$ is an indication of the onset of molecular mobility in the matrix and at the interface. Typical results from such a test are shown in Figure 2.14 [Garton & Daly 1985]. The behavior of the composite improves (the peak appears at a higher temperature) as the amount of moisture on the fibers is reduced.

2.7.3 Microscopic analysis

(a) Optical microscopy

Optical analysis of samples from single fiber fragment test can be used to obtain information about fiber fragmentation and stress transfer across the interface [Drazal et al. 1983, Drazal & Rich 1988]. The degree
Figure 2.14 Typical DMA results of carbon-epoxy composites

$\Delta$ : reinforced with "conditioned" fibers;

○ : reinforced with "semi-dry" fibers;

△ : reinforced with "vacuum dried" carbon fibers

[Garton & Daly 1985]
of stress transfer is measured by the amount of birefringence and the fiber fragment lengths. Higher the stress at the interface, lower the average and median fiber fragment length and stronger the birefringence. Optical microscope using polarized transmitted light are used to obtain micrographs displaying birefringence patterns at the interface. Figure 2.15 shows a typical micrograph [Rohatgi 1991]. It exhibits the various characteristics that can be studied qualitatively using such a photoelastic study and the inferences that can be drawn from it. Birefringence patterns due to stresses occur at the interface and in the surrounding matrix. The birefringence is strongest at the point of fiber breakage (easily discernible as the short, dark bands on the fiber) and weakest at halfway points between two breaks. The degree of birefringence (and hence level of stress) has been linked to the extent of stick - slip occurring at the interface [Drazal et al. 1983]. If there is very little slip at the interface, the stress transfer to the fiber will be high. Hence stronger birefringence implies lesser stick - slip and better compatibility at the interface.

(b) Other microscopic techniques

Scanning electron microscopy (SEM) is amongst the most popular techniques for analyzing the interface. It is used to observe failed surfaces to evaluate interfacial behavior. The degree of interaction is gauged by the amount of fiber pull out and matrix resin adhesion to fibers [Tse et al. 1986]. Transmission electron microscopy (TEM) has been used to observe failure paths at the interface in graphite fiber - epoxy composites [Drazal et al. 1983].
Figure 2.15 Typical optical micrograph showing birefringence pattern [Rohatgi 1991]
2.8 Environmental effects on composite materials

Composite materials must survive in the environment to which they are subjected at least as well as the conventional materials they replace. Moisture and temperature are two key environmental concerns in designing composite structures [Schwartz 1984]. Composites undergo degradation in mechanical properties upon exposure to water. Degradation may occur in both strength and stiffness. Increasing the temperature tends to accelerate effects of degradation. This provides a basis for short time tests to obtain an estimate of the effects of extended immersion at normal temperatures. It is generally accepted that a "two hour water boil" is equivalent to about one month's exposure to water at room temperature [Fred 1967].

2.8.1 Effect of water on different components of composite

(a) Effect on resins

To a varying extent, resins used in composites are water sensitive. In general resins such as, epoxy, polyester, absorb water and suffer some degree of degradation both in strength and stiffness. At room temperature these effects are only slight and the water absorption process may continue for a long period of time and for some resin systems equilibrium may not be attained for months or even years [Lubin 1982]. Strength degradation tends to level off at long time. It has been noted that many types of resins show "recovery" effects in that samples which show
degradation in properties upon water immersion recover from this deterioration upon drying [Fred 1967].

(b) Effect on glass fibers

Glass fibers may also be degraded by water immersion. Immersion in water acts to reduce the strength of glass fibers by reducing the effective cross section. Since the attack progresses inwards from the surface, the smaller the fiber diameter, the more marked the effect. This type of degradation is not reversible, since it is corrosive in nature. The effect on glass fiber also depends on the presence (or absence) of different coupling agents, which are applied to glass fibers to improve bonding and increase water resistance.

(c) Effect on fiber - resin interface

It has been long recognized that the interaction at the interface exerts a strong influence on wet - strength retention of the composites. Composite fabricated with untreated fibers are particularly sensitive to water immersion. Use of coupling agents have been shown to improve the wet strength retention [Fred 1967].

The water sensitivity of composites is also affected by resin content. In general, it has been found that increasing resin content tends to decrease water sensitivity [Schwartz 1984]. Even more important factor is void content, which, if excessive, can seriously increase the water sensitivity of a composite.
2.8.2 Mechanism of water penetration

Penetration of composite materials by water can occur by the following two general processes:

(a) Diffusion

The transport of water through a composite free of defects normally occurs by a process of activated diffusion. The permeate dissolves in the surface layers of the composite and migrates into the bulk of the material under a concentration gradient. The penetration rate in diffusion process increases exponentially with temperature but is essentially independent of hydrostatic pressure [Chamberlain 1967].

(b) Poiseuille flow

The penetration of water into a composite structure through cracks or pinholes in the matrix is generally considered to occur by capillary or poiseuille type of flow [Chamberlain 1967]. This type of flow could also occur at the glass fiber - resin interface, resulting in the so called "wicking effect". The rate of water penetration by this mechanism is a direct function of hydrostatic pressure. The water penetrates composites more readily at the resin - fiber interface than by diffusion through the matrix.

2.8.3 Mechanism and effect of water attack

The mechanism of degradation of composites by water is complex. A number of mechanistic theories have been proposed and these are discussed below.
(a) The resin phase

Water immersion can cause resin swelling, plasticization, and degradation in strength and stiffness. In the case in which no chemical changes occur due to water immersion (such as hydrolysis of chemical bonds) these effects are reversible.

(b) The reinforcement phase

The effect of water immersion on reinforcement was discussed earlier. Any decrease in properties of fibers will result into the decrease in composite properties. Also this type of degradation is not reversible.

(c) The interface

The most important factor in degradation of composite in water is the action of the water at the fiber - resin interface. It has been proposed that a primary effect of water entering composite is chemical interaction at the interface. Thus, if a coupling agent acts to form an Si--O--Si bond at the glass surface, water could cause bond scission which could result into complete debonding between the matrix and the glass fibers. This would result in a decrease in stress transfer efficiency. This type of mechanism requires reformation of Si--O bonds between the coupling agent and the glass fibers, or at least formation of secondary bonds of some type, to explain recovery of composite properties on drying [Chamberlain 1967].
If it is assumed that interaction at the interface does not involve primary chemical bonding, but rather secondary bonding, such as hydrogen bonding or van der Waal's force interactions, then the interposition of medium of high dielectric constant, such as water, could cause effective lessening of the interactions by weakening of Coulomb forces. Also the water molecule might offer a competitive interaction in which hydrogen bonding could occur between the water molecules and silane groups on the glass on the one end, and polar groups in the resin phase on the other. This mechanism would also tend to weaken the resin-fiber bond and result in degradation of composite properties. Interactions of these types also require reversibility upon removal of water to explain recovery effects.

