EFFECTS OF MOLD TEMPERATURE AND VACUUM IN RESIN TRANSFER MOLDING

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ABSTRACT

EFFECTS OF MOLD TEMPERATURE AND VACUUM IN RESIN TRANSFER MOLDING

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The purpose of this study was to investigate the effects of mold temperature, initial resin temperature, and the vacuum, applied at resin exit ports, on the mechanical properties of epoxy matrix woven glasss fiber reinforced composite specimens produced by Resin Transfer Molding (RTM).

For this purpose, six different mold temperatures (25º, 40º, 60º, 80º, 100º, and 120ºC), two initial resin temperatures (15º and 28ºC), and vacuum (0.03 bar) and without vacuum (~1 bar) conditions were used. Specimens were characterized by using ultrasonic (C-Scan) inspection, mechanical tests (Tensile, Flexural, Impact), thermal analyses (Ignition Loss, TGA) and scanning electron microscopy (SEM).

It was generally observed that mechanical properties of the specimens produced with a mold temperature of 60ºC were the best (e.g. 16%, 43%, and 26% higher tensile strength, Charpy impact toughness and flexural strength values, respectively). When vacuum was not applied, the percentage of “voids” increased leading to a decrease in mechanical properties such as 26% in Charpy impact toughness and 5% in tensile and flexural strength. Lower initial resin temperature also decreased mechanical properties (e.g. 14% in tensile strenght and 18% in Charpy impact toughness).

Keywords: Epoxy, Woven Glass Fibers, RTM, Mold Temperature, Vacuum, Initial Resin Temperature

ÖZ

REÇİNE AKTARIM KALIPLAMASI (RTM) YÖNTEMİNDE KALIP SICAKLIĞININ VE VAKUMUN ETKİLERİ

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Bu çalışmanın amacı kalıp sıcaklığının, reçine başlangıç sıcaklığının ve kalıp reçine çıkış kanallarına uygulanan vakumun Reçine Aktarım Kalıplaması (RTM) Yöntemi ile üretilen epoksi matriksli dokuma cam elyaf takviyeli kompozit numunelerin mekanik özelliklerine etkisini araştırmaktır.

Bu amaç için, altı farklı kalıp sıcaklığı (25º, 40º, 60º, 80º, 100º ve 120°C), iki farklı reçine sıcaklığı (15º ve 28°C), vakumlu (0.03 bar) ve vakumsuz (~1 bar) koşulları kullanılmıştır. Üretilen numuneler ultrasonik muayene (C-Scan), mekanik testler (Çekme, Eğme, Darbe), termal analizler (Yanma kaybı, TGA) ve tarama elektron mikroskobu (SEM) ile incelenmiştir.

Genel olarak, 60°C kalıp sıcaklığı ile üretilen numunelerin mekanik özelliklerinin en yüksek olduğu gözlemlenmiştir (örneğin çekme dayancı, Charpy darbe tokluğu ve eğme dayancı değerleri sırasıyla %16, %43, ve %26 daha yüksek). Vakum uygulanmadığı zaman, mekanik özelliklerde düşüşe (Charpy darbe tokluğunda %26, çekme ve eğme dayançlarında ise %5) neden olan "boşlukların" yüzdesinde artış olmuştur. Başlangıç reçine sıcaklığının düşmesi de mekanik özellikleri, örneğin Charpy darbe tokluğunu %18, çekme dayancını ise %14, düşürmüştür.

Anahtar Kelimeler: Epoksi, Dokuma Cam Elyaf, RTM, Kalıp Sıcaklığı, Vakum, Başlangıç Reçine Sıcaklığı

To My Family

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INTRODUCTION

Polymer matrix composites are now an important class of engineering materials. They offer outstanding mechanical properties and unique flexibility in design capabilities. Additional advantages include light weight, corrosion resistance, impact resistance, and excellent fatigue strength. Today, fiber reinforced composites are routinely used in such diverse applications as automobiles, aircrafts, space vehicles, off-shore structures, containers and piping, sporting goods, electronics, and appliances.

A simple classification of polymers is as three classes: thermosets, thermoplastics and rubbers. It has been estimated that over three-quarters of all matrices of PMCs are thermosetting polymers. Thermosets are resins which readily cross-link during curing. Polyesters, Epoxies, Phenolics, Polyimides are the most widely used thermoset matrix resins. In this study epoxy resin was preferred.

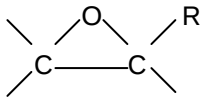
1.1 Epoxy Matrix Resins

Epoxy resins are used extensively in composite materials for a variety of demanding structural applications. They are the most versatile of the commercially available matrices. Unsaturated polyesters may cost less, and polyimides may perform better at elevated temperatures, but epoxy resins have a broad range of physical properties, mechanical capabilities, and processing conditions that makes them invaluable by comparison [1].

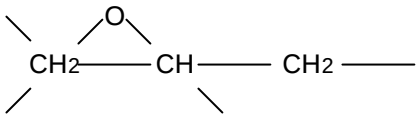
Depending on the chemical structures of the resin and the curing agent, the availability of numerous modifying reactants, and the conditions of cure, it is possible to obtain toughness, chemical and solvent resistance, mechanical responses ranging from extreme

flexibility to high strength and hardness, resistance to creep and fatigue, excellent adhesion to most fibers, heat resistance, and excellent electrical properties. No by-products are formed during the cure. Shrinkage that is due to cure is low. The uncured resins have a variety of physical forms. Ranging from low-viscosity liquids to nontacky solids, which, combined with a large selection of curing agents, affords the composite fabricator a wide range of processing conditions [1].

By definition epoxy is a polymerizable thermoset polymer containing one or more epoxide groups and curable by reaction with amines, alcohols, phenols, carboxylic acids, acid anhydrides, and mercaptans. An epoxide group is:



where R represents the point of attachment to the remainder of the resin molecule. The epoxide function usually appears in the form:



called the glycidyl group, which is attached to the remainder of the molecule by an oxygen, nitrogen, or carboxyl linkage [1].

1.2 Curing Reactions and Curing Agents

Three chemical reactions are of major importance to the curing of epoxy composite matrices: the amine/epoxide reaction, the anhydride/epoxide reaction, and the Lewis acid-catalyzed epoxide homopolymerization.

(a) Lewis acid-catalyzed epoxide homopolymerization and Curing Agents

The principal Lewis acid used in epoxy composites is boron trifluoride in the form of its monoethylamine complex (BF3-MEA). This curing agent is characterized by a long pot life and a high *Tg*. Samples of DGEBPA (diglycidyl ether of bisphenol A) with BF3-MEA, although showing considerably increased viscosity, are still usable after storage for 6 months at room temperature [1].

(b) Anhydride / Epoxide Reaction and Curing Agents

The chemistry of curing with anhydrides is more complex than curing mechanism with amines. It was initially proposed that the anhydride reacts with an alcohol to form a half-acid ester, which in turn reacts with the epoxide to form a second ester linkage resulting in a new hydroxyl. The reaction continues in this manner until all of the reactive groups were consumed. This mechanism was based on the logic that some hydroxyl groups always present, either in the resin itself or as an impurity, such as water. Optimum properties for this system results at an anhydride/epoxide ratio of 0.85/1, indicating that a side reaction was occurring, probably epoxide homopolymerization was catalyzed by the acid, giving rise to some polyether formation [1].

It was later found that Lewis acids and bases act as catalysts for this reaction. In this system the anhydride/epoxide stoichiometry was found to be 1/1. This leads to a second mechanism in which the anhydride reacts with the catalyst to form a carboxyl anion, and the anionic process continues to the completion of the cure. This latter curing system is now preferred since it leads to somewhat better elevated-temperature properties in these cured composites [1].

Acid anhydrides are characterized by a long pot life, better heat aging in air at elevated temperatures, and better electrical properties. Their composite applications are generally the same as those of the aromatic amines, and they are chosen to impart specific

properties to the laminating system. Cures normally involve an added accelerator, such as benzydimethylamine (BDMA) [1].

(c) Amine / Epoxide Reaction and Curing Agents

The most common curing agents are amines, in which each of the amino hydrogens reacts with an epoxide group. The reaction mechanism is given in the following figure.

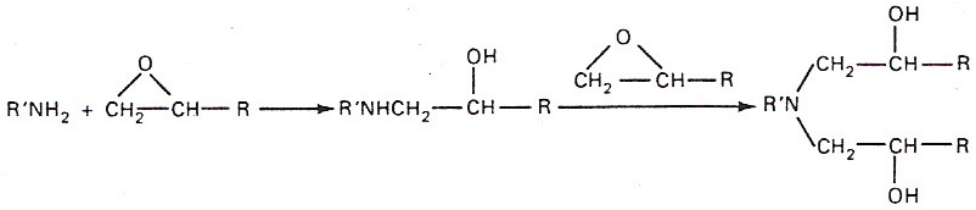


Figure 1.1 Amine/Epoxide curing reaction [1].

Depending on the number of amino hydrogens on the curing agent, their reactivity, the number of epoxide groups per resin molecule, and the supporting structures of each, a wide variety of mechanical properties can be obtained and various laminating processes can be used [1].

The aliphatic amines and their derivatives are recommended for ambient temperature curing. Consequently, they would be expected to have a limited pot life or shelf life. Typical applications include wet lay-up laminating operations such as tank linings, wet filament winding, repairs, tooling, certain air frames and radomes, and electrical insulation [1].

The moderate temperature cured cycloaliphatic and tertiary/primary aliphatic amines offer a compromise between the room-temperature curing agents and the higher-temperature curing aromatic amines. They can be cured under milder conditions than the

aromatic amines, but their elevated-temperature performance, solvent resistance, and chemical resistance are generally superior to those obtained from the ambient temperature cured aliphatic amines [1].

The aromatic amines are widely used in composite fabrication in both wet and dry lay-up applications for filament winding, electricals, piping, tooling, and whenever maximum chemical resistance and electrical properties, and good elevated-temperature performance. Higher-temperature cures and longer cure times are required to obtain these advantages [1].

1.3 Glass Fiber Reinforcements and Used Forms

The role of the reinforcement in a composite material is fundamentally one of increasing the mechanical properties of the neat resin system. All of the different fibers used in composites have different properties and so affect the properties of the composite in different ways. The mechanical properties of most reinforcing fibers are considerably higher than those of un-reinforced resin systems. The mechanical properties of the fibre/resin composites are therefore dominated by the contribution of the fiber to the composite [2].

By blending quarry products (sand, kaolin, limestone, colemanite) at 1600°C, liquid glass is formed. The liquid is passed through micro-fine bushings and simultaneously cooled to produce glass fiber filaments from 5-24 μm in diameter. The filaments are drawn together into a strand (closely associated) or roving (loosely associated), and coated with a size to provide filament cohesion and protect their surface from abrasion [2].

By variation of the formulation different types of glass fibers can be produced. The types used for structural reinforcements are: E-Glass, C-Glass, R, S or T-Glass. E-Glass (electrical) consists of lower alkali content, and is stronger than A-Glass (alkali). It has good tensile and compressive strength and stiffness, good electrical properties and

relatively low cost. But impact resistance is relatively poor. E-glass is the most common reinforcing fiber used in polymer matrix composites including this study.

E-Glass fiber is available in the following forms:

- **Strand:** a compactly associated bundle of filaments. Strands are rarely seen commercially and are usually twisted together to give yarns.
- **Yarns:** a closely associated bundle of twisted filaments or strands. Each filament diameter in a yarn is the same, and is usually between 4-13 μm. Yarns have varying weights described by their 'tex' (the weight in grammas of 1000 linear meters) with the typical tex ranges usually between 5 and 400.
- **Roving:** a loosely associated bundle of untwisted filaments or strands. Each filament diameter in a roving is the same, and tex range is usually between 300 and 4800.

Woven fabrics are produced by the interlacing of warp (0°) fibers and weft (90°) fibers in a regular pattern or weave style. The fabric's integrity is maintained by the mechanical interlocking of the fibers. Drape (the ability of a fabric to conform to a complex surface), surface smoothness and stability of a fabric are controlled primarily by the weave style. The area weight, porosity and resin wet out are determined by selecting the correct combination of fiber tex and the number of fibers/cm. The following is a description of some of the more commonly used weave styles (Figure 1.2):

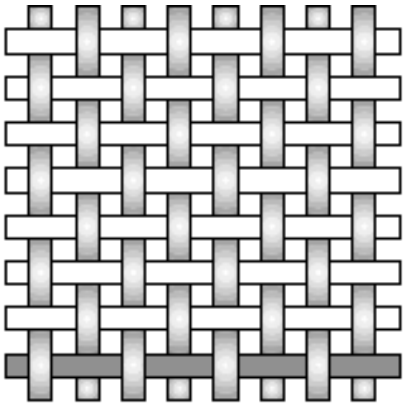
(i) Plain: Each warp fiber alternately weave under and over each weft fiber (Fig. 1.2(a)). The fabric is symmetrical, with good stability and reasonable porosity. However it is the most difficult of the weaves to drape, and the high level of fiber crimp imparts relatively low mechanical properties compared with other weave styles. With large fibers (high tex) this weave style gives excessive crimp and therefore it tends not to be used for very heavy fabrics [2].

(ii) Twill: One or more warp fibers alternately weave over and under two or more weft fibers in a regular repeated manner (Fig. 1.2(b)). This produces the visual effect of a straight or broken diagonal rib to the fabric. Superior wet out and drape is seen in the twill weave over the plain weave with only a small reduction in stability. With reduced crimp, the fabric also has a smoother surface and slightly higher mechanical properties [2].

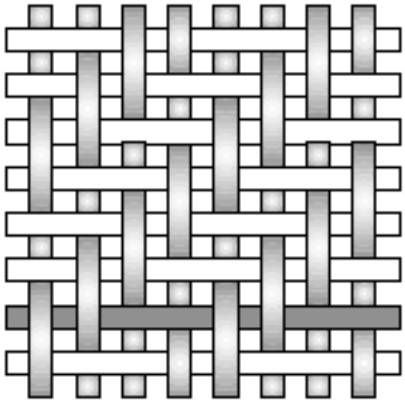
(iii) Satin: Satin weaves are fundamentally twill weaves modified to produce fewer intersections of warp and weft (Fig. 1.2(c)). The 'harness' number used in the designation (typically 4, 5 and 8) is the total number of fibers crossed and passed under, before the fiber repeats the pattern. A 'crowsfoot' weave is a form of satin weave with a different stagger in the repeated pattern. Satin weaves are very flat, have good wet out and a high degree of drape. The low crimp gives good mechanical properties. Satin weaves allow fibers to be woven in the closest proximity and can produce fabrics with a close 'tight' weave. However, the style's low stability and asymmetry needs to be considered [2].

(iv) Basket: Basket weave is fundamentally the same as plain weave except that two or more warp fibers alternately interlace with two or more weft fibers (Fig. 1.2(d)). An arrangement of two warps crossing two wefts is designated 2x2 basket, but the arrangement of fiber need not be symmetrical. Therefore it is possible to have 8x2, 5x4, etc. Basket weave is flatter, and, through less crimp, stronger than a plain weave, but less stable. It must be used on heavy weight fabrics made with thick (high tex) fibers to avoid excessive crimp [2].

(v) Leno: Leno weave improves the stability in 'open' fabrics which have a low fiber count. A form of plain weave in which adjacent warp fibers are twisted around consecutive weft fibers to form a spiral pair, effectively 'locking' each weft in place (Fig. 1.2(e)). Fabrics in leno weave are normally used in conjunction with other weave styles because if used alone their openness could not produce an effective composite [2].



(a)



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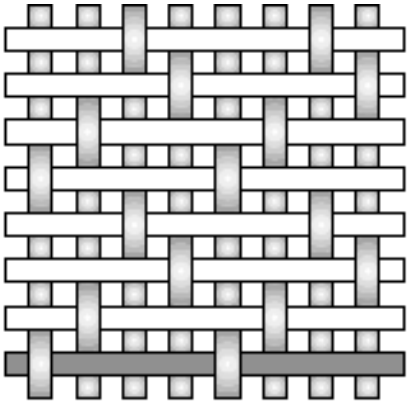

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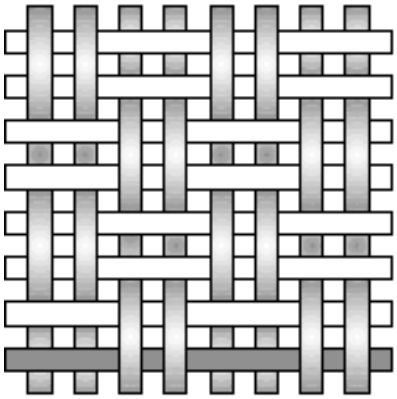
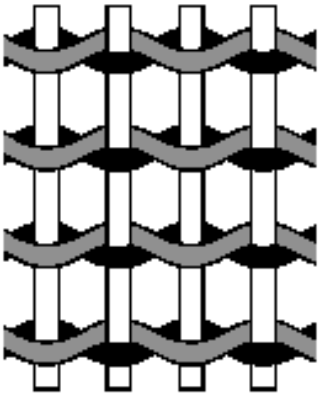


(d)



(e)

Figure 1.2 Woven glass fiber weave styles: (a) Plain, (b) Twill, (c) Satin, (d) Basket, and (e) Leno [2]

1.4 Resin Transfer Molding

PMC manufacturing methods are chiefly characterized by the method of placing the uncured composite material into or onto a mold so that the material can be shaped into the final product. The main manufacturing methods are: Hand lay-up, vacuum press molding, autoclave molding, filament winding, compression molding, pultrusion and resin transfer molding (RTM) [3].

Resin transfer molding (RTM) process is also known as liquid transfer molding process. In the RTM process, a preform is placed into the mold cavity. A matching mold half is mated to the first half and the two are clamped together. Then, using dispensing equipment, a pressurized mixture of thermoset resin, a catalyst, color, filler, etc., is pumped into the mold using single or multiple ports in the mold. After curing, depending on the cure kinetics of the mixture, the part is then removed from the mold. Thus, RTM results in the production of structural parts with good surface finish on the both sides of the part [3].

The main issues in the RTM process are resin flow, curing, and heat-transfer in porous media. The process involves injecting a precatalyzed thermosetting resin under pressure into a heated mold cavity that contains a porous fiber preform. During mold filling, the resin flows into the mold and experiences exothermic curing reactions, causing its viscosity to increase over time and finally solidification. After the fiber preform is completely saturated with resin, cure reactions continue past the gel-point to form a cross-linked polymer [3].

1.4.1 Materials and Tooling in RTM Process

For the RTM process, fiber preforms or fabrics are used as reinforcements. There are several types of preforms (e.g., thermoformable mat, conformal mats, and braided preforms) used in the RTM process. The thermoformable mats are produced by more or less randomly swirling continuous yarns onto a moving carrier film or belt and applying

a binder, which is typically a thermoplastic polymer, to loosely hold the mat together. The mat is cut to the desired size and formed under heat and pressure to the shape of the mold. In this process, scraps are produced to get the final shape preform because complicated three-dimensional shapes are produced by cutting the flat mat and then forming it under heat and pressure. Once a shape is formed, the preform maintains its shape. In conformal mats, fabrics or chopped strand are placed on the outer layer and spun-bonded core material is placed as core materials. These layers are stitched together to form conformal mats. Spun material is placed as a core material to create a low-permeability region in the inside region. In braided preforms, fibers are woven over a mandrel to obtain a three dimensional fiber architecture. For low-volume applications, weaves, braids, and mats are utilized; and for high-volume applications, random fiber preforms are used. Glass, carbon, and Kevlar are used as reinforcing fibers to make the preform, E-glass being the most common [3].

A wide range of resin systems can be used, including polyester, vinylester, epoxy, phenolic, and methlymethacrylate, combined with pigments and fillers including alumina trihydrate and calcium carbonates. The most common resin used for the RTM process is unsaturated polyester and epoxies. Epoxy with carbon fiber is very common in aerospace industry. The use of epoxies and other high-viscosity resins require changes in equipment to meter and condition the resin prior to injection. New epoxy resins are being developed to provide fast cure, thus increasing the production rate [3].

1.4.2 Mold Design for RTM Process

The mold for the RTM process is typically made of aluminum and steel but for prototype purposes plastic and wood are also used. The mold is generally in two halves containing single or multiple inlet ports for resin injection and single or multiple vents for air and resin outlet. In the mold design stiffness is critical. The wall thickness of the mold should be sufficiently rigid to take all the pressure exerted during processing. The mold design should also take into account handling and thermal considerations. Thermal properties of the mold and composite materials affect the dimensional tolerances of the

finished part and therefore the coefficients of the thermal expansion for the mold and part need to be considered while designing the mold. The tool should be designed to ensure that it can be clamped and sealed properly [3].

1.4.3 Production with RTM Process

In the RTM process, a preform of dry fiberglass mat or fabric is positioned in the cavity of a matched mold as shown in Figure 1.3 below. All the variations of RTM follows the general process outline depicted in Figure 1.3, except that in some cases the pressure drawdown operation is not performed.

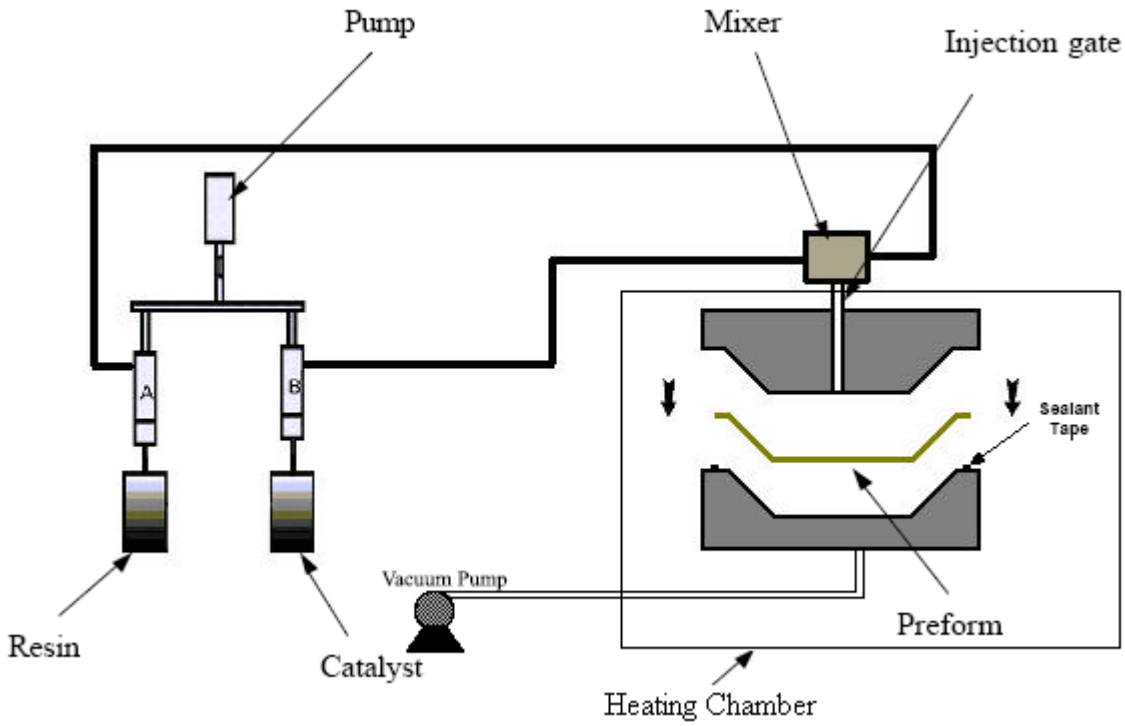


Figure 1.3 Vacuum-assisted resin transfer molding process showing the preform being inserted into a matched metal mold for a pressure drawdown operation, using the vacuum pump and a resin transfer pump.

Cores and inserts are inserted into the preform as required. Once the reinforcing and core materials are placed into the cavity, then the mold is closed. The mold can be closed using hydraulic or pneumatic presses or by using clamps along the edges. After closing the mold, liquid resin is pumped under low to moderate pressure into the mold cavity using dispensing equipment. In a typical dispensing equipment, resin and catalyst are stored in tanks A and B and mixed through a static mixer just before injection. Single or multiple ports are used for resin injection. For small components, a single port is typically used. For long and large structures, multiple ports are used for uniform resin distribution as well as for faster process cycle time. In general, the resin is injected at the lowest point of the mold and flows upward against gravity to minimize entrapped air. Vents are located at highest point of the mold [3].

The steps during the RTM process are summarized below:

1. A thermoset resin and catalyst are placed in tanks A and B of the dispensing equipment.
2. A release agent is applied to the mold for easy removal of the part. Sometimes, a gel coat is applied for good surface finish.
3. To avoid vacuum leakage a proper sealing is applied.
4. The preform is placed inside the mold and the mold is clamped.
5. The mold is heated to a specific temperature.
6. Resin is mixed either by a fixed mixer which is at the tip of the injection unit or by a mechanical mixer.
7. Mixed resin is injected with positive pressure through inlet ports at selected temperature and pressure. Sometimes, a vacuum is created inside the mold to assist in resin flow as well as to remove air bubbles.
8. Resin is injected until the mold is completely filled. The vacuum is turned off and the outlet port is closed. The pressure inside the mold is increased to ensure that the remaining porosity is collapsed.
9. After curing for a certain time, depending on resin chemistry, the composite part is removed from the mold [3].
10. If required, post-cure is applied.

1.4.4 Advantages of the RTM

RTM provides opportunities to use continuous fibers for the manufacture of structural components in low-to medium- volume environments. Some of its major advantages over other composites manufacturing techniques include: [3]

1. Initial investment cost is low because of reduced tooling costs and operating expenses as compared to compression molding and injection molding. For this reason, prototypes are easily made for market evaluation.
2. Moldings can be manufactured close to dimensional tolerances.
3. RTM processing can make complex parts at intermediate volume rates. This feature allows limited production runs in a cost-effective manner. This lends benefits to the automotive market, in which there is a growing need toward lower production volumes per car model and quicker changes to appeal to more niche markets.
4. RTM provides for the manufacture of parts that have a good surface finish on both sides. Sides have similar or dissimilar surface finishes.
5. RTM allows for production of structural parts with selective reinforcement and accurate fiber management.
6. Higher fiber volume fractions, up to 65%, can be achieved.
7. Inserts can be easily incorporated into moldings and thus allows good joining and assembly features.
8. A wide variety of reinforcement materials can be used.
9. RTM offers low volatile emission during processing because of the closed molding process.
10. RTM offers production of near-net-shape parts, hence low material wastage and reduced machining cost.
11. The process can be automated, resulting in higher production rates with less scrap [3].

1.4.5 Limitations of RTM Process

Although RTM has many advantages compared to other fabrication processes, it also has the following limitations [3].

1. The manufacture of complex parts require good amount of trial-and-error experimentation or flow simulation modelling to make sure that porosity- and dry fiber- free parts are manufactured.
2. Tooling and equipment costs for the RTM process are higher than for hand lay-up and spray-up processes.
3. The tooling design is complex.

A comparison of RTM with other molding processes is presented in Table1.1 [3].

Table 1.1 Comparison of RTM with Other Molding Processes [3].

Molding Process	Production Rate/Year	Cycle Time (min)	Emission
RTM	200 – 10000	6 – 30	No
Open Mold (hand lay-up, spray-up)	100 – 500	60 – 180	Yes
SRIM	> 10000	3 – 20	No
Compression molding (SMC, BMC)	> 10000	1 – 20	No
Injection molding	> 20000	0.5 – 2	No (very safe)

1.5 Previous Works on RTM & RTM Parameters

In RTM process, main parameters and features are: permeability of the media, fiber fraction, fiber architecture, injection pressure, location of injection and ventilation gates, void content, pressure during cure, vacuum level (if exists), mold preheat temperature and resin temperature. All these variables are dependent on each other. Previous works on these parameters are given below.

1.5.1 Permeability

In RTM process, resin flow and fiber wet-out are very important. Some of parameters which determine resin flow within RTM process are injection pressure, vacuum in the mold, resin temperature, viscosity, and preform permeabilities. Preform permeability depends on fiber material type, fiber architecture, fiber volume fraction, and several other factors. During mold filling, the resin follows the path of least resistance and experiences difficulty when impregnating tightly packed yarns and reinforcing fibers.

Flow through fibrous preforms by an externally applied pressure is often modeled using Darcy's law. It states that the volumetric flow rate *(Q)* through a constant area reinforcement is proportional to the cross-sectional area *(A)*, to the pressure gradient across the reinforcements *(ΔP)*, inversely proportional to the viscosity *(μ)* and to the length in the flow direction *(z)*:

$$\frac{Q}{A} = V_z = -\frac{K_{zz} \cdot \Delta P}{\mu . z}$$

In the above equation K_{zz} is the permeability of the porous material in the direction *z* and V_z is the average superficial velocity. This law is used to determine the in-plane and transverse permeabilities of reinforcements, from the measurements of the flow rate at a given pressure gradient. Darcy's law is defined for saturated porous media. Since the fibrous materials used in RTM are dry, the mold filling stage is an unsaturated flow process. However, because it is easier to implement, the permeability measurement is often carried out with a steady flow condition by saturating the specimen [4].

Jinlian *et.al* [5] found a relation between permeability and void content during their research on void formation in multi-layer woven fabrics. They suggested two simplified unit cells for in-plane impregnation in multi-layer fabrics to develop a mathematical model in order to describe the mechanism of void formation during RTM processes. They performed experiments to measure the formation of voids and their location. They used three plies of plain woven fabrics as reinforcement and a two-part epoxy/amine

resin, LY564/HY2954 from Ciba-Geigy as matrix material. Resin was injected at a constant pressure (0.6 MPa) into the mold and the longitudinal cross-section was examined using a microscope. The location of the void predicted by the model agreed quite well with the experimental results. The Voids observed in microstructure of the composite plates were mainly located at the end of the warp since the transverse permeability of the warp is lower than the axial permeability of the weft direction. Their model showed that the ratio of weft's axial permeability and warp's transverse permeability is determinant for the formation and size of void.

1.5.2 Fiber Fraction

An investigation of effects of fiber fraction on the performance of the glass fiber reinforced epoxy composites molded by RTM was done by Lee and Wei [6]. The resin used was a two-part epoxy/amine resin LY564/HY2954 supplied by Ciba-Geigy. The fabric reinforcement used was a highly permeable glass fabric from Brochier, Ijectex EF420-E01-100, with a surface density of 420gr/m². A flat rectangular aluminum mold with the dimensions of 0.325x0.325x0.003m was used for the preparation of the RTM composites. Ten and eight layers of glass fabrics of EF420 were used to produce 3 mm thick plates of a 55 and 44% fiber volume fraction, respectively. Although the fiber volume fraction is one of the most important factors affecting the mechanical strength of high-performance composites, more fibers can result in decrease of the flow viscosity of resin in the RTM process. Lee and Wei observed an increase in mold filling time by 35% when the fiber volume fraction increased from 44 to 55%. The 44% fiber fraction composite had a higher flexural strength and a higher ILSS than that of the 55% fiber fraction composite as a result of a reduction of voids in the resulting composites. They also indicated that the decreased fiber fraction leads to a lower flexural modulus due to the increased resin content and the significant loss of stiffness in the composites [6].

1.5.3 Fiber Architecture

Pearce *et al.* [7] studied to relate variations in permeability, and in the laminate mechanical properties, to differences in microstructure. They used SP Systems Ampreg 26 epoxy with Ampreg 26SL slow hardener as the resin matrix and four carbon-fiber fabrics were woven specifically for their study by Carr Reinforcements Limited using a 372 gr/m² 2x2 twill weave as the reference fabric. One of the fabrics did not contain any high permeable tows where others contained them with varying amounts. After producing plates with same process parameters, they performed tension and compression tests. The compression strengths were found to be unaffected by the changes in fabric architecture. They attributed this result to that since compression strength could be related to the maximum curvature in the axial direction; maximum value would be unchanged with the introduction of those flow enhancing tows. However, the values of tensile strength in the weft direction were found to be dependent on the fiber architecture. The strength for fabric containing 7% modified tows was lower than the strength for the fabric containing 10% modified tows.