Water at the interface also acts as a lubricant and reduces stress transfer efficiency. Recovery effects would occur upon removal of water. In general all these mechanisms contribute to degradation to a varying extent [Lubin 1982].
CHAPTER III
EXPERIMENTAL

3.1 Materials

In this study, E-glass fiber reinforcements were used: a continuous random fiberglass mat (OCF M8610) and a stitched unidirectional fiberglass mat (CoFab A0108). These fiber mats are shown in Figure 3.1. They will be referred to as random and unidirectional fiber mats. The fibers in these mats are sized with a combination consisting of a silane coupling agent and components aimed at improving compatibility with unsaturated polyesters. These are used widely in present applications with SRIM and RTM.

The two matrix resins used in this study were polyurethane (PU) and polyurethane-unsaturated polyester (PU-UPE) hybrid. The polyurethane resin is based on a liquid form of diphenylmethane diisocyanate (MDI, 143-L, Dow Chemicals, f = 2.3, "A" side) and a polyester based triol (TONC - 310, Union Carbide, f = 3.0, "B" side) at stoichiometric ratio. The triol, TONE 310, has an average molecular weight of 900 and the diisocyanate has a molecular weight of 287. Stoichiometric ratios of these materials are given in the following table.
Figure 3.1 Reinforcements used in the study (a) continuous random fiberglass mat (OCF M8610) and (b) stitched unidirectional fiberglass mat (CoFab A0108)
Table 3.1  Materials used in urethane reaction

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins : Triol (TONE - 310, f = 3.0)</td>
<td>67.21</td>
</tr>
<tr>
<td>MDI (143 - L, f = 2.0)</td>
<td>32.79</td>
</tr>
</tbody>
</table>

The basic reaction which forms the urethane linkage is shown below:

- NCO + HO \[\xrightarrow{\text{Catalyst}}\] - H - C - O -

The polyurethane - unsaturated polyester hybrid was obtained by adding 50 % by weight of unsaturated polyester resin to the polyurethane resin and mixing them thoroughly. It forms an interpenetrating polymer network (IPN). The unsaturated polyester resin used was based on Ashland Chemicals' Q 6585 whose structure is shown below:
\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{\[C - CH = CH - C\]} & \quad \text{CH}_3 \\
\text{Maleic anhydride} & \quad \text{Propylene glycol}
\end{align*}
\]

This resin is a 1:1 mixture of propylene glycol and maleic anhydride containing 35% by weight styrene, which has an average of 10.13 vinylene groups per polyester molecule. The average molecular weight of the polyester is 1580 gm / mole and the equivalent molecular weight / (mole C=C) is 150 gm / mole.

Both polyester and styrene monomer were used as received without removing the inhibitor. The molar ratio of styrene / polyester resin was chosen to be 2:1. The Q 6585 resin and styrene were weighed and mixed in a flask with the appropriate weight ratio, which is given in the following table.

<table>
<thead>
<tr>
<th>Material</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q 6585</td>
<td>64.1</td>
</tr>
<tr>
<td>Styrene</td>
<td>35.9</td>
</tr>
</tbody>
</table>
The prepared UPE resin was stored in refrigerator.

A low temperature initiator system, 2,5 dimethyl-2,5 bis (2-ethyl-hexanoyl-peroxy) hexane (USP 245) was used to hasten the polyester reaction at a concentration of 1.0 % by weight of UPE resin. USP 245 has a molecular weight of 431. Dibutyltin dilaurate (T - 12) was used as the catalyst for polyurethane reaction at a concentration level of 1.64 % by weight of polyurethane resin. The composition of polyurethane - unsaturated polyester hybrid is shown in Table 3.3.

Table 3.3 Composition of PU - UPE hybrid

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU resin : Triol (TONE - 310)</td>
<td>33.61</td>
</tr>
<tr>
<td>MDI (143 - L)</td>
<td>16.40</td>
</tr>
<tr>
<td>UPE resin (2:1 mole ratio of Q6585 to styrene)</td>
<td>50</td>
</tr>
<tr>
<td>Catalyst : T - 12</td>
<td>1.64 % by weight of PU resin</td>
</tr>
<tr>
<td>Initiator : USP 245</td>
<td>1.0 % by weight of UPE resin</td>
</tr>
</tbody>
</table>

The triol was degassed at 333.15 K (60°C) for 5 hours and MDI at room temperature for 3 hours to get rid of dissolved moisture and air. Care was taken during mixing and pouring resins to avoid formation of
bubbles. All chemicals used in tests involving comparison came from the same batch. This was necessary to avoid minor variations that could occur between batches. Table 3.4 is a summary of materials used in this work.

3.2 Rheological measurements

A Rheometrics Dynamic Analyzer (RDA model 700) in the oscillatory mode was used to follow the rheological changes and gelation. The sample was assumed to gel at the point at which the storage shear modulus (G') and the loss shear modulus (G'') intersected.

RDA - 700 consists of a test station, computer and optional input / output devices for entry, display and storage of test parameters and results. The test station consists of an environmental chamber, servo motors, transducer and electronics to monitor the temperature and deformation history of the sample under test and to detect the resulting stress. The computer controls the test sequence, makes measurements, and analyzes the resulting data. The test sequence and parameters are programmed by the operator from the computer front panel or from the optional data terminal.

The sample cell used in the RDA consists of a set of serrated aluminum parallel plates. The lower plate was rotated a few degrees at a constant oscillation and the amount of torque transferred to the upper plate was measured from which G' and G'' were calculated. The gap between the two plates was fixed at 1.1 mm and the frequency used was 10 radians / sec. The strain ratio was set at 10 %.
<table>
<thead>
<tr>
<th>Description</th>
<th>Commercial name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester polyol</td>
<td>TONE - 310</td>
<td>Union Carbide</td>
</tr>
<tr>
<td>Diphenylmethane diisocyanate</td>
<td>MDI, 143 - L</td>
<td>Dow Chemical</td>
</tr>
<tr>
<td>Polyester in 35 % by weight styrene</td>
<td>Q 6585</td>
<td>Ashland Chemical Co.</td>
</tr>
<tr>
<td>Styrene</td>
<td>Lab. grade styrene</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Catalyst for PU system</td>
<td>T - 12</td>
<td>Air Products</td>
</tr>
<tr>
<td>Initiator for UPE system</td>
<td>USP 245</td>
<td>Lucidol Div., Pennwalt Co.</td>
</tr>
<tr>
<td>Random glass fiber mat</td>
<td>OCF M8610</td>
<td>Owens Corning Fibers Co.</td>
</tr>
<tr>
<td>Unidirectional glass fiber mat</td>
<td>CoFab A0108</td>
<td>Composite Reinforcements Inc.</td>
</tr>
</tbody>
</table>
3.3 Sample preparation for tensile testing

Composite samples were prepared using a rectangular mold of length 320 mm (12.6") and width 200 mm (7.87") (Figure 3.2). For samples prepared using polyurethane resin and random fiber mats, a spacer of dimensions 165 mm (length) X 125 mm (breadth) X 5.78 mm (thickness) (6.5" X 4.9" X 0.23") was used. The load cell used for tensile testing could be used only upto 1000 lbs and therefore it was necessary in some cases to reduce thickness of the samples. In these cases a spacer of dimensions 165 mm (length) X 125 mm (breadth) X 1.35 mm (thickness) (6.5" X 4.9" X 0.05") was used.

The mold was sprayed with a Teflon (Frekote 1711) mold release agent. The fiber mats were heated in an oven for an hour at 353.15 K (80°C) to ensure that all the absorbed moisture evaporated. This was necessary to prevent excessive void formation. Presence of voids and moisture is detrimental to composite strength and stiffness.

The fiber mats were placed in the mold such that area near the injection point was not covered with fiber mats (Figure 3.3). This ensured that the flow inside the fiber mats was axial and not radial. The degassed resin component were thoroughly hand mixed using a glass rod, before injection. The resin was injected into the mold using a SEMCO model 550 sealant gun operated on nitrogen gas. The experimental set up is shown in Figure 3.4. After mold filling, the inlet and outlet were plugged and the mold was placed in a preheated oven at 353.15 K (80°C) to allow the resin to cure. Cure was carried out at 353.15 K (80°C) for 16 hours.
Figure 3.2  Schematic of mold used to prepare composite samples for tensile testing (all dimensions are in mm)
Figure 3.3  Schematic diagram showing placement of fiber mats in the mold
This was necessary to ensure that the reaction went to completion. The cured samples were allowed to cool to room temperature and dogbone coupons were cut out using a die cutter with appropriate dimensions.

Both random and unidirectional fibers were used with polyurethane resin matrix for the preparation of composite samples. Unidirectional fiber mats were placed in the mold such that fibers were in the direction perpendicular to the flow. For each type of fiber mats, four sets of experiments were run. Two different injection pressures; 30 psi and 60 psi and two different fiber mat / mold temperatures; room temperature and 353.15 K (80°C) were used. For samples prepared using 80°C, mold along with fiber mats was preheated in an oven at 353.15 K (80°C) for 4 hours.

A previous study [Damani & Lee 1990] on single fiber fragmentation test had shown that resin - fiber interface obtained using polyurethane as matrix was not very good. Similar results were obtained in this study. The reason for this is that glass fiber mats used had sizing that was incompatible with polyurethane. However it is compatible with unsaturated polyester resin. Hence in order to enhance interfacial interactions a polyurethane - unsaturated polyester hybrid was used as matrix. In this case T - 12 was used as a catalyst for polyurethane reaction and USP 245 was used as an initiator for the polyester reaction. When unidirectional fiber mats were used, fiber wash occurred during injection. Hence only samples prepared using random fiber mats were used in the analysis. The experimental procedure for the preparation of samples using polyurethane - unsaturated polyester hybrid resin was
same as that using polyurethane resin. The only difference was in the curing step. The samples prepared using polyurethane - unsaturated polyester hybrid resin were cured at 353.15 K (80°C) for 4 hours and post cured at 393.15 K (120°C) for 16 hours. This was necessary to ensure that polyester reaction went to completion.

In order to compare the tensile strength of reinforced samples with unreinforced ones, samples were also prepared without using reinforcement by the same procedure.

3.4 Tensile testing

For the tensile testing, composite samples in the shape of a dogbone coupon having an overall length of 138.7 mm (5.5") with a 12.7 mm (0.5") wide by 63.5 mm (2.5") long gauge section were used (Figure 3.5). The coupons were subjected to a ramp loading using Instron Universal Testing Instrument (model 1137) in tension mode.

The Instron model 1137 is shown in Figure 3.6. It incorporates a highly sensitive electronic load weighing system with load cell that uses strain gages for detecting tensile or compressive loads. A specimen is physically attached to the load cell by grips for tensile testing and tensile forces are applied by a moving crosshead operated by two vertical lead screws. Digitally commanded crosshead speeds are pushbutton selectable. Positional control of the crosshead is provided by an analog error signal developed from resolver feedback in a closed loop system. Direction and sequence of crosshead movement may be manual or automatically controlled. The load weighing system includes a solid state
Figure 3.5  Schematic of dogbone coupon used for tensile tests
(all dimensions are in mm)

$t = 5.84 \text{ mm for PU-Random fiber mat composite samples}$

$= 1.27 \text{ mm for all other cases}$
Figure 3.6  Instron Universal Testing Instrument (Model 1137)
load cell signal conditioning amplifier, providing a wide selection of full scale load ranges. The amplifier controls provide for adjustment and calibration of the load weighing system to give accurate and reliable test data. The output of the load cell amplifier is in a signal form suitable for controlling the pen servo system of a recorder. Test results may be presented on a strip chart recorder. The recorder pen provides a trace describing specimen loading, while the chart movement is indicative of lapsed time at a pushbutton - selectable speed.