Lee and Wei [8] in their another study investigated the effects of permeability on static and dynamic mechanical behavior by comparing two fabric structures which have different permeabilities because of their different fiber architecture. In their study, they used the epoxy resin PR500, from 3M, is a one-part epoxy and an epoxy-amine resin, LY564/HY2954 from Ciba-Geigy. The fabric reinforcement used in their study was a highly permeable glass fabric from Brochier, Injectex EF420-E01-100, with a surface density 420 gr/m², and an eight-harness satin woven glass fabric 1581 from Clark-Schwebel Co. with a surface density of 293.3 gr/m². They injected the resins into a 32.5x32.5 cm Aluminum flat mold. The preforms prepared for experiments were 10 plies of EF420 for 3 mm thickness and 10 plies of 1581 to give 3 mm and 2 mm thickness respectively to get the same fiber fraction, 55% in volume. They observed that the plates containing 1581 eight-harness satin fabric have less void content than the plates containing EF420. The resin flow in the highly permeable fabric EF420 was much faster in the x-direction than in the y-direction. As the resin flow front had reached the

mold edge, a gap developed between the fabric and the mold edge. This gap can create a preferential flow path for the resin (edge effect), and the mold edge, which disrupts filling the mold cavity.

The ILSS values that they measured showed decrease with increase in void content. When they investigated the dynamic mechanical behavior of the specimens they found distinct difference between the two fabric architecture. The storage modulus of EF420 fabric composites were 32-60% lower than those for 1581 fabric composites. In addition, the flexural modulus of 1581 fabric plates was 18% higher than that of the EF420 plates.

1.5.4 Injection Pressure

The pressure applied during the RTM process in the mold is the resin injection pressure. This injection pressure helps the resin to flow inside the mold through porous media and allows the resin to fill the cavity. The RTM system have compressors that inject resin at a certain pressure. The injection pressure determines the flow rate of the resin, and thus the mold filling time. Resin injection pressure depends on the resin viscosity, mold size, permeability of porous media, mold fill time needed, and cure kinetics of the resin.

Kaynak and Kas [9] studied on the effects of injection pressure in RTM of woven carbon fiber/epoxy composites. In order to investigate effects of injection pressure they produced woven carbon composite layers with a small laboratory size RTM machine. They used Ciba Araldite LY5052/HY5052 resin system as matrix material and Torayca T-300-Fiberite 2x2 twill carbon weave as reinforcement. They injected resin mixture into a flat mold filled with woven carbon fiber layers with injection pressures of 1, 2, 3, 4, and 5 atm. They made mechanical testing and microscopic examination. They observed that an injection pressure level of 2 atm resulted in the best mechanical performance of the specimens due to better fiber impregnation by the uniform resin flow, minimizing void formation. Increasing the resin injection pressure level above 2

atm, they observed differences between macroflow and microflow leading to non-uniform resin flow and void formation, hence a reduction in the mechanical properties.

Olivero *et al.* [10] investigated effects of injection rate on the mechanical properties of resin molded disks. They used an epoxy resin, EPON 815C, manufactured by Shell Chemicals, and chopped-strand glass mats as reinforcement materials. An experimental molding setup was constructed to fabricate fiber-reinforced, center-gated, disk-shaped composite parts. Disks were molded at four different injection rates in order to observe the effects of these on the mechanical properties and void content of the final part. The related flow rates were 0.067, 0.2, 0.6 and 1.0 cm^3/s. They found that increased injection rate had a detrimental effect on the mechanical properties of resin transfer molded composite disks. Both the stiffness and tensile strength were measured to decrease by 14 and 13%, respectively with the increase in injection rate. They explained this result by the fluid flow front. The fluid flow front moves faster and traps more air leading to increased void formation.

Rudd *et al.* [11] studied on the effects of process variables on cycle time during resin transfer molding process. In their study they also investigated the injection pressure as a process parameter. They used a 558 x 550 mm plaque mold made of aluminum with an injection gate in the upper half. They applied two different injection pressures of 2 and 5 bar to the moulds having the same amount of fiber reinforcement. They observed 20% increase in overall cycle time by the decrease in injection pressure from 5 to 2 bar. They also noted that the peak temperatures recorded in the laminates with 2 bar injection pressure were approximately 25°C less than those recorded at the higher resin injection pressure due to longer cure cycle, which releases the heat of reaction over a longer period.

1.5.5 Location of Injection and Ventilation Gates

Gating and venting are very practical design issues in RTM. It is not possible to mold a composite part without at least one gate to inject resin and one vent to let the displaced air out of the mould. Poorly designed gate and vent locations can yield a part with dry spots.

Liu *et al.* [12] studied on the modeling and simulation of RTM process. After modeling, they verified their model with experiments. For experimental verification a mold with 203 x 140 x 102 mm dimensions and 3.18 mm cavity thickness was used. For the first experiment, they injected dyed corn syrup at a constant flow rate at the centre of one of the ends of the box, the preform consisting of random fiberglass mat with a volume fraction of 14%. In this experiment, a dry spot has formed due the race tracking, an effect caused by areas of relatively high porosity in the preform, or air channels. The fluid was drawn into the the dry spot by capillary forces, and it appeared to close up. They also observed air gaps formed at the four edges of the base of the box. In their second experiment, they injected the fluid at a constant flow rate at the end of the box and simultaneously at the centre of the central face, the preform consisting of bidirectional fiberglass mat with a volume fraction of 35%. At this particular instance, dry spot was formed between the merging flow fronts existing within the mold. In this experiment, a dry spot had formed due to the complications introduced through multiple injection sites, and also the presence of race tracking. Unlike from the first experiment, the region in which the dry spot occurred was not fully saturated with fluid and hence represented a defective portion of the finished product. As in the first experiment air gaps formed at the four edges of the box.

Lee and Wei [6] also investigated the effects of location of gates to the resin flow. In order to make observations they used two different gate arrangements which were center inlet and perimeter inlet systems. In their experiment, they found a sudden decrease in mold filling time , 65%, for the moldings with the perimeter inlet as compared to that with the center inlet. They explained this decrease as the much higher flow rate in the

perimeter inlet. This difference between flow rates of moldings with different gate locations resulted a 28% lower void content and a 6% higher flexural strength within plates produced with the perimeter inlet system when compared with plates which were produced by using the center inlet arrangement.

1.5.6 Void Content

Voids (or improper wet-out) are the most important problem in the RTM process. Existence of voids in composite is detrimental to mechanical properties such as, ILSS, compressive strength and fatigue. On the other hand, an increase in impact strength with increasing void content has also been reported. This is explained by the weakened bonding contributing to the formation of a more extensive yielding zone at a propagating crack tip. Greater toughness then arises because of debonding and pulling out of fibers and to a limited extent by delamination.

Varna *et al.* [13] studied the effects of voids on the global mechanical behaviour of laminates in transverse tensile loading. They also studied micromechanisms of failure in order to explain the effect of void content on mechanical behaviour. They used Palatal A430 vinylester from BASF AG as a polymer matrix and unidirectional glass fiber fabric Brochier Lyvertex 21130 from Brochier as the reinforcement. Approximately 5% of the total amount of fibers was aligned perpendicular to the major fiber direction. Twelve layers of predominantly unidirectional glass fiber fabric, were placed in a rectangular mold of 0.2 x 0.88 x 0.003 m. The mold and matrix were heated to 35°C and the matrix was injected into the mold from a pressure vessel at 0-6 MPa absolute pressure. They observed two types of voids in the specimens produced. Large spheroidal voids formed between transverse fiber bundles at positions where weft bundles cross transverse bundles. Long, cylindrical voids with smaller diameter formed within fiber bundles and were orientated in the flow direction. Laminates with the highest average content of voids also had the highest content of large spherical voids. These laminates had a transverse strain to failure as high as 2% whereas low void content laminates failed at 0-3%. Only a few large and well-defined transverse cracks formed in low void

content laminates before final failure. Multiple transverse cracks with irregular shape as well as numerous smaller cracks formed in the high void content laminates. The irregularity of these cracks resulted in lower stress concentrations and stress level in the weft bundles.

Ghiorse [14] observed the mechanical property changes by the presence of different levels of void content. He produced 24 epoxy laminates plates with wet lay-up, vacuum bagging and autoclave methods. Epoxy prepregs of 0.13 mm thickness and carbon fibers were used for production of composites. He reported a void content variation of ±2% in the production of carbon/epoxy composite would cause an approximate ±20% swing in the interlaminar shear strength and flexural strength, accompanying with a ±10% variation in the flexural modulus. Therefore he deduced that in the range of 0-5% void content, each 1% increase in void content would lead to a 10% decrease in flexural and inter laminar shear strength and 5% in flexural modulus.

Lundstrom and Gebart [15] performed an experimental series to investigate the change in void content during filling. In these experiments they cut the reinforcement in different lengths (0.2, 0.4, and 0.55 m) and made injection with a flat mold by a parallel flow from one edge of the laminate to the other. Then they observed the resin flow and void content through preforms measuring 6.5, 5.2, and 7.4% average void contents respectively. From these results, they concluded that bubbles were continuously created during mold filling since the total void increased with increasing length. They suggested continuing filling after the reinforcement had been completely wet by resin to reduce void content.

1.5.7 Pressure During Curing

Olivero *et al.* [10] investigated also the effects of pressure during curing on the mechanical properties of resin molded disks. They observed that, increasing the pressure level applied during curing increases the mechanical performance of the specimens due to the lowered void fraction, for instance the increase in tensile strength was 15% when

they increased the pressure from 0 to 683 kPa leading to void fractions of 0.72 and 0.35 respectively.

Lundstrom and Gebart [15] also made a similar study by using an extra pressure of 0.2 MPa during curing after the resin injection. They observed a reduction of about 60% in void content compared to a laminate cured at atmospheric pressure. They claimed that pressure during curing compressed voids leading to lower void content.

1.5.8 Post Cure Condition

When a reinforced epoxy resin starts to cure, the internally developed loads tend to deform the product and give rise to residual strains. Restrained deformations lead to internal stress build up, which have a damaging effect on the quality of the product, mainly in the form of cracks and fiber-resin debonding.

Nowak *et al.* [16] presented a novel simulation procedure for stress and shrinkage calculations for post cure conditions, as well as the simulation results. They selected an embedded pole which was a heart of the vacuum circuit breaker, as the product analysis. They used silica–filled-epoxy based casting resin system, Araldite, produced by Vantico Ltd. They tested different post curing conditions.

Their simulation predicted that a postcuring schedule characterized by fast cooling within the first few hours gave rise to lower curing degrees. This incomplete curing retained till the end of the process. For mechanical performance, the case of which the temperature of the whole component was stabilized at 60°C was found to be better than the case of which the component cooled to room temperature. The cases in which, the high temperature of the resin was maintained during the first 4 hours of the total 8 hours of post curing stage, products completed their curing very rapidly. From the comparison of the maximum stress and deformation values estimated for the different cases, they concluded that the values achieved for natural convection cooling were slightly lower than values obtained for controlled cooling cases.

1.6 Previous Works on the Effects of Mold Temperature, Vacuum and Initial Resin Temperature

1.6.1 Mold Temperature

Chang *et.al.* [17] investigated the effects of process variables on the quality of compression resin transfer molding. One of the parameters they studied was pre-heated mold temperature. They used Ciba-Geigy epoxy resin LY564/HY2954 and the bi-directional fiber mat TGFW-600 (a woven roving glass fiber mat). The upper part of the mold had dimensions of 200x180x45 mm and the lower mold had 300 x 270 x 30 mm. They injected the resin into the mold by using a pressure pot connected to a compressed air source. Specimens were made of five plies of TGFW-600 fiber mats. For comparisons of mechanical properties, various specimens were fabricated under different process conditions. The pre-heated mold temperatures used with different combinations of other process variables were 25, 50 and 75°C. Tensile test was employed to measure the ultimate tensile strength and modulus of elasticity in this study. They concluded that when compared to the other process parameters such as vacuum level, injection pressure and resin temperature, the influence of mold temperature on mechanical properties of the laminates was rather slight.

Yu and Young [18] studied on the optimum RTM process parameters. One of the process parameters they take into account was mold temperature. They studied with both epoxy and polyester resin systems. For epoxy resin system, they used a rectangular mold with dimensions 102.4 x 90 x 2 cm and as reinforcement TGFC 7628-38N fiber glass cloth. They made injections at different mold temperatures. They concluded that under the same injection pressure, mold filling time was shorter for higher mold temperature and resin injection temperature. However, they observed that the filling temperature was too high, the mold might not be completely filled because of the premature resin gel.

Johnson and Pitchumani [19] studied to improve permeation of the medium by induction heating which would give decrease in resin viscosity in low permeable regions. They developed a process to investigate the effects of process parameters such as induction heating of the mold. Materials used in their work were a glycerin-water mixture as the working fluid in lieu of an actual resin-catalyst system, Owens Corning M8610 continuous strand mat and COFAB A1118B bi-directional stitched mat. In their work, they used three different preform lay-ups having low permeability bi-directional mat, and high permeability random mat. They applied injections with various vacuum levels and with various heating levels by different coil positions. Their experiments showed that the effects of mold heating on the void fraction changes according to the location of the heated mold. They indicated that above a certain heating level, for many combinations of permeability difference and coil location, the void fraction could be reduced to zero leading to complete fiber wet-out. On the other hand, increased heating level of the mold might lead to premature gelling of the resin and cause even higher unfilled volume fractions.

Gonzalez-Romero and Macosko [20] presented some design suggestions for the RTM process. While they described the criterion for selection of process parameters for optimization they observed the resin flow in RTM process. They claimed that during resin injection into the hot mold, the incoming fluid picks up heat from the porous bed and carries it as it flows. By the end of filling, the material closer to the injection gate had the lowest temperature and the material at the outlet of the mold has the highest temperature; thus, the resin at the gate cured last.

1.6.2 Vacuum

In order to aid good resin flow and to avoid voids, vacuum at the vents can be applied to displace air within the reinforcements. Vacuum also helps in rapid mold filling.

In the research of the effect of process variables on the quality of compression resin transfer molding, Chang *et.al.* [17] made a specimen without vacuum while all the other

specimens were made with vacuum assistance. By that specimen they validated the effect of vacuum assistance in the RTM process. The ultimate strength of the specimen without vacuum assistance decreased by about 30% as compared with those with vacuum assistance. They explained this result by the decrease of void content when they used vacuum.

Hsiao *et al.* [21] investigated the influence of air pressure gradients at the flow front, due to the presence of two air vents under different vacuum pressures for Resin Transfer Molding (RTM) and Vacuum Assisted Resin Transfer Molding (VARTM) and they introduced an analytical model to predict the pressure distribution. Their analytical model showed that there was pressure variation along the flow front resulting from the introduction of the sink and source vents. The model claimed that the significance of pressure variation depended on the geometry of the mold, location and strength of the sink and source, air viscosity, and permeability of the preform. This sink and source model suggested that pressure variation was favorable to low permeability preforms and increases linearly as the distance between the two vents increased.

Abraham and Mcllhagger [22] made investigation on various methods for resin transfer and gating to maximize fabric wet out and minimize void content. For their experiments, they used two piece 550 mm² Aluminum mold. The resin system used was Ciba LY-564 and a HY-2954 hardener. A series of 18% volume fraction preforms with 295 gr/m² plain weave glass fiber CS-Interglass and a series of 50% volume fraction preforms with 196g/m² CS-Interglass were used as reinforcements. They performed tests with different vacuum levels (0.75 bar, 1 bar), fiber volume fractions (18 and 50%) and gating systems (peripheral and radial). They concluded that maximum flexural strength was achieved when vacuum and peripheral gating was utilized. This method of vacuum and gating system eliminated the problems of edge tracking as the gap between the fabric and the tool was used to feed the reinforcement with resin. Their study also demonstrated that peripheral gating using vacuum was not affected by the anisotropic permeability for the stacked laminate and dimensions used in experiments. Radial gating, however, for a similar preform construction, suggested that flow modeling was required to determine

vent location accurately, which was necessary to achieve high quality and complete wet out.

Lundstrom and Gebart [15] compared the void content with different outlet pressures i.e. different levels of vacuum assistance. The pressure differences between inlet and outlet were kept constant at 0.5 MPa to eliminate any influence on the void content from different pressure gradients or, equivalently, different injection speeds. The length of the reinforcement, which they used, was 0.55 m and the temperature of the resin and the mold had been 35°C. They observed a decrease in void content by increasing vacuum level. For the highest vacuum level (~0.001 MPa) the void content was practically negligible.

Hayward and Harris [23] investigated effects of process variables on the quality of RTM moldings with polyester resin. In their study, they found that, 70% vacuum assistance made the amount of void content decrease significantly. Because of that minimization in void content, shear strength and flexural strength of parts produced with RTM increased. The reason of this increase was the reduction of pressure in trapped air pockets. They indicated that when the pressure in trapped air pockets reduced the degree of penetration of resin into those regions under vacuum increased.

1.6.3 Resin Temperature

Johnson *et al.* [24] described the application of a purpose-built, in-line microwave system to preheat resin and reduce RTM cycle time. Building their microwave preheating equipment they produced two series of moldings with resin injected at a constant elevated temperature to determine the effect on RTM cycle. They used Synolac 6345 initiated with 2% bis t-butyl peroxy dicarbonate as the resin mixture. They injected the resin mixture at 22, 30, 40, 45 and 50°C to the mold which was preheated to 60°C. They observed a 41% reduced impregnation time when raising the resin temperature from 22 to 40°C. Increasing resin temperature to 45°C caused no additional reduction in the impregnation time, while a further temperature increase to 50° extended the

impregnation time by 14 seconds. They explained this extension to the rise in viscosity within the mold prior to the end of injection as indicated by the flow of coagulated resin from the mold vents. They suggested that for the resin system and molding parameters used in the series of trials, 40°C was the optimum resin preheat temperature. This aroused from the interaction of resin viscosity and gel time, both of which were temperature dependent.

Lee and Wei [8] also studied on effects of injection temperature in RTM process. They used EF420 (a highly permeable glass fabric) and 1581 fabrics (an eight harness satin woven glass fabric) and epoxy matrix. For both of the fiber architecture they injected resin from a center inlet at 160°C and from a perimeter inlet at 150°C. They observed that the parts produced at 150°C injection temperature showed a 7-11.5% lower flexural strength for both fabrics than the parts produced at 160°C. Furthermore, composite plates which produced with 150°C injection temperature had 41% less storage modulus than the composites produced with 160°C injection temperature. They explained the reductions in the flexural modulus and storage modulus observed for the composites produced at 150°C by the insufficient mixing of the resin resulting from particulate filtration of hardener by fabric preform during the mold filling stage via the perimeter inlet. Since the peak melting temperature of the resin was around 155°C, the melting of the solid hardener could not be complete at 150°C.

1.7 The Aim of This Research

In resin transfer molding (RTM) production technique there are many process parameters that affect the product quality. Some of the main process parameters are: permeability of the preform, fiber fraction, fiber architecture, injection pressure, location of injection and ventilation gates, pressure during curing, resin temperature, mold temperature and vacuum level. Many of these parameters were investigated in the References [4 through 26] as explained in the above sections. Kaynak and Kas [9, 25] previously studied the effects of resin injection pressure, part location, and post-curing on the properties of RTM composite plates.

The main aim of this study was to investigate the influences of mold temperature and use of vacuum during resin injection. For this purpose, epoxy/woven glass fiber composite plates were produced with six different mold temperatures (25, 40, 60, 80, 100º and 120ºC), two different initial resin temperatures (15º and 28ºC), and under vacuum (0.03 bar) and without vacuum (~1 bar) conditions.

After the production of composite plates by RTM, C-scan ultrasonic inspection, mechanical tests, thermal analyses and scanning electron microscopy were conducted to evaluate the influences of mold temperature, initial resin temperature and vacuum.

CHAPTER 2

EXPERIMENTAL WORK

In this study, as explained in the following sections in detail, in order to investigate the effects of mold temperature and vacuum level on the properties of Resin Transfer Molded composite specimens, first six plates were produced with different mold temperatures (25º, 40º, 60º, 80º, 100º, 120ºC), then another six plates were produced under vacuum (0,03 bar) and without vacuum (~1 bar) conditions only for three mold temperatures (25º 60º, 120ºC). In the first set, initial resin temperature was 28ºC (in summer), while in the second set it was 15ºC (in winter).

Before specimen cutting, all the plates were non-destructively evaluated by C-Scan analysis. Then, specimens were characterized by using mechanical tests (Tension, Flexural, Impact), thermal analyses (Ignition Loss, TGA), and scanning electron microscopy (SEM).

2.1 Materials Used

(i) Epoxy Resin and Hardener

In this study the matrix material used was made up of a special low-viscosity epoxy resin / hardener mixture Araldite LY5052/HY5052 produced by *Vantico* (Switzerland) which was especially developed for RTM applications. LY5052 is the base resin containing 1,4-butanediol diglycidylether, and HY5052 is a hardener based on modified cycloaliphatic amines. Their properties, viscosities and gel times, determined by the producer are given in Table 2.1, 2.2, and 2.3, respectively.

Table 2.1 Properties of the Resin and Hardener

Property	Epoxy Resin (Araldite LY 5052)	Hardener (Araldite HY 5052)
Aspect (Visual)	Clear liquid	Clear liquid
Color (Gardner, ISO 4630)	≤ 2	≤ 4
Viscosity at 25°C (ISO 9371B)	1000 – 1500 mPa.s	40 – 60 mPa.s
Density at 25°C (ISO 1675)	1.17g/cm³	0.94 gr/cm³
Flash Point (ISO 2719)	≥ 140 °C	≥ 110 °C

Table 2.2 Initial Mix Viscosity of the Resin and Hardener Mixture (ISO 9371B)

Temperature (ºC)	Initial Mix Viscosity (mPa.s)
18	1150 – 1350
25	500 – 700
40	200 – 250

Table 2.3 Gel Times of the Araldite LY5052/HY5052 Epoxy Resin/Hardener Mixture

Temperature (°C)	Gel Time (min.)
25	420 – 500
40	150 – 170
60	40 – 55
80	14 – 17
100	4 – 6
120	2 – 3

(ii) Woven Glass Fiber

Woven glass fiber used as the reinforcement material in this study was CD 125-300 produced by *Camelyaf* (Turkey). It was 1x1 plain weave type (Figure 2.1) with a surface density of 300 gr/m².

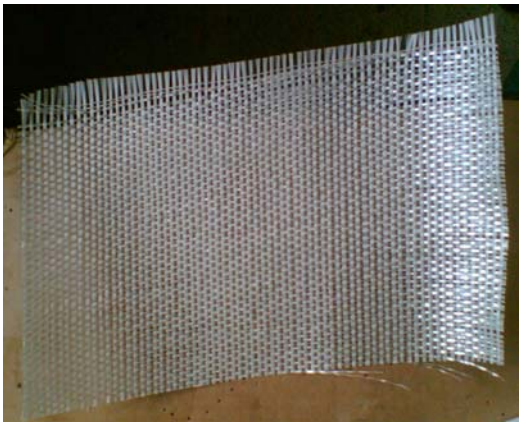


Figure 2.1 1x1 Plain weave glass fiber used

(iii) Mold Releasing Agent

In order to prevent sticking, in other words for easy demolding of the composite plates, *Vantico* QZ 13 mold releasing agent was used.

2.2 RTM System Used

In order to produce composite plates, ISOJET RTM System (Figure 2.2) at BARIS Electrical Ind.Inc (Ankara, Turkey) was used.

(i) Capabilities of the RTM System

- 15 lt resin capacity
- $2x10^{-3}$ mbar vacuum level
- 4 bar max injection pressure
- Resin flow rate control and monitoring
- Furnace for mold heating, resin injection and curing
- Temperature control and monitoring

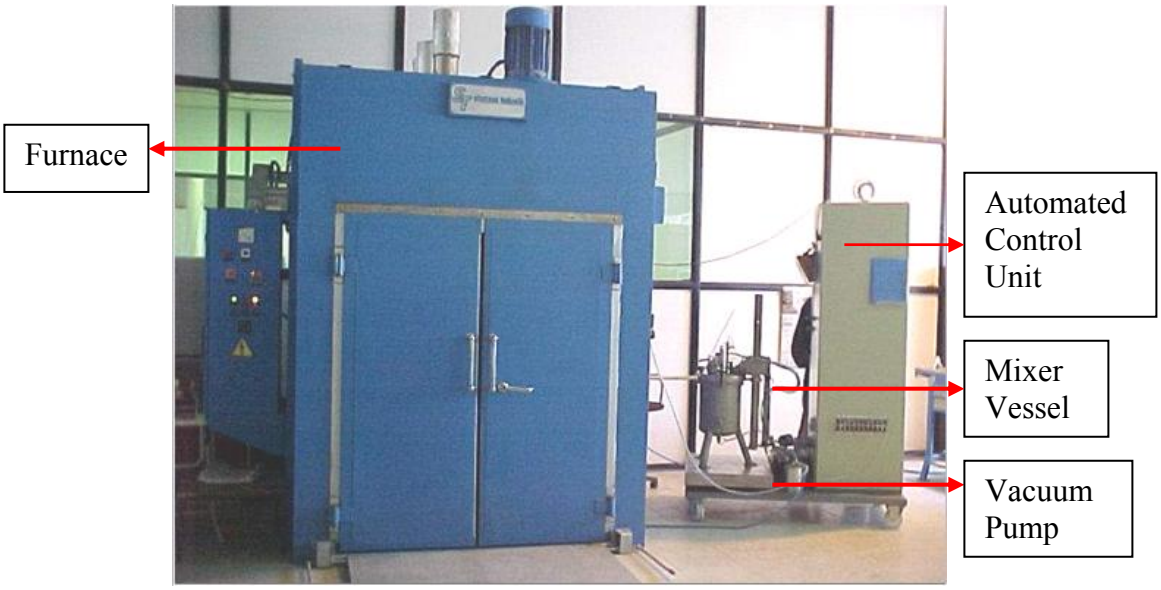
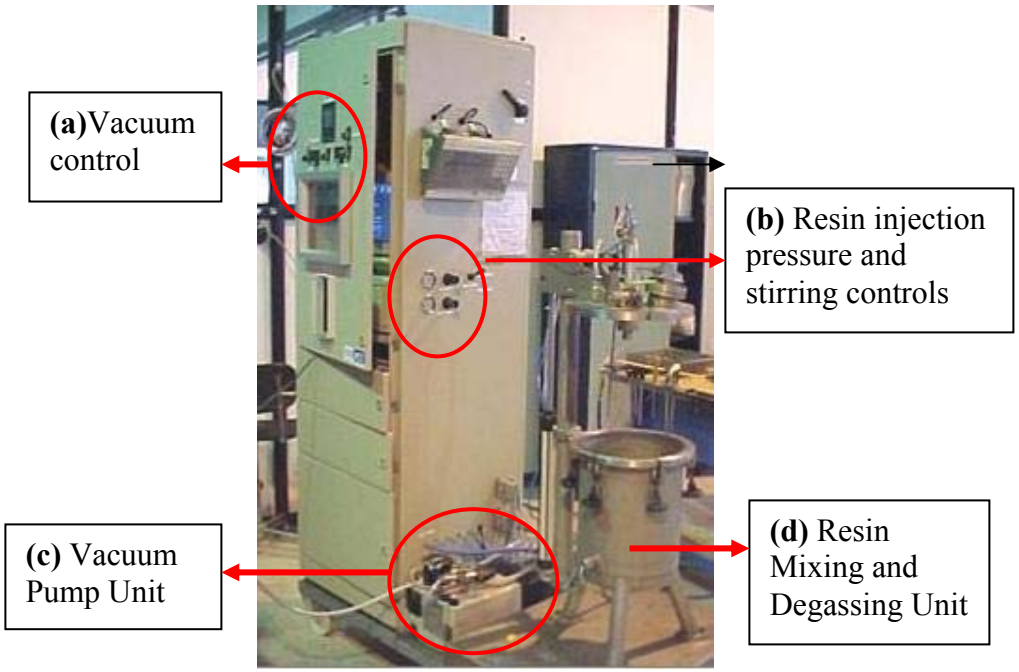


Figure 2.2 General view of the RTM system used

(ii) Parts of the RTM System

The system is composed of four main parts. First part is the automated control unit for adjusting, the vacuum levels and resin stirring and injection pressures as shown in Figure 2.3 (a) and (b).



(a) **(b)**

Figure 2.3 Main parts of the RTM System (a) Vacuum control units, (b) Resin stirring and injection pressure control units, (c) Vacuum pump unit, (d) Resin mixing and degassing unit

The second part, vacuum pump unit (Figure 2.3(c)) is used for two purposes, first for degassing over the resin mixing unit during stirring, and second in the mold (located in the furnace) during resin injection.

The third part is the mixing unit (Figure 2.3(d)) which is used to stir the epoxy resin and hardener mechanically. During stirring in order to minimize bubble formation, vacuum degassing can be also used. Then, resin mixture is injected into the mold located in the furnace.

The final part of the system is furnace (Figure 2.2), which is especially used for the temperature control of molds and resin curing. There are various connection pipes through the walls of this furnace for resin injection, mold vacuum, and resin outlet.

(iii) The Mold

In this study in order to produce composite plates, a two piece flat mold made of steel was used (Figure 2.4). Upper mold part has one inlet hole for resin injection and two outlet holes for excess resin, while lower mold part has a rectangular cavity of 300x200x4 mm for plate production.

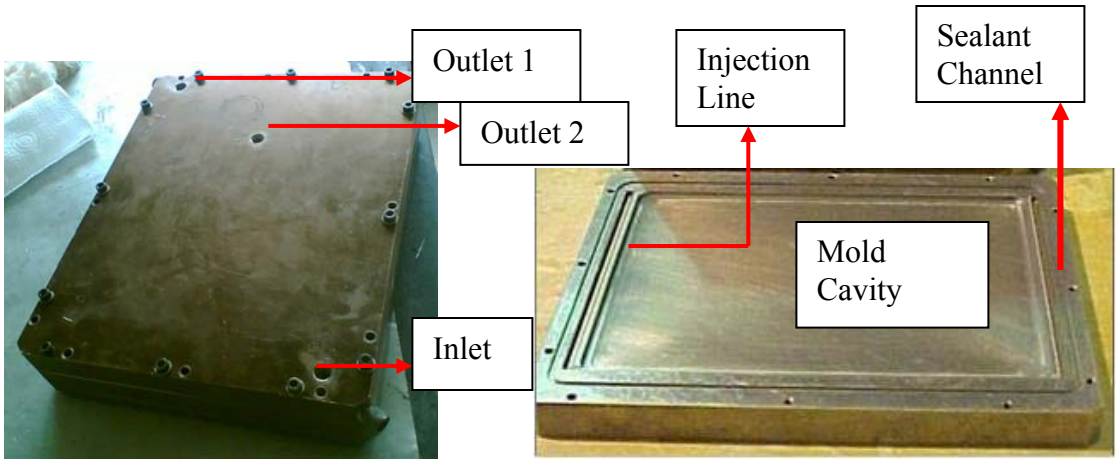


Figure 2.4 The two piece steel flat mold used (a) closed mold, (b) open lower mold

2.3 Production of the Composite Plates

General flowchart of the production of the composite plates is given in Figure 2.5. First of all, inner faces of the mold halves were cleaned and waxed with the mold releasing agent. Then, lower mold cavity was filled by laying up 14 layers of woven glass fiber as shown in Figure 2.6.