Two clamps were used to place the coupon perfectly vertical during testing. It is necessary to ensure that the axis of the coupon is aligned perfectly in the direction of loading. Otherwise results obtained may be erroneous. Of the two clamps, one is stationary and the other is attached to the moving crosshead which moves at the specified rate of loading. The movement of crosshead is controlled by crosshead limit stops. As the crosshead comes in contact with a stop, it trips a load cell that automatically stops the machine. This is necessary to ensure safe operation and to control amount of extension. In this study crosshead speed of 1.27 mm / min (0.05" / min) was used and tensile force was applied till the sample broke. Due to statistical nature, it was necessary to test multiple samples to arrive at accurate results. Consequently four samples were tested for each conditions and tensile strength was calculated as tensile force required to break the sample divided by cross sectional area of the specimen.
3.5 Fracture surface analysis

To analyze the interphase of composite samples, fracture surface analysis using scanning electron microscope (SEM) was used. SEM is an extremely popular tool for the analysis of fracture surfaces because it possesses the advantages of a large magnification range, greater depth of focus, higher contrast, appropriate resolution and easy handling of samples [Hawkes 1985]. A Hitachi S-510 scanning electron microscope with a resolution of 70Å, a magnification range of 150,000X and an accelerating voltage of 25 KV was used to observe fracture surfaces at magnification of 400X. The samples were gold coated to provide a conductive layer. The presence of such a layer prevents the buildup of electronic charge in the vicinity of the sample, which can cause distortion in the image. A silver based ink was used to glue the sample onto the holder to provide a conducting path from the sample to the sample holder. The sample chamber was maintained under high vacuum (5 microns) and the image was viewed on a cathode ray tube. Photomicrographs were taken using an installed Polaroid camera.

3.6 Water boil test

Water and temperature are two key environmental concerns in designing composite structures. Water attacks composites by migrating along fiber - resin boundaries and destroying the interface. It may also affect resin and fibers. The result is a decrease in strength and stiffness. High temperature accelerates the effect of water. Water boil test is often used to study the effect of long term exposure on composite strength.
Samples were prepared by the procedure described in Section 3.3 and then boiled in water (at 100°C) for different time period. Tensile tests were carried out by the procedure described in Section 3.4. Fracture surface analysis using SEM was also carried out for some of the samples.
CHAPTER IV
RESULTS AND DISCUSSION

Although there are a number of studies available in literature on mold filling and curing process (macro mechanics aspects), very little attention has been paid to fiber impregnation and interface bonding (micro mechanics aspects). Most studies on resin - fiber bonding and wetting have been for the traditional prepreg layup / autoclave cure type processes where the process is slow and the interactions between macro and micro mechanics are relatively unimportant. In this study, the effect of material and processing variables on wetting and bonding and hence on the ultimate mechanical properties of composite materials were studied. Presented below are some of the results.

4.1 Results obtained using fiberglass reinforced polyurethane composites

Polyurethane is the most common resin and glass fibers are the most popular reinforcement in commercial application of SRIM. Hence experiments were carried out using polyurethane resin and glass fibers.

Figure 4.1 and 4.2 show random fiberglass mat and two sides of a unidirectional fiberglass mat at 12X magnification, respectively. In Figure
Figure 4.1 Continuous random fiberglass mat at 12X magnification
Figure 4.2  Two sides of stitched unidirectional fiberglass mat at 12X magnification
4.2, the bright white strips are the fiber bundles, while the dark areas are the channels between the fiber bundles. The thin gray cross-hatching is the stitching which binds the fiber bundles together. Each fiber bundle has a large number of fibers. Thus the interstitial space within the fiber bundles is much smaller than the spaces between the fiber bundles. Thus the permeability of a fiber bundle to resin impregnation is much less than that of the fiber mat. During the mold filling process, as the advancing flow front encounters a fiber bundle, it may flow around it. After the front surrounds and bypasses a fiber bundle, the fiber bundle is slowly impregnated with the resin by capillary action. That is the rate of fiber impregnation is much smaller relative to the motion of the advancing flow front. Any mechanism that favours the flow into the fiber bundles will improve wetting. Also any mechanism that will favour the interface reaction between sizing and resin will improve bonding. These will result in improvements in the mechanical properties

4.1.1 Tensile tests

Table 4.1 shows the properties of unreinforced polyurethane samples. Mold temperature was varied at two specified levels. It was found that the mold temperature did not have any significant effect on the tensile strength of unreinforced polyurethane samples. Four samples were tested for each condition and the reported value is an average of four values.

Table 4.2 shows the tensile strengths of random fiberglass mat reinforced polyurethane composite samples for all combinations of the
Table 4.1  Properties of unreinforced polyurethane samples

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Curing Temperature (°C)</th>
<th>Gel Time (Minutes)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp.</td>
<td>80</td>
<td>39.0</td>
<td>5.1 ± 0.5</td>
</tr>
<tr>
<td>80</td>
<td>80</td>
<td>17.5</td>
<td>5.3 ± 0.6</td>
</tr>
</tbody>
</table>

Table 4.2  Tensile strength of random fiberglass mat reinforced polyurethane samples (Fiber weight fraction = 16%)

<table>
<thead>
<tr>
<th>Injection Pressure (Psi)</th>
<th>Mold/Fiber mat Temperature (°C)</th>
<th>Mold Filling Time (Sec)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Room Temp.</td>
<td>5</td>
<td>19.7 ± 1.0</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>2</td>
<td>23.8 ± 0.9</td>
</tr>
<tr>
<td>30</td>
<td>Room Temp.</td>
<td>15</td>
<td>21.8 ± 1.2</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>10</td>
<td>25.4 ± 1.2</td>
</tr>
</tbody>
</table>
manipulated variables. Table 4.2 illustrates that the lowest tensile strength was obtained when composites were prepared using high injection pressure (60 psi) and low mold/fiber mat temperature (room temperature). On the other hand, tensile strength was the highest when low injection pressure (30 psi) and high mold/fiber mat temperature (80°C) was used.

(a) Effect of mold/fiber mat temperature

Choice of mold temperature in general is made on the basis of resin characteristics (i.e. gelation time at a given temperature) rather than on an assessment of its effect on the resulting properties [Hayward & Harris 1990]. These experiments clearly showed that at the same injection pressure, a higher fiber temperature resulted in a higher tensile strength. Also in the experiments with unreinforced polyurethane samples, it was observed that the temperature does not affect the tensile strength of resin itself. Thus the resin is not responsible for the observed behavior. The enhancement of the composite properties at a higher molding temperature may be attributed to several phenomena.

When the fiber temperature is maintained significantly higher than that of the incoming resin, chemical bonding between the sizing and the matrix resin at the fiber surface may be favoured. Also the resin in contact with the hot fibers will have lower viscosity than that in the bulk. This will enhance the flow of resin into the fiber bundle (the micro flow) as compared to bulk resin flow around fiber bundles (the macro flow).
Enhancement in the micro flow results in improved wetting and bonding at the interface and hence better mechanical properties.

(b) Effect of injection pressure

The effect of injection pressure on mold filling has been viewed differently amongst injection molders. Some have favoured the use of low pressures, essentially to improve wetting of the fibers by resin, while others favoured high pressures, said to expel trapped air [Hayward & Harris 1990]. Table 4.2 gives evidence that at the same mold / fiber mat temperature, low pressure injection gives higher tensile strength.