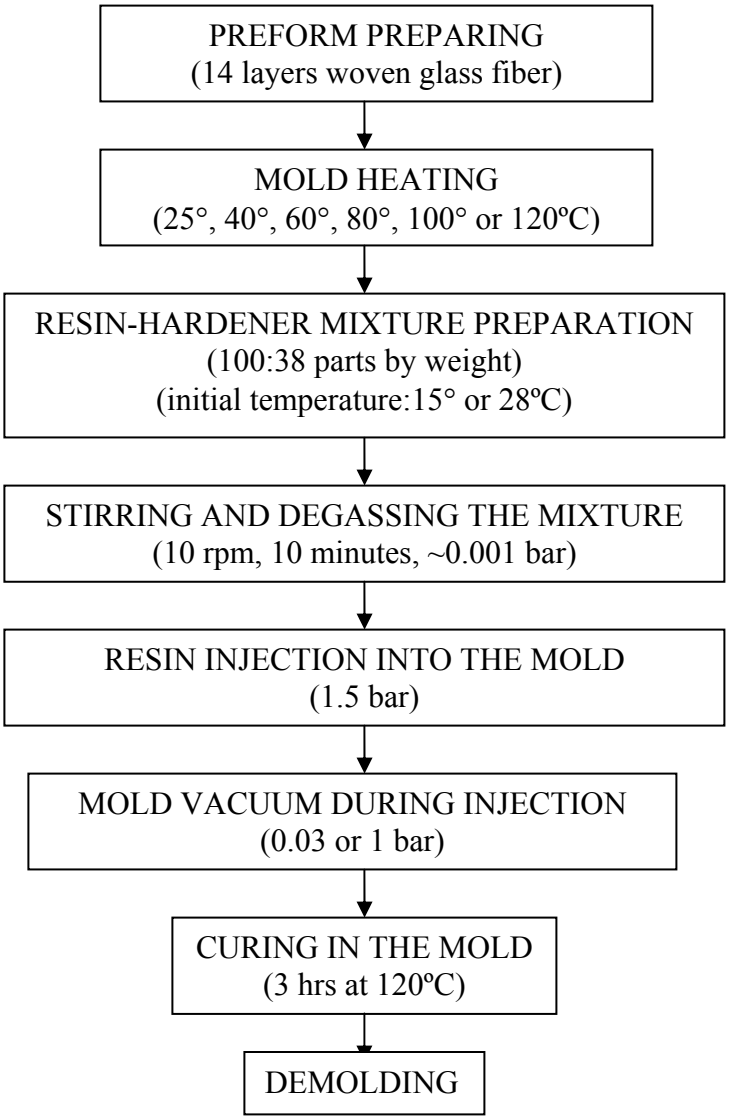


Figure 2.5 General flowchart of the production of composite plates

Figure 2.6 Lower mold filled with woven glass fiber layers

Second, upper face of the mold was closed and fastened, and then the mold was put in the furnace. After making inlet and outlet connections (as shown in Figure 2.7), the furnace was turned on to heat the mold to the required temperature. In this study in order to see their effects, six different mold temperatures were used: 25º, 40º, 60º, 80º, 100º and 120ºC.

Figure 2.7 Inlet-Outlet connections and standing position of the closed mold in the furnace

In the mean time, the resin and hardener mixture was prepared with a ratio of 100:38 parts by weight as indicated by the producer. In this study, a ratio of 500/190 gr was used for the production of one plate. In this set the temperature of the resin mixture was 28ºC (in summer). Then, the mixture was stirred mechanically with a speed of 10 rpm for 10 minutes (Figure 2.8) in order to prevent inhomogeneous mixture of the resin and hardener due to their density differences. During mixing, in order to minimize bubble formation, vacuum degassing under ~0.001 bar was also accomplished.

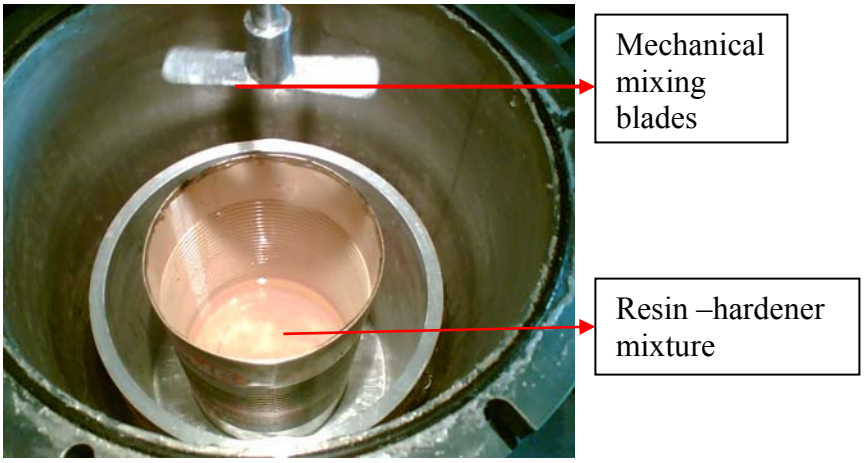


Figure 2.8 Mechanical stirring of the Epoxy-Hardener mixture

After all these preparations, the resin-hardener mixture was injected into the closed mold at 1.5 bar injection pressure. During resin injection, the mold cavity was vacuumed down to 0.03 bar.

In this study in order to investigate the effects of mold vacuum, another set of six plates were produced at three different mold temperatures (25º, 60º, and 120ºC) under vacuum (0.03 bar) and without vacuum (~1 bar) conditions. In this set the temperature of the resin mixture was 15ºC (in winter).

Following the mold filling, matrix resin system was cured in the mold by increasing the furnace temperature to 120ºC. Curing time was set to 3 hours at 120ºC. After curing, composite plates produced were de-molded.

2.4 Ultrasonic Inspection of the Plates (C-Scan)

After the production, the composite plates were evaluated by a non-destructive testing method called C-scan by *Tecal Auto-Ultra Scanning System,* with a scanning program called *Sara 8.2* and an evaluation software called NDEVAL 1.02 at TAI (Tusas Aerospace Industries, Ankara). The frequency of the probe used was 5 MHz. C-scan inspection parameters used in this study is given in Table 2.4.

Table 2.4 C-scan Inspection Parameters Used in this Study

Parameter	**Value**
Velocity	200
Index	1
Part to Nozzle Distance 1	20 mm
Part to Nozzle Distance 2	20 mm
Transducer Receiver	5 MHz
Transducer Transmitter	5 MHz
Nozzle Diameter	4/5 mm

C-scan is one of the ultrasonic non-destructive testing methods used for polymer matrix composite parts. In this method, first the composite part is fixed to a bar. Then two probes approach to the part from each side, by leaving the thickness of the part between them. One is emitting ultrasonic waves and the other is receiving them. But in order for the ultrasonic waves to move there must be a suitable medium. Ultrasonic waves loose their energies and speed when they pass through air. So, there is a flush of water coming out of the nozzles of both probes.

Because all the parts have a thickness, there will always be an energy loss (dB loss) through the thickness of the composite plate. But the amount of dB loss will alter if there is a defect in the structure, such as; resin rich regions, places where wrinkles occur in the fiber orientation, large voids entrapped inside the composite or the parts where the resin impregnation on to the fibers is not sufficient.

2.5 Specimen Preparation

After C-scan inspection of the composite plates, specimens for mechanical tests and thermal analyses were cut by a circular saw cutting machine (Delta) at TAI machining shop.

Specimens for each test were cut from different locations of the plates in order to have random sampling condition. By using the C-scan images of the composite plates, regions having large defects (especially edges of the plates, sometimes also central regions) were not used for the specimen cutting, and discarded as scrap.

2.6 Mechanical Tests

For each plate produced, at least three tension tests, and at least five flexural and Charpy impact tests were conducted at materials testing laboratories of TEMSA Automotive Industry Corporation, Adana. In order to calculate mechanical properties of the specimens precisely, thickness and width of the central part of each specimen were measured from five different locations.

(i) Tension Tests

Tension tests were conducted according to ISO 527-4 Standard [26] by using a 10 kN Shimadzu AGS-J universal testing machine with a loading rate of 2 mm/min. Type 1B specimens (with a 10mm width of a narrow portion and 115 mm length between grips) were machined from the samples of 250 x 25 x 4 mm.

(ii) Flexural Tests

Flexural (three point bending) tests were performed according to ISO 14125 Standard [28] by using the same Shimadzu testing machine with a loading rate of 1 mm/min. Dimensions of the specimen bars were 80x15x4 mm with a span length of 64 mm.

(iii) Charpy Impact Tests

Charpy impact tests were conducted according to ISO 179-1 standard [29] by using Ceast Resil Impactor 6959 with a hammer of 50 Joules. Dimensions of the un-notched specimen bars were 80x10x4 mm with a span length of 62 mm.

2.7 Thermal Analyses

In order to determine resin content, fiber content, and thermal stabilities of the specimens, two thermal analyses namely Ignition Loss and TGA were performed at TEMSA laboratories.

(i) Ignition Loss Analysis

Ignition loss of the cured and reinforced matrix resin was determined according to the standard ASTM D-2584 [30]. Specimens of 25x25x4 mm was put in a crucible and ignited at 565ºC by using Nuve MF120 muffle furnace. Specimens were weighed by using, Mettler Toledo, AB304-S, balance, precisely before and after ignition.

(ii) Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the specimens were conducted by using Perkin Elmer Pyris 6 TGA equipment according to ISO 11358 standard [31]. Specimens of ~10 mg were heated from 50º to 900ºC with a heating rate of 20ºC/min.

2.8 Scanning Electron Microscopy (SEM)

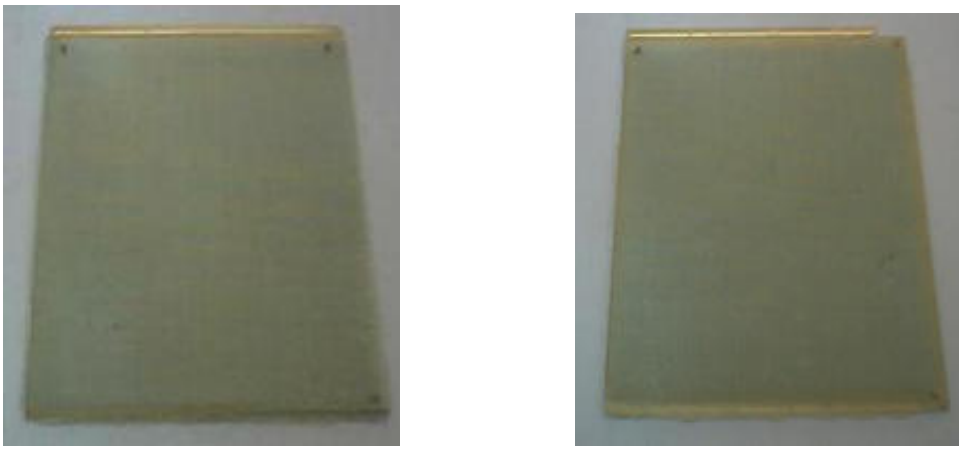
Scanning electron microscopy was conducted especially to observe microvoids formed and other morphological features of the fracture surfaces. SEM analysis was performed by using Jeol JSM-6400 microscope at METU Metallurgical and Materials Engineering Department Specimens were first gold spattered to avoid charging.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Effects of Mold Temperature

As explained before, in the first part of this study, RTM composite plates were produced by using six different mold temperatures (25º, 40º, 60º, 80º, 100º, and 120ºC) with an initial resin/hardener mixture temperature of around 28ºC (in summer) under vacuum (0.03 bar) condition. Figure 3.1 shows examples of these plates.



(a) **(b)**

Figure 3.1 Two examples of the composite plates produced with a mold temperature of (a) 60ºC and (b) 100ºC

3.1.1 Mold Filling Time

During resin injection the time interval required to fill the mold was recorded. This data together with the gel time of the epoxy-hardener mixture determined by the producer were given in Table 3.1.

This table indicates that increasing the mold temperature decreases both gel time of the resin mixture and mold filling time. The reason for the decreased gel time is the more effective cross linking, while for the decrease in mold filling time is the decreased resin mixture viscosity.

Table 3.1 Effect of Mold Temperature on the Resin Mixture Gel Time and Mold Filling Time

Mold Temperature (ºC)	**Resin Mixture Gel Time (min)**	**Mold Filling Time (sec)**
25	420 – 500	~ 420
40	150 – 170	~ 300
60	40 – 55	~ 60
80	14 – 17	~ 50
100	4 – 6	~ 35
120	2 – 3	~ 30

3.1.2 C-Scan Inspection

After the production of these six composite plates, they were inspected by ultrasonic C-scan analysis. C-scan equipment used in this study was computer controlled producing output images by assigning a color for each dB loss level. C-scan images obtained for each composite plate are given in Figure 3.2.

Light colored regions in these images represent macro defects such as large voids or insufficiently impregnated fiber zones. In this set, C-scan images were especially used to avoid specimen cutting from these regions with macro defects.

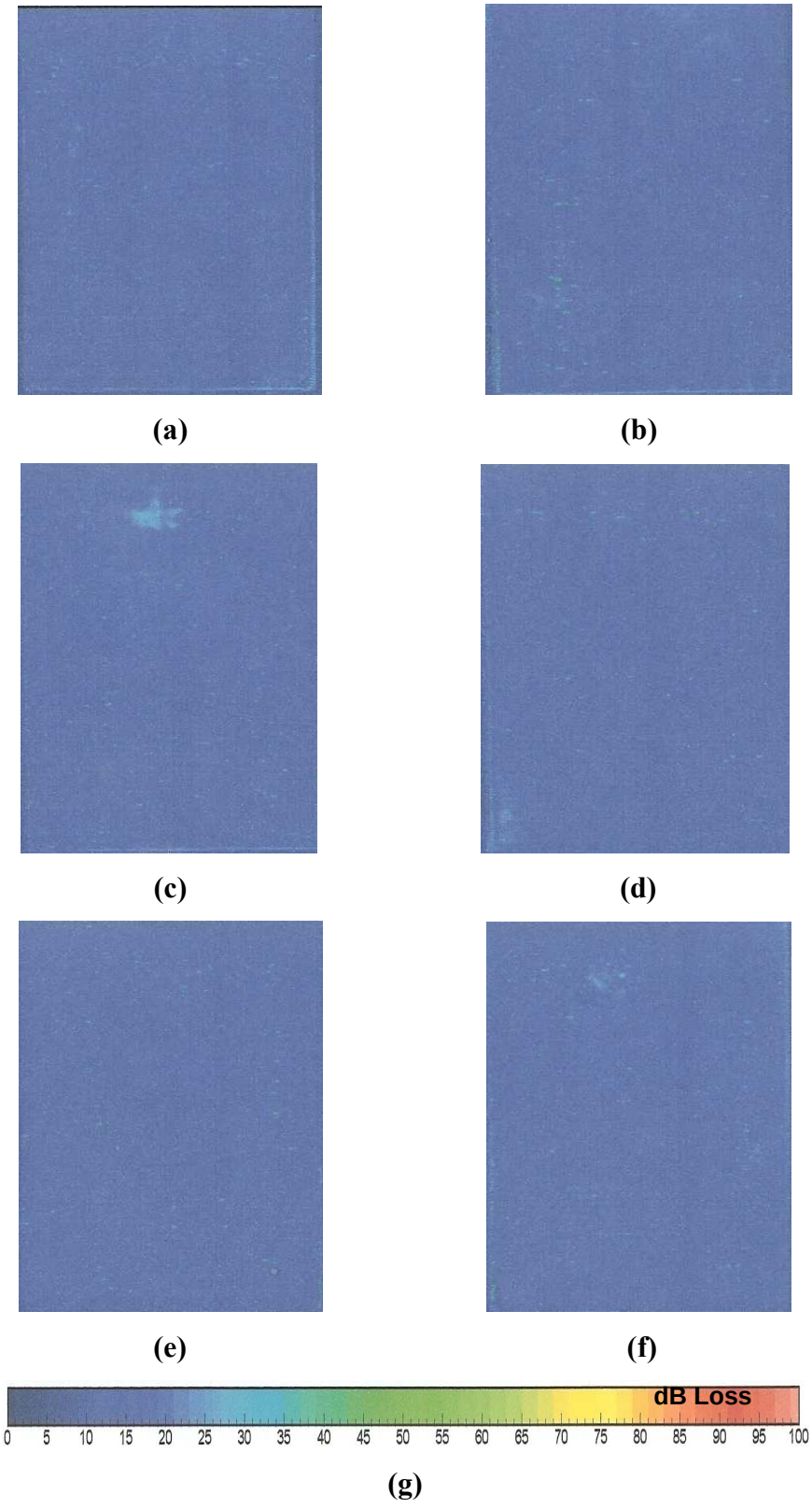


Figure 3.2 C-scan images of the composite plates produced with a mold temperature of (a) 25º, (b) 40º, (c) 60º, (d) 80º, (e) 100º, (f) 120ºC and (g) color spectrum of the dB loss

3.1.3 Mechanical Properties

In order to determine mechanical properties of the composite plates produced with six different mold temperatures, Tension Test, Charpy Impact Test and Flexural Test were conducted. Their results are given below.