Lowering the pressure, increases the time required to fill the mold cavity at constant temperature. It has been shown that more mold filling time provides a longer distance travelled by the resin into the fiber bundles by capillary action [Macosko 1989]. In other words, lower pressure enhances the flow around the fibers in the fiber bundle (the micro flow) leading to better wetting of fibers and hence better composite properties.

In the case of random fiber mats, as the name suggests, the fibers are oriented randomly. Hence it was very difficult to define the micro and macro flow directions. In unidirectional fiber mats since the fibers are oriented in one direction, the macro and micro flow directions can be defined very well. Hence in order to further investigate the effects of injection pressure and mold / fiber mat temperature on the quality of molded composites, unidirectional fiber mat reinforced polyurethane composite samples were prepared. Unidirectional fiber mats were placed in such a way that the fibers were perpendicular to the axial flow
direction. Thus, capillary action operates along the fiber, perpendicular to the bulk flow direction.

Table 4.3 shows the tensile strength data for unidirectional fiber mat reinforced polyurethane composite samples. Results show that there is statistically no difference in the longitudinal tensile strengths of composites prepared under the four combinations of processing conditions. The reason for this is that the properties in this direction (which is the direction of fibers) is governed primarily by the properties of fibers. The matrix resin and the interface wetting and bonding have very little effect on the properties.

However, transverse tensile strength data clearly agree with the previous conclusions made for the random fiber mat reinforced composites. That is, the highest tensile strength was obtained when samples were prepared using low injection pressure and high mold / fiber mat temperature. It has been reported in the literature that the transverse tensile strengths of composite materials will be lower than the tensile strength of unreinforced samples. However, in this study the opposite results were obtained. The reason for this behavior is that the presence of stitches in the transverse direction (in the direction perpendicular to fibers) gives additional strength to the composites over the unreinforced samples.

4.1.2 Fracture surface analysis

Figures 4.3 and 4.4 show the scanning electron micrographs of fracture surfaces of composite samples prepared using random and
Table 4.3  Tensile strength of unidirectional fiberglass mat reinforced polyurethane samples (Fiber weight fraction = 35%)

(a) Longitudinal tensile strength

<table>
<thead>
<tr>
<th>Injection Pressure (Psi)</th>
<th>Mold/Fiber mat Temperature (°C)</th>
<th>Mold Filling Time (Sec)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Room Temp.</td>
<td>8</td>
<td>142.3 ± 10.1</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>5</td>
<td>147.6 ± 14.3</td>
</tr>
<tr>
<td>30</td>
<td>Room Temp.</td>
<td>12</td>
<td>147.2 ± 12.5</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>10</td>
<td>145.7 ± 6.9</td>
</tr>
</tbody>
</table>

(b) Transverse tensile strength

<table>
<thead>
<tr>
<th>Injection Pressure (Psi)</th>
<th>Mold/Fiber mat Temperature (°C)</th>
<th>Mold Filling Time (Sec)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Room Temp.</td>
<td>8</td>
<td>12.4 ± 1.0</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>5</td>
<td>15.3 ± 0.9</td>
</tr>
<tr>
<td>30</td>
<td>Room Temp.</td>
<td>12</td>
<td>14.1 ± 0.7</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>10</td>
<td>16.3 ± 0.3</td>
</tr>
</tbody>
</table>
Figure 4.3 Scanning electron micrographs of fracture surfaces of random fiberglass mat reinforced polyurethane composites for (a) 60 psi / room temperature and (b) 30 psi / 80°C.
Figure 4.4 Scanning electron micrographs of fracture surfaces of unidirectional fiberglass mat reinforced polyurethane composites for (a) 60 psi / room temperature and (b) 30 psi / 80°C
unidirectional fiber mats respectively, for the two extreme cases, i.e. 60 psi / room temperature and 30 psi / 80°C. These micrographs confirm the conclusions drawn from tensile strength data. The wetting and bonding were better in the samples prepared using injection pressure of 30 psi and mold / fiber mat temperature of 80°C than for the 60 psi - room temperature case. However, these photos reveal that the fiber wetting and bonding was poor even for the best operating variables. For comparison, fracture surface analysis of composites prepared by compression molding of sheet molding compound (SMC) was carried out. Figure 4.5 shows the micrograph of fracture surface of SMC sample. As can be seen from this figure, there is a great amount of resin adhering to fibers. Contrast between the interface of SMC sample and that of polyurethane composite samples is apparent.

As mentioned earlier, the sizing used on the commercial glass fibers is based on unsaturated polyester resin and polyvinyl ester. Hence it is not compatible with polyurethane. Thus poor interface is obtained when polyurethane resin is used. One solution is to use urethane based sizing. The other way is to modify resins to suit the existing sizing to provide for adequate chemical interactions.

4.2 Results obtained using fiberglass reinforced polyurethane - unsaturated polyester hybrid composites

Unsaturated polyester resin is a commonly used resin in RTM process for commercial applications. In order to improve the compatibility with sizing, polyurethane - unsaturated polyester hybrid resin was used
Figure 4.5  Scanning electron micrographs of fracture surface of SMC sample
and the experiments were repeated. In this case a catalyst, T-12 was used for the polyurethane reaction and an initiator for the unsaturated polyester reaction.

4.2.1 Tensile tests

Table 4.4 shows the properties of unreinforced polyurethane - unsaturated polyester hybrid resin samples. The data show that the tensile strength is higher for the lower molding temperature. This result can be explained as follows.

Polyurethane - unsaturated polyester hybrid resin is an interpenetrating polymer network (IPN). The unsaturated polyester reaction is a thermally activated free radical polymerization and is more temperature sensitive than the polyurethane reaction, a mixing activated step growth polymerization. At different temperatures, relative rates of formation of polyurethane and unsaturated polyester are different and the IPN formed will be different.