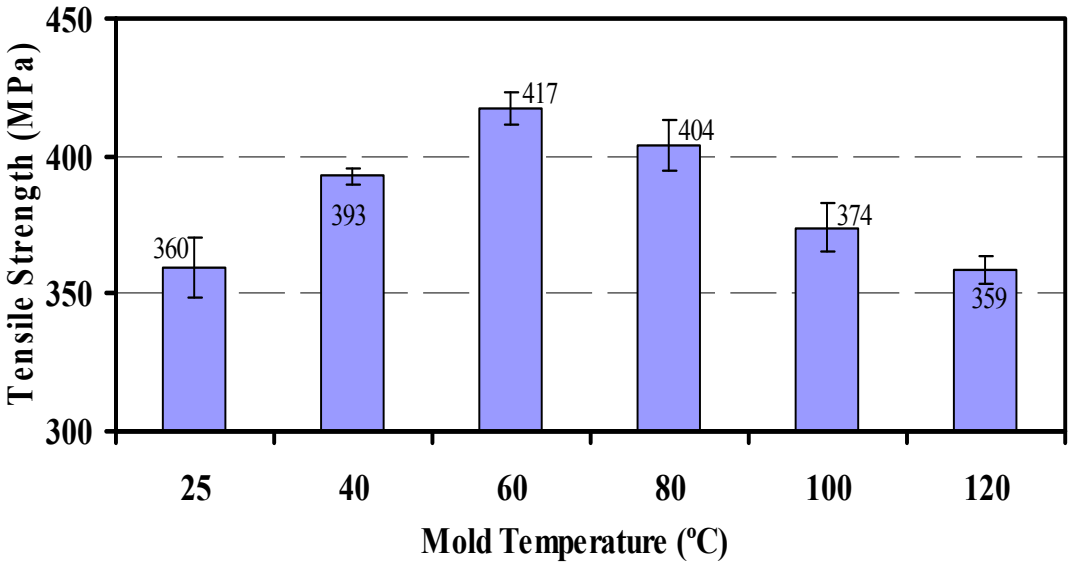
(i) Tensile Strength

For each condition 3 tension tests were performed, then their stress versus strain curves were obtained. One example of these curves for each condition are given in Appendix A. Tensile strength of the specimens were determined by taking their mean values, and are tabulated in Table 3.2 and compared in Figure 3.3(a).

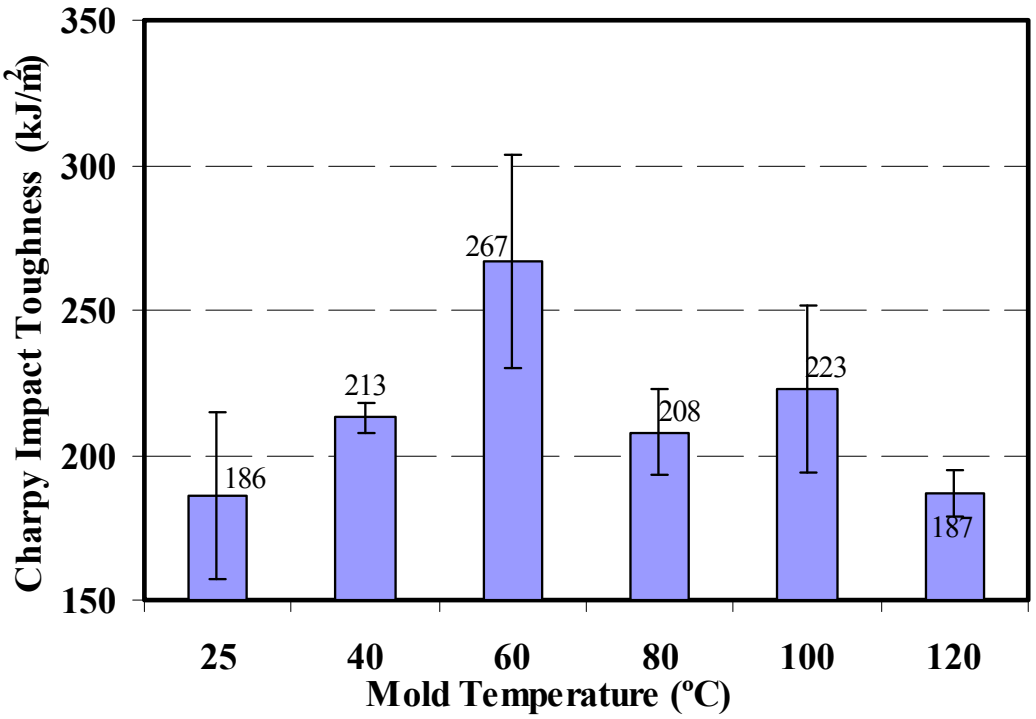
Figure 3.3(a) shows that tensile strength of the specimens has an increasing trend from 25º to 60ºC mold temperature while a decreasing trend from 60º to 120ºC, in which specimens with 60ºC mold temperature have 16% higher tensile strength values than the specimens produced at 25º and 120ºC mold temperatures.

Table3.2 Tensile Strength and Charpy Impact Toughness of the Specimens Produced with Six Different Mold Temperature

Mold Temperature (ºC)	**Tensile Strength (MPa)**	**Charpy Impact Toughness (kJ/m²)**
25	360 ± 11	186 ± 29
40	393 ± 3	213 ± 5
60	417 ± 6	267 ± 37
80	404 ± 9	208 ± 15
100	374 ± 9	223 ± 29
120	359 ± 5	187 ± 8



(a)



(b)

Figure 3.3 (a) Tensile Strength and (b) Charpy Impact Toughness of the specimens produced with six different mold temperatures

(ii) Charpy Impact Toughness

Four impact tests were conducted for each condition, then their Charpy impact toughness values were determined by taking their mean values, and these data are tabulated in Table 3.2 and compared with each other in Figure 3.3(b).

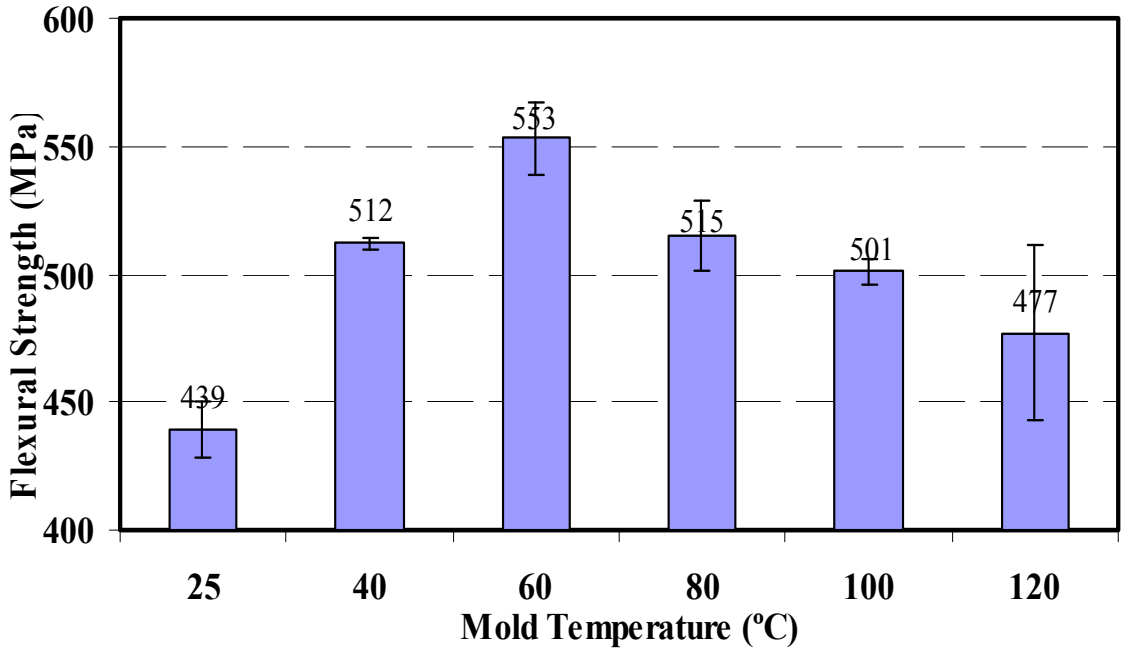
Figure 3.3(b) indicates that there is a similar trend observed in the tensile strength values. In this case, specimens produced at 60ºC mold temperature had very high value which was 43% more than the specimens produced at 25º and 120 ºC mold temperatures.

(iii) Flexural Properties

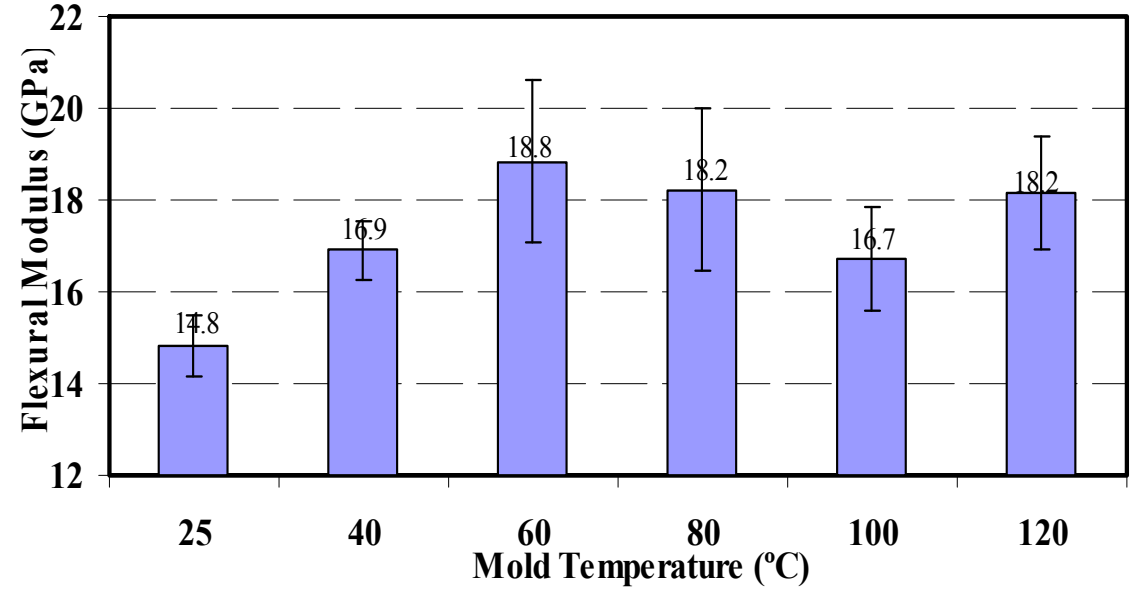
In order to determine flexural properties of the specimens at least five three point bending tests were performed, then their flexural stress versus flexural strain curves were obtained. One example of these curves for each condition are given in Appendix B. By using these curves, flexural strength, flexural modulus, and flexural strain at break values of the specimens were determined. Their mean values are tabulated in Table 3.3 and compared in Figure 3.4.

Table 3.3 Flexural Properties of the Specimens Produced with Six Different Mold Temperatures

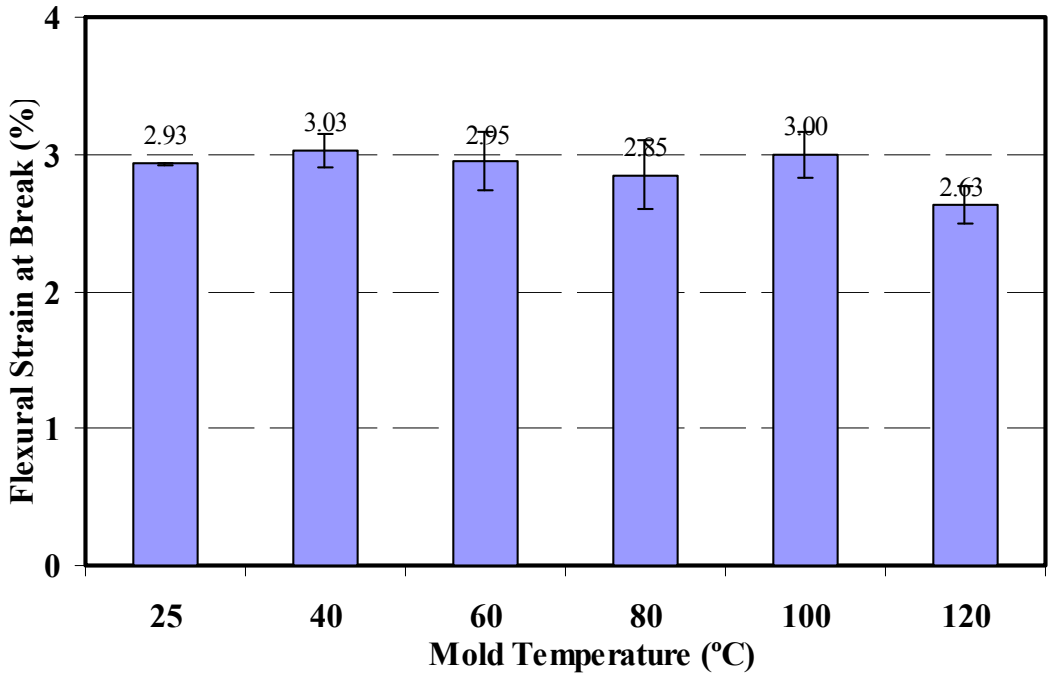
Mold Temp. (ºC)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Flexural Strain at Break (%)
25	439 ± 11	14.8 ± 0.68	2.93 ± 0.01
40	512 ± 2	16.9 ± 0.64	3.03 ± 0.12
60	553 ± 14	18.8 ± 1.77	2.95 ± 0.21
80	515 ± 14	18.2 ± 1.77	2.85 ± 0.25
100	501 ± 5	16.7 ± 1.12	3.00 ± 0.17
120	477 ± 34	18.1 ± 1.22	2.63 ± 0.14


600
550
500
450
400
Flexural Strength (MPa)
439
512
553
515
501
477
25
40
60
80
100
120
Mold Temperature (ºC)

(a)


22
20
18
16
14
12
Flexural Modulus (GPa)
14.8
16.9
18.8
18.2
16.7
18.2
25
40
60
80
100
120
Mold Temperature (ºC)

(b)



(c)

Figure 3.4 Flexural properties of the specimens produced with six different mold temperatures (a) Flexural strength, (b) Flexural modulus, and (c) Flexural strain at break

Figure 3.4(a) shows that effect of the mold temperature on the flexural strength of the specimens had the same trend with tensile strength, it increases from 25º to 60ºC and then decreases from 60º to 120ºC. This time, the increase in flexural strength from 25º to 60ºC mold temperature is as much as 26%. This increase for the flexural modulus value is very similar (27%) as shown in Figure 3.4(b). There were no significant differences in the values of flexural strain at break (Figure 3.4(c)).

(iv) Discussion

Increased mold temperature above RT basically can have three important effects on the resin mixture injected into the mold; decrease in resin viscosity (see Table 2.2), decrease in resin gel time (see Table 2.3) and thermal expansion of the micro bubbles present in the resin mixture.