Table 4.5 shows the results of tensile tests conducted on random fiberglass mat reinforced polyurethane - unsaturated polyester hybrid resin composite samples. Tensile strength data shown in Table 4.5 corroborate the conclusions made for the polyurethane composites in Table 4.2. The composite strength is lowest for high pressure injection (60 psi) combined with low mold / fiber mat temperature (room temperature). The composite gains strength using a low injection pressure (30 psi) and a room temperature mold / fiber mat. Tensile
Table 4.4  Properties of unreinforced polyurethane - unsaturated polyester hybrid resin samples

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Curing Temperature (°C)</th>
<th>Gel Time (Minutes)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp.</td>
<td>80</td>
<td>12.5</td>
<td>49.7 ± 1.1</td>
</tr>
<tr>
<td>80</td>
<td>80</td>
<td>1.0</td>
<td>45.4 ± 0.8</td>
</tr>
</tbody>
</table>

Table 4.5  Tensile strength of random fiberglass mat reinforced polyurethane - unsaturated polyester hybrid resin samples (Fiber weight fraction = 29%)

<table>
<thead>
<tr>
<th>Injection Pressure (Psi)</th>
<th>Mold/Fiber mat Temperature (°C)</th>
<th>Mold Filling Time (Sec)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Room Temp.</td>
<td>3</td>
<td>84.5 ± 1.8</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>2</td>
<td>90.5 ± 1.1</td>
</tr>
<tr>
<td>30</td>
<td>Room Temp.</td>
<td>4</td>
<td>88.1 ± 1.5</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>3</td>
<td>96.1 ± 2.0</td>
</tr>
</tbody>
</table>
strength is even higher for the combination of high injection pressure (60 psi) and high mold/fiber mat temperature (80°C). The maximum strength is achieved when low pressure injection (30 psi) and high mold/fiber mat temperature (80°C) are used. Note that for the unreinforced samples, tensile strength decreased when molding temperature was increased, whereas reverse results were obtained for the composite samples. The explanation for the results is similar to that for the polyurethane samples. Low injection pressure favours the micro flow, thereby improving wetting. Higher temperature favours the matrix-sizing reaction thereby promoting bonding. It also favours the micro flow due to reduction in viscosity in the vicinity of fibers and hence improves wetting. Improvement in wetting and bonding are directly reflected in tensile strength of composite samples.

When experiments were carried out using unidirectional fiber mats an interesting result was obtained. Examination of cured composite samples indicated that there was movement of the reinforcement during injection process (Figure 4.6). This phenomenon is known as "fiber wash" [Hayward & Harris 1990]. Tendency for this to occur is related to the nature of the reinforcement (weave, binder, lay-up, etc), the injection pressure and the resin viscosity. Loose weave reinforcements have a greater tendency to wash than tighter weaves, such as satin weave fabrics. In the case of reinforcement held in place by binding agents, the lower the strength of the binder, more is the tendency to move. The solubility and rate of dissolution of binder also affect the level of wash. For example, if the binder dissolves too quickly when in contact with the
Figure 4.6  Samples showing phenomenon of fiber wash
resin, then the fibers move freely under the pressure of incoming resin. Higher viscosity resins have a greater tendency to cause fiber wash in weakly bound fiber reinforcement. Higher injection pressure during molding also induces the movement of fibers.

When fiber wash occurs there is non uniform distribution of fibers resulting in variation in properties from point to point in the molded composite. Hence these sample were not used in the analysis. Since the primary aim of this study was to analyze wetting and bonding in RTM / SRIM, no further analysis of fiber wash was carried out.

4.2.2 Fracture surface analysis

The scanning electron micrographs for the polyurethane - unsaturated polyester hybrid composite fracture surfaces illustrate the degree of wetting and bonding on individual fibers. Figure 4.7 shows four micrographs corresponding to the four combinations of operating variables. The results obtained support the tensile strength data. The degree of wetting is the greatest for the composite samples prepared using 30 psi and 80°C as illustrated in Figure 4.7 (d). There is a great amount of resin adhering to the individual fibers, and the covering is fairly uniform. In contrast to this, as can be seen from Figure 4.7 (a), the poorest wetting is observed in the case of samples prepared using 60 psi and room temperature. The fiber surfaces in Figure 4.7 (a) are covered with patches of resin and the interface film of resin is thin. Figure 4.7 (b) and (c) show intermediate wetting and bonding. It is rather difficult to
Figure 4.7 Scanning electron micrographs of fracture surfaces of random fiber glass mat reinforced PU-UPE composites for (a) 60 psi / room temperature and (b) 60 psi / 80°C
Scanning electron micrographs of fracture surfaces of random fiber glass mat reinforced PU-UPE composites for (c) 30 psi / room temperature and (d) 30 psi / 80°C.
differentiate or judge the interface quality in these two cases. However, the difference between Figure 4.7 (a) for high pressure injection and room temperature molding condition and Figure 4.7 (d) using low pressure injection and 80°C molding temperature is strikingly clear. Also from Figure 4.7 it is clear that at the same mold / fiber mat temperature, low injection pressure results in improved wetting (a vs c and b vs d) and at the same injection pressure, high mold / fiber mat temperature leads to improved wetting and bonding (a vs b and c vs d).

The results obtained for high temperature molding are rather interesting, especially so because a parallel study using single fiber fragmentation test indicated that interface bonding was inferior at high mold temperature [Rohatgi 1991]. This apparent contradictory results can be explained as follows. In single fiber fragmentation test, a single fiber filament is used. Hence although hot mold would increase the temperature of the fiber, due to the negligible thermal mass, incoming resin at room temperature would cool down the fiber. Thus the interface reaction between fiber sizing and resin would not be favoured as compared to matrix curing. On the other hand, in the case of fiber mat, due to high fiber loading, the resin in the vicinity of fibers would be at higher temperature than the bulk temperature.

Comparison of Figures 4.5 and 4.7 show that polyurethane - unsaturated polyester hybrid composites prepared using room temperature molding conditions have inferior interface for both levels of injection pressure as compared to SMC sample. Interface quality of
samples prepared using 60 psi / 80° C conditions is more or less similar to the SMC sample. However, 30 psi / 80° C sample has greater amount of resin adhering than the SMC sample.

It was suggested earlier that the use of sizing compatible resin would improve adhesion at the interface. Comparison of Figures 4.3 (b) and 4.7 (d) proves this. These figures show scanning electron micrographs of fracture surfaces of composite samples prepared using identical processing conditions and using polyurethane and polyurethane - unsaturated polyester hybrid as the matrix respectively.

The observed results can be explained using Figure 4.8, which is a schematic diagram of the possible interactions between a polyurethane - unsaturated polyester hybrid and fiber sizing. In the matrix, the polyol reacts with the diisocyanate to form the urethane network, while styrene monomer serves as a chain - linking agent for C=C bonds on adjacent polyester molecules. The diisocyanate may also react with the hydroxyl groups on the end of polyester chains leading to grafting between the two networks [Yang & Lee 1987]. In the region of the interface, the styrene could cause linkage between adjacent polyester molecules of the matrix and the sizing. Some chemical interaction may also occur between the matrix isocyanate and the hydroxyl groups on the sizing polyester. In addition to the possible chemical bonding, there may be physical or inter - molecular interactions between the matrix resins and the sizing. This scheme explains the observed improvement in the interface adhesion in the case of polyurethane - unsaturated polyester hybrid composites over that in polyurethane resin composites.
Figure 4.8  Schematic of interactions at the resin - fiber interphase of a PU - UPE system  
[Yang & Lee 1987]
4.3 Water boil test

Composite materials must be able to withstand the great diversity of environment to which they are exposed, such as large variation in temperature and moisture. The effect of moisture on the composite material's properties is a function of matrix and fiber type, time, component geometry, temperature, relative humidity, and exposure conditions. Water boil test is a popular test to determine the effects of moisture on composite materials.

4.3.1 Tensile tests

Unreinforced polyurethane - unsaturated polyester resin samples were subjected to the water boil test and the results are shown in Table 4.6. It was found that the tensile strength of samples prepared using room temperature mold was higher than that for 80°C molding condition, before and after 8 hour water boil test. The results were explained earlier as due to different IPNs formed at different temperatures.

Figure 4.9 shows the results of water boil test for composites prepared using the two extreme conditions (60 psi / room temperature and 30 psi / 80°C). It was found earlier that before the water boil test the composite tensile strength was the highest for the injection pressure of 30 psi and mold / fiber mat temperature of 80°C. After half an hour of exposure to the boiling water, the same trend was found. However, after a two hour water boil test, there was a reversal. That is, tensile strength for the 60 psi / room temperature combination was higher than the 30 psi / 80°C combination. These results can be explained as follows.
Table 4.6  Tensile strength of unreinforced polyurethane - unsaturated polyester hybrid resin samples before and after water boil test

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Curing Temperature (°C)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before water boil test</td>
</tr>
<tr>
<td>Room Temp.</td>
<td>80</td>
<td>49.7 ± 1.1</td>
</tr>
<tr>
<td>80</td>
<td>80</td>
<td>45.4 ± 0.8</td>
</tr>
</tbody>
</table>
Figure 4.9  Results of water boil test for random fiber mat reinforced PU-UPE composite samples
When the composite samples are subjected to boiling water, water penetrates into the sample and attacks the interphase. As a result interface debonding occurs. After 2 hour of water boil test, the interphase is more or less destroyed. The difference in tensile strengths of composite samples prepared using different combinations of processing conditions after 2 hour water boil test could be due to the difference in the properties of matrix resin rather than the interphase.

If the above mentioned hypothesis is correct then further exposure of composite samples to boiling water should give the same results. Water will attack only the fibers and the resin, since the interphase is completely destroyed. After 8 hour water boil test, the tensile strength of composites prepared using 60 psi / room temperature combination was found to be more than that for 30 psi / 80°C combination. The difference in the tensile strength values between the two cases was approximately the same for 2 hour and 8 hour water boil test. Also this difference was approximately equal to the difference in tensile strength values for the unreinforced polyurethane - unsaturated polyester resin. These results support the hypothesis that 2 hour exposure to boiling water destroyed the interphase. Further drop in strength of composite samples was due to the drop in resin and fiber properties.

Figure 4.10 shows the ratio of tensile strengths of reinforced to unreinforced polyurethane - unsaturated polyester resin samples before and after 8 hour water boil test. Before the water boil test, this ratio for the 30 psi / 80°C sample was the highest due to better interface bonding
Figure 4.10 Ratio of tensile strengths of reinforced to unreinforced PU-UPE hybrid resin samples
and wetting. However, after the 8 hour water boil test, the ratios for the
two cases were approximately the same, supporting the hypothesis that
the exposure to boiling water destroyed the interphase completely.

4.3.2 Fracture surface analysis

Figure 4.11 shows scanning electron micrographs of fracture
surfaces of composite samples subjected to 2 hour water boil test.
Comparing Figure 4.11 (a) and (b), it can be seen that the interface
wetting is more or less the same in the two cases. Also there is very little
resin adhering to the fiber surfaces, indicating that the interface bonding
was destroyed by boiling water. As against this, before the exposure to
boiling water, composite samples prepared using 30 psi / 80°C exhibited
much better interface than the 60 psi / room temperature samples (Figure
4.7 (a) vs (d)). The difference between Figures 4.7 (d) and 4.11 (b),
which are micrographs for the same processing conditions, is clear.

Figure 4.12 shows the micrographs of fracture surfaces of
composites after 8 hour water boil test for the same two cases. Again
there is little difference in the resin - fiber wetting and bonding in the two
cases. Also the interface is more or less the same after 2 hour and 8 hour
water boil test (Figure 4.11 vs 4.12). The fracture surface analysis thus
supports the results obtained from the tensile tests.

4.4 Comparison of RTM / SRIM processes with traditional processes

The question now arises as to whether the composites prepared by
RTM / SRIM processes are as good as that produced by conventional
Figure 4.11 Scanning electron micrographs of fracture surfaces of random fiberglass mat reinforced PU-UPF composites after 2 hour water boil test for (a) 60 psi / room temperature and (b) 30 psi / 80°C
Figure 4.12 Scanning electron micrographs of fracture surfaces of random fiberglass mat reinforced PU-UPE composites after 8 hour water boil test for (a) 60 psi / room temperature and (b) 30 psi / 80°C
manufacturing methods such as prepreg process. Composite prepared by RTM / SRIM processes have been considered to have properties intermediate between SMC and chopped strand mat products at the one extreme, and high quality composites manufactured by prepreg on the other [Wilder 1989]. In order to make a fair comparison between RTM / SRIM and conventional processes, random fiberglass mat reinforced polyurethane - unsaturated polyester composite samples of same glass loadings were prepared using very long mold filling time. This was an attempt to provide long time for the impregnation and interface bonding process. This would result in very good interphase and hence better properties.

In order to test the interphase the samples were subjected to water boil test and results are shown in Table 4.7. Although composites prepared using very slow mold filling have higher tensile strength, they also show drop in strength on exposure to boiling water. Retention ratio (ratio of tensile strength before and after water boil test) in this case is similar to that in the case of samples prepared using RTM / SRIM processes. Thus given the ease of processing and economic advantages of RTM / SRIM processes over the conventional prepreg processes, the RTM / SRIM processes seem to have high potential in future for composite manufacturing.
<table>
<thead>
<tr>
<th>Injection pressure</th>
<th>Mold / Fiber mat Temperature</th>
<th>Tensile strength (MPa)</th>
<th>Before water boil test</th>
<th>After 2 hour water boil test</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 psi</td>
<td>Room Temp.</td>
<td>74.7 ± 1.9</td>
<td>58.4 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>very low pressure</td>
<td>Room Temp.</td>
<td>88.4 ± 2.1</td>
<td>64.1 ± 1.0</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

RTM / SRIM technology has come a long way since its early days. These processes fill the gap between high volume processes such as compression molding and lower volume fabrication techniques like hand layup. Although a lot of attention has been paid to macro mechanics (mold filling and curing), very little literature is available on the micro mechanics (fiber impregnation and interfacial adhesion) of these processes. In this study wetting and bonding in RTM and SRIM were studied. Following conclusions can be made from this study.