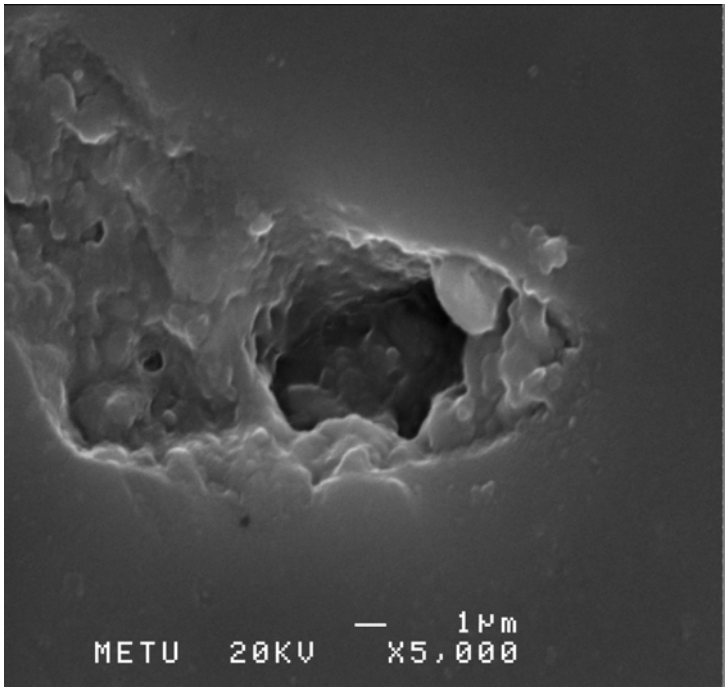
Although matrix and hardener mixture was mechanically stirred in a mixing vessel having degassing ability with a high level vacuum (-0.8 bar) action, it is not possible to obtain a bubble free mixture, there will be always micro bubbles which will lead to the formation of microvoids in the structure of the composite plates produced. Another source of micro bubble or microvoid formation is due to the insufficient wetting of the fiber surface by the matrix resin system.

These bubbles in hot mold may expand and form large voids. However, when the resin enters into the hot mold, its viscosity decreases, since there is a vacuum action (0.03 bar) in the mold, these mobile bubbles can be easily taken out of the mold.

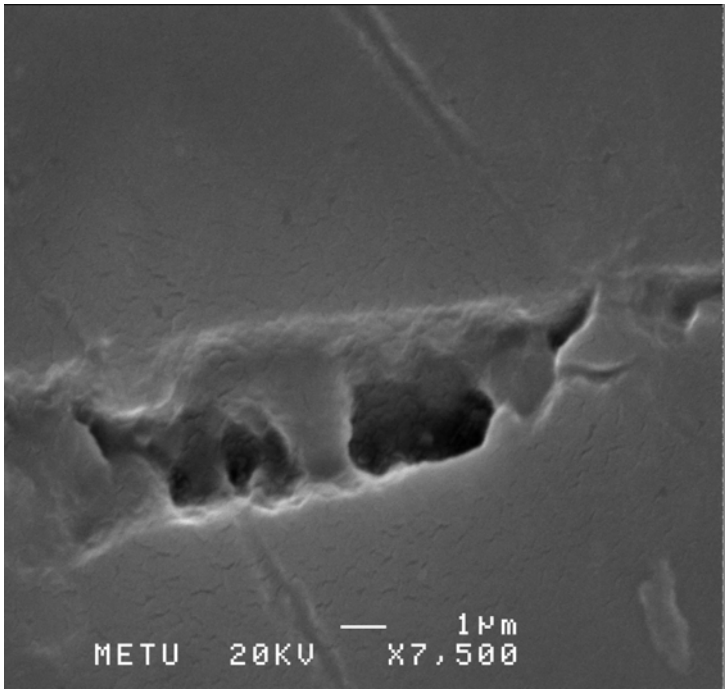
However, when the temperature of the mold is increased, gel time of the resin decreases, i.e. resin becomes more and more jelly due to cross linking reaction. Therefore, decreased gel time also decreases the mobility of the bubbles which prevent their ventilation through outlets.

Therefore, in order to ventilate micro bubbles, there should be an optimum mold temperature for the optimum resin viscosity and optimum resin gel time.

In this study as indicated in the previous sections, all mechanical properties of the specimens produced with a mold temperature of 60ºC, were much higher compared to the specimens produced with a mold temperature below (25º and 50ºC) and above (80º, 100º, 120ºC) this temperature.



(a)



(b)

Figure 3.5 SEM fractographs showing microvoids formed in the matrix if the specimens produced with a mold temperature of (a) 25ºC, and (b) 120ºC.

Therefore, it may be concluded that 60ºC is an optimum mold temperature for this matrix resin system. As shown in Figure 3.5, SEM analysis also confirmed that conclusion which indicated formation of more microvoids in the specimens below and above this optimum mold temperature.

3.2 Effects of Vacuum

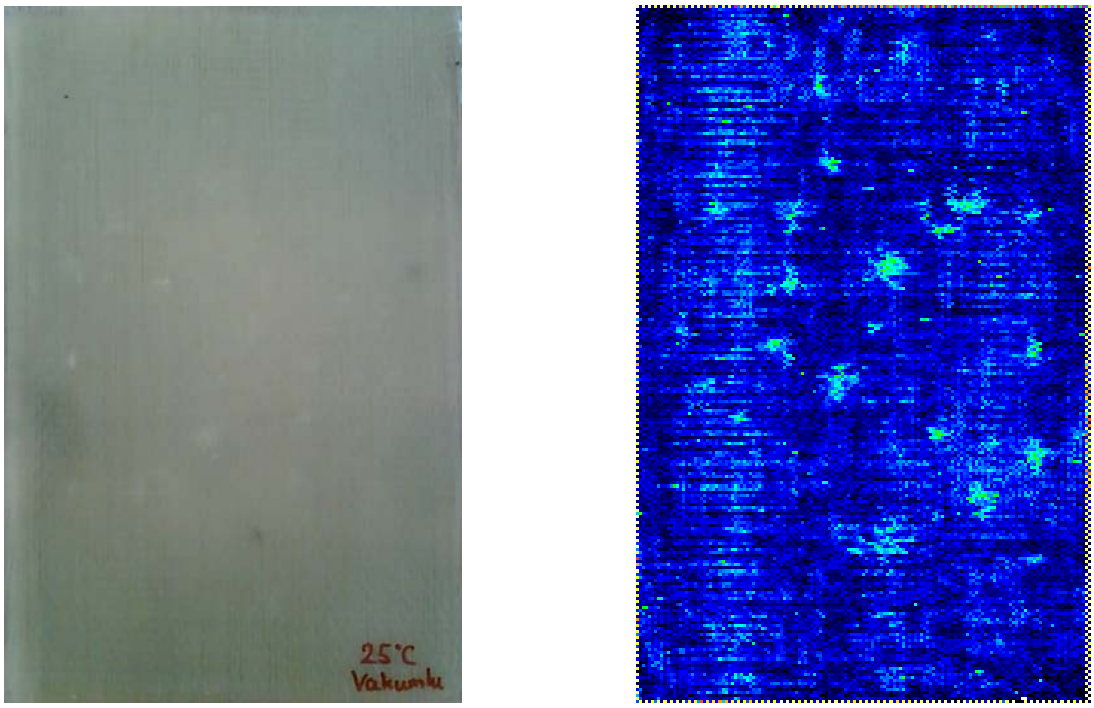
In the second part of this study, another 6 plates were produced to investigate the effects of vacuum applied during molding. This time only 3 different mold temperatures (25º, 60º, 120ºC) were used. Composite plates at these mold temperatures were first produced by applying vacuum (0.03 bar) and then without using vacuum (~1 bar). Since these productions were in winter, the initial resin/hardener mixture temperature was around 15ºC.

3.2.1 C-Scan Analysis

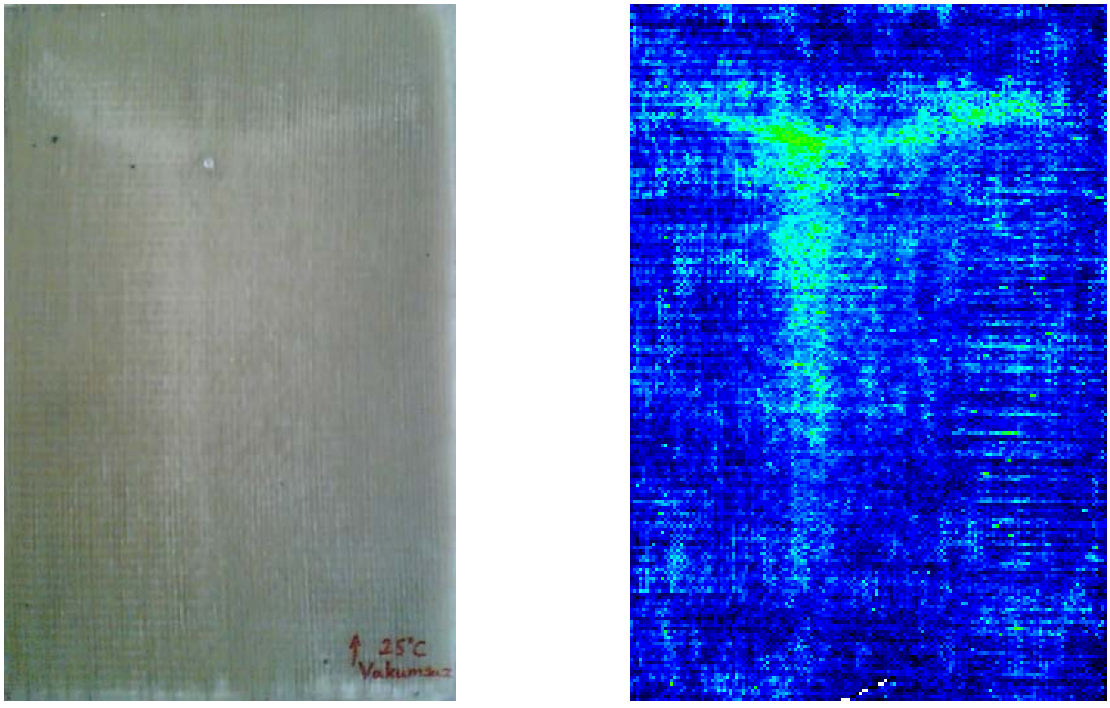
After the production of these six composite plates, they were inspected by ultrasonic C-scan analysis. Real images and C-scan images of these plates are given in Figures 3.6 to 3.8. In this part of the study, C-scan images were first used to avoid specimen cutting from large light colored regions which represent “defects”. Then, since C-scan technique incorporates the effects of Ultrasonic attenuation (dB loss), histograms of these dB losses were also obtained for each composite plate (Figures 3.9 to 3.11).

In C-scan analysis, there is a maximum tolerable dB difference from the average dB loss value. Thus, the regions having a dB loss higher than the maximum tolerable loss can be referred as “voids” or “defects”.

As shown in Figures 3.9 to 3.11, C-scan histograms of composite plates indicated that the min dB loss value was 27 dB. In order to evaluate these histograms, a tolerance of 15 dB (the tolerance level used at TAI) was added, and then the values equal and greater than 42 dB losses were determined.

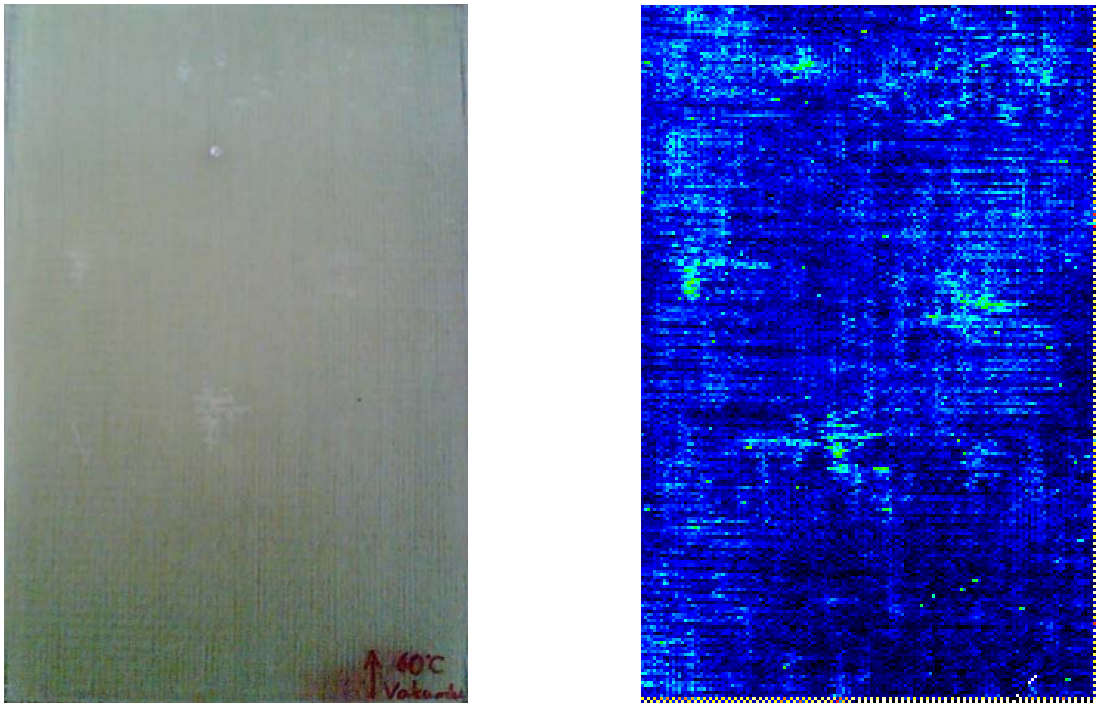


(a)

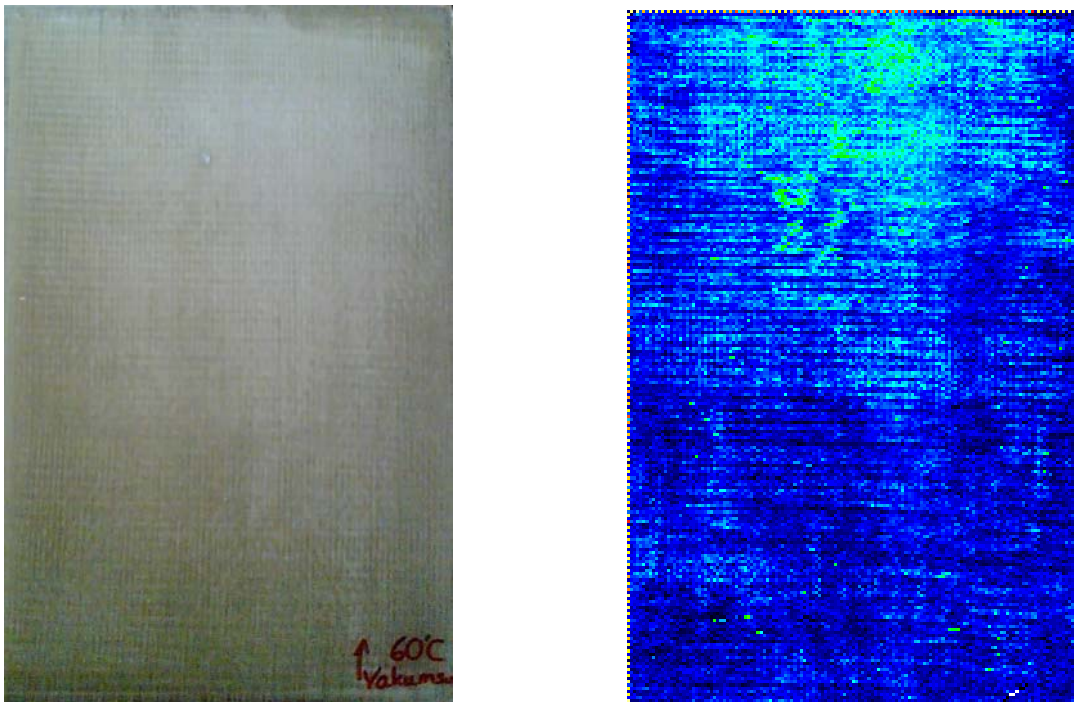


(b)

Figure 3.6 Real and C-scan images of the composite plates produced with a mold temperature of 25ºC, (a) with vacuum, and (b) without vacuum