5.1 Conclusions

(1) Improved interfacial behavior can be obtained by using lower injection pressure and higher molding temperature. Scanning electron micrographs of fracture surfaces clearly show that low injection pressure favours wetting of individual fibers and high fiber mat temperature leads to better wetting and bonding. These tests display the importance of maintaining a high fiber mat temperature. If fibers are not preheated for a significant period of time before injection of the resin, their temperature could be lower than desired and this could affect interphasial behavior. The study also elucidates the importance of using low pressure injection.
However, since cycle time considerations dictate the use of high pressure, optimum value should be used.

(2) Results of tensile tests show the effect of processing variables on the composite mechanical properties. Significant improvements were found in tensile strength when low pressure injection and high mold/fiber temperature were used. This is a direct consequence of improved interface bonding and wetting.

(3) In the case of unidirectional fiber mat reinforced composites, longitudinal tensile strength depends largely on the fiber strength and interface wetting and bonding has very little effect on it. The transverse tensile strength, on the other hand, is sensitive to the interface.

(4) Comparison of scanning electron micrographs of fracture surfaces of composite samples overwhelmingly point in favor of improved interphasial behavior with the polyurethane - unsaturated polyester hybrid resin as compared to polyurethane. The study displays how crucial the resin-fiber interphase can be. In absence of sufficient compatibility, void formation and poor adhesion could pose problems.

(5) Water boil test is a popular test to study the effect of moisture on the composite properties. Unfortunately, due to the absence of any standardization, results obtained by different researchers can not be compared directly. Water attacks the interphase and destroys it. Resin and fiber strength also decreases due to the attack of water. As a result, composite as a whole records degradation in properties. Continued exposure to water results in complete destruction of interphase and any
further drop in strength is because of the drop in resin and/or fiber strength.

(6) Results of tests conducted using very slow mold filling indicate that RTM/SRIM may be able to compete with traditional processes for the manufacture of complex structural parts in future. Although composites prepared using very long mold filling had higher tensile strength as compared to RTM/SRIM molded composites, on exposure to boiling water, similar retention ratios of tensile strengths were obtained.

5.2 Recommendations

The focus of this study was to characterize wetting and bonding in RTM/SRIM processes. This work, however, was by no means exhaustive. Other avenues for future work are listed below.

(1) The goal of this study was to study quality of composites molded under different conditions. In this study only two levels of operating variables, injection pressure and mold/fiber mat temperature were used. It is necessary to try more values to generate useful knowledge for producing composites with desirable mechanical properties. The effect of resin injection and curing on the mechanical properties of molded composites can also be quantified. For this purpose, tensile and impact strength of composites molded with various reinforcements, resin systems and processing conditions have to be measured.

(2) In order to facilitate resin flow, some investigators have tried to evacuate the mold before resin injection. Hayward and Harris [1990]
have reported that vacuum assistance leads to improved mechanical properties of composites. The results, however, may not always be favorable. Vacuum molding may enhance the macro flow more than the micro flow. Recently it has been suggested that a small back pressure in the mold cavity during resin injection may improve fiber wetting process because it may slow down the macro flow more than the micro flow [Robertson 1988]. It would be interesting to study the effect of evacuating mold cavity and back pressure on wetting and on mechanical properties. Other suggested process innovations in literature, such as injection-compression molding, bladder molding, hot-gas assisted curing could also be tried.

(3) In this study, the mold was end-gated. As a result, flow was in the planar direction. In commercial RTM / SRIM applications, molds are often center-gated. Near the gate, resin has to penetrate through the reinforcement stack before flowing in the planar directions. It has been found that the reinforcement stack can not be considered as a rigid porous block in this type of flow. The viscoelastic type compressibility of the fiber reinforcement and interactions between adjacent fiber mats need to be considered. Measurement of process profile in the thickness direction during the resin injection can provide information regarding the micro flow mechanism in the thickness direction.

(4) Resin injection process has been generally modelled by D'Arcy's law, which is found to be acceptable for predicting macro flow front progression. However, it can not explain the actual mold filling, which is a transient phenomenon. For this purpose, it is necessary to include both
the macro and the micro flow. Parnas and Phelan [1991] have developed a model that includes the fiber impregnation. But it does not consider the capillary forces. Also the model is for a simple geometry of unidirectional fiber mat. It would be very useful to model the injection process for a complicated geometry and take into account wetting process in the mold filling. For this purpose fiber wettablility need to be determined. Resin surface tension could be measured by standard ring pull method and contact angle by the droplet spreading method or the forced dynamic wetting method [Elliott & Riddiford 1967, Elmendorp & During 1990]. One of the difficulties of combining the two flows in the model is, to determine the boundary conditions at a permeable wall (i.e. the bundle surface). Beavers & Joseph [1967] have proposed a slip velocity boundary condition that can be used here. Interaction of competitive micro and macro flow could be studied using flow visualization techniques [Molnar 1989].

(5) It is also important to quantify the competitive reaction, interface bonding vs matrix curing. Modeling of the reaction kinetics at the interface can be done by using a FTIR spectroscopy in the reflection mode. Reaction kinetics of the bulk can be followed either by an FTIR in the transmission mode or by differential scanning calorimetry (DSC). The corresponding viscosity changes can be followed by a RDA and a Haake viscometer. These results can be used to propose appropriate kinetic models for interface reaction (which controls bonding) and rheo - kinetic models for matrix curing (which governs wet time).
(6) In this study fiber weight fraction of composites was low. In high performance composites the fiber weight fraction can be as high as 60%. High fiber loading may affect some of the results. Increasing the fiber content could change the macro flow lengths. It would be necessary to analyze high fiber content composites in order to study the feasibility of using RTM for high performance composites.

(7) Gel times of resin systems used in this study were much higher than the mold filling times. As a result after the mold filling process, the resin had time to penetrate into the fiber bundles. It would be interesting to carry out study using resin systems with a very short gel time. For this purpose a RIM machine may have to be used for mold filling.
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