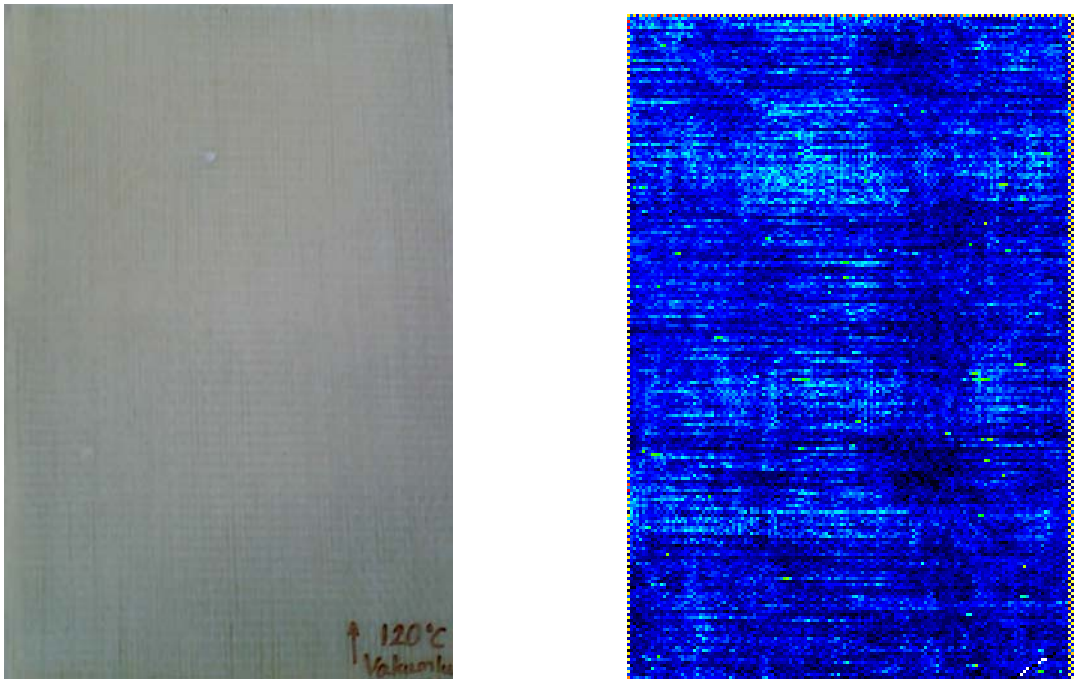


(a)

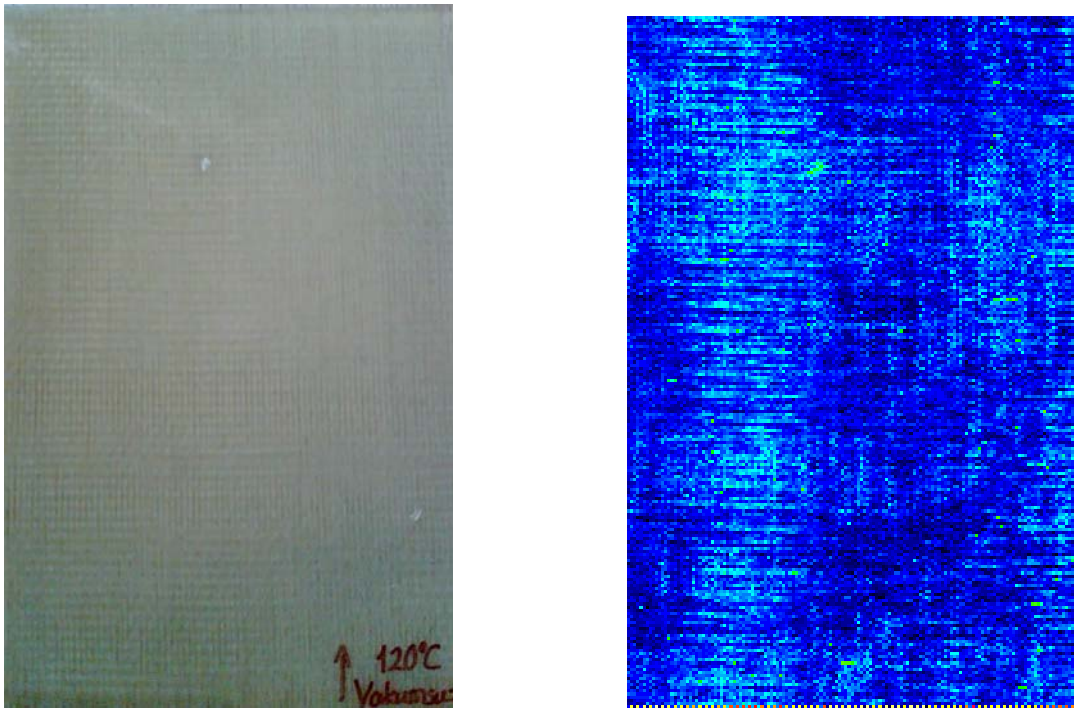


(b)

Figure 3.7 Real and C-scan images of the composite plates produced with a mold temperature of 60ºC, (a) with vacuum, and (b) without vacuum

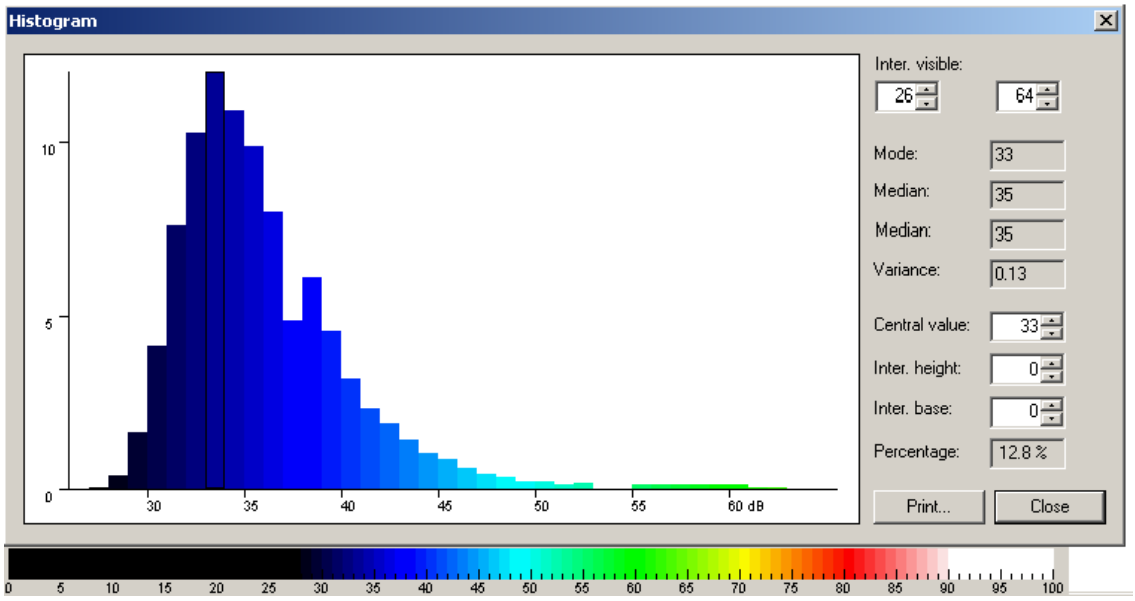


(a)

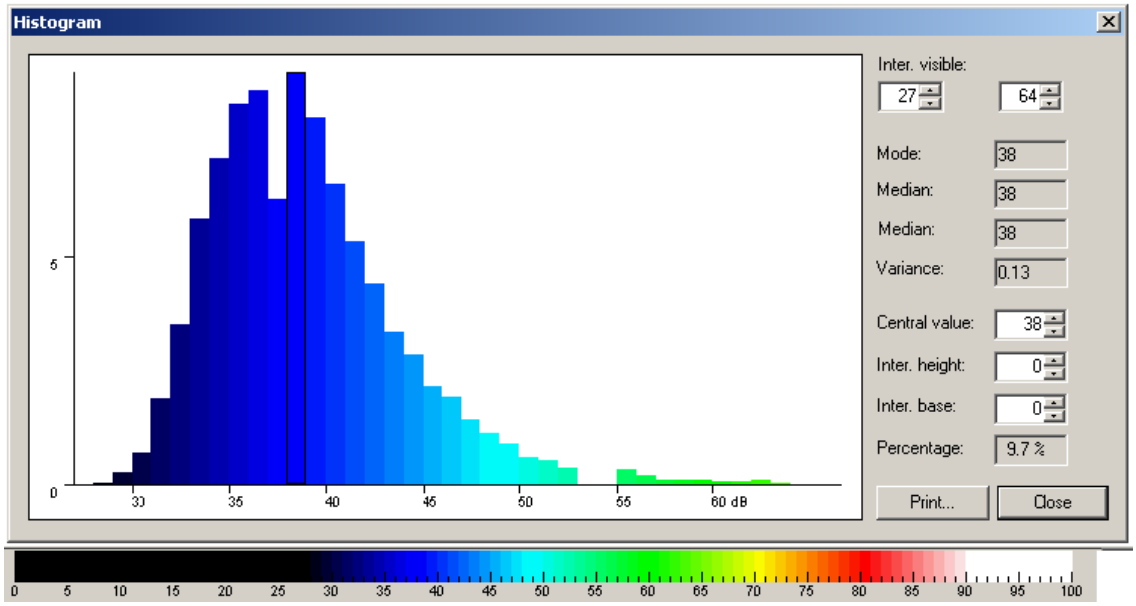


(b)

Figure 3.8 Real and C-scan images of the composite plates produced with a mold temperature of 120ºC, (a) with vacuum, and (b) without vacuum

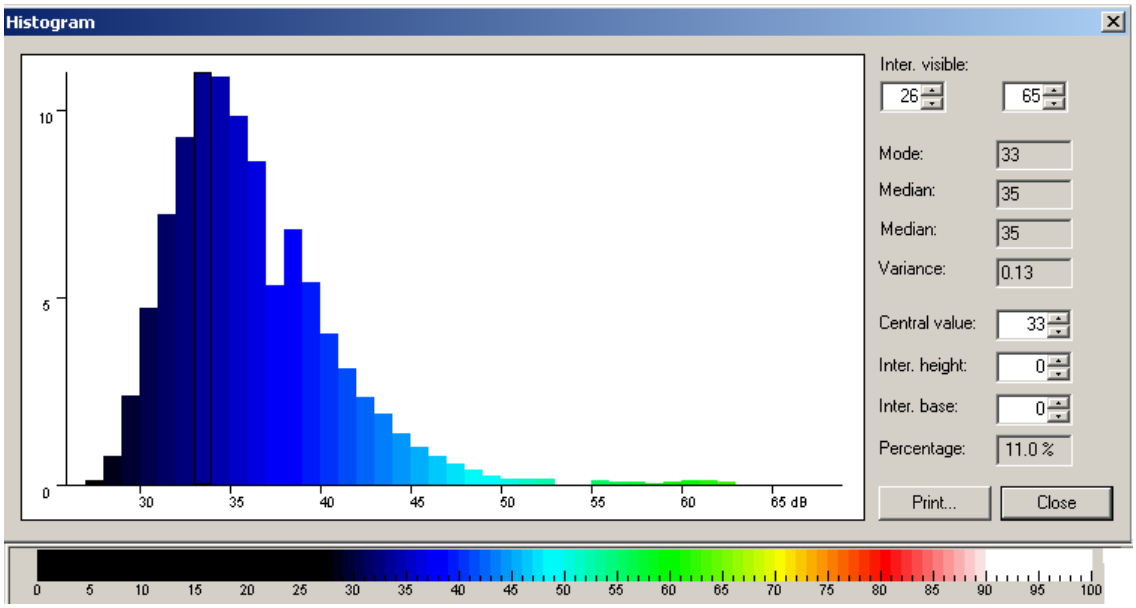


(a)

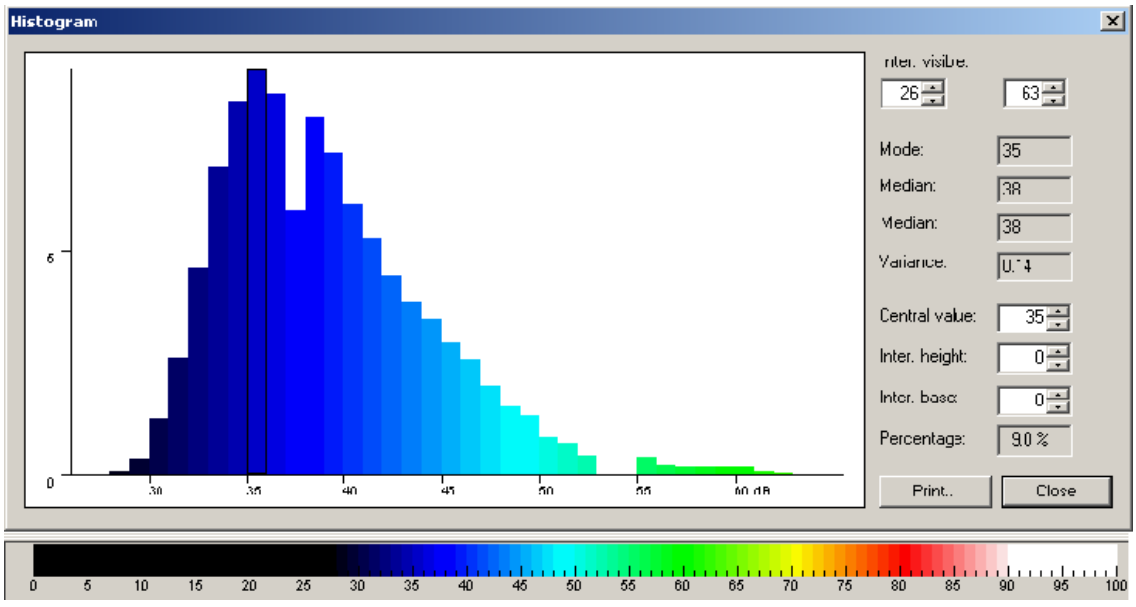


(b)

Figure 3.9 C-scan histograms showing dB loss percentages of the composite plates produced with a mold temperature of 25ºC, (a) with vacuum, and (b) without vacuum

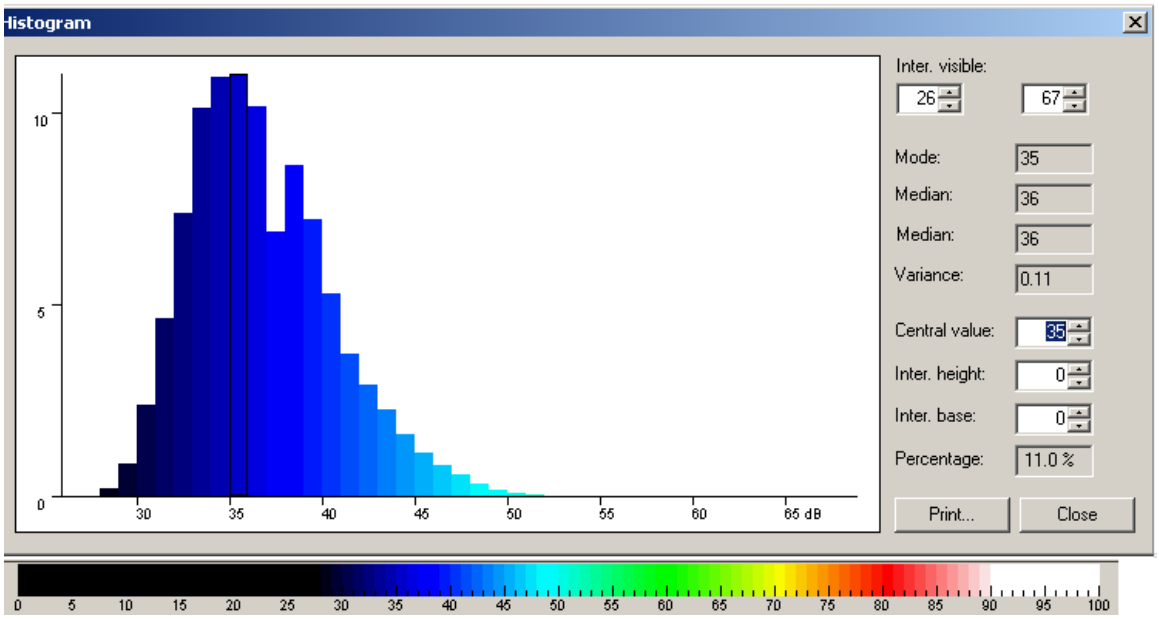


(a)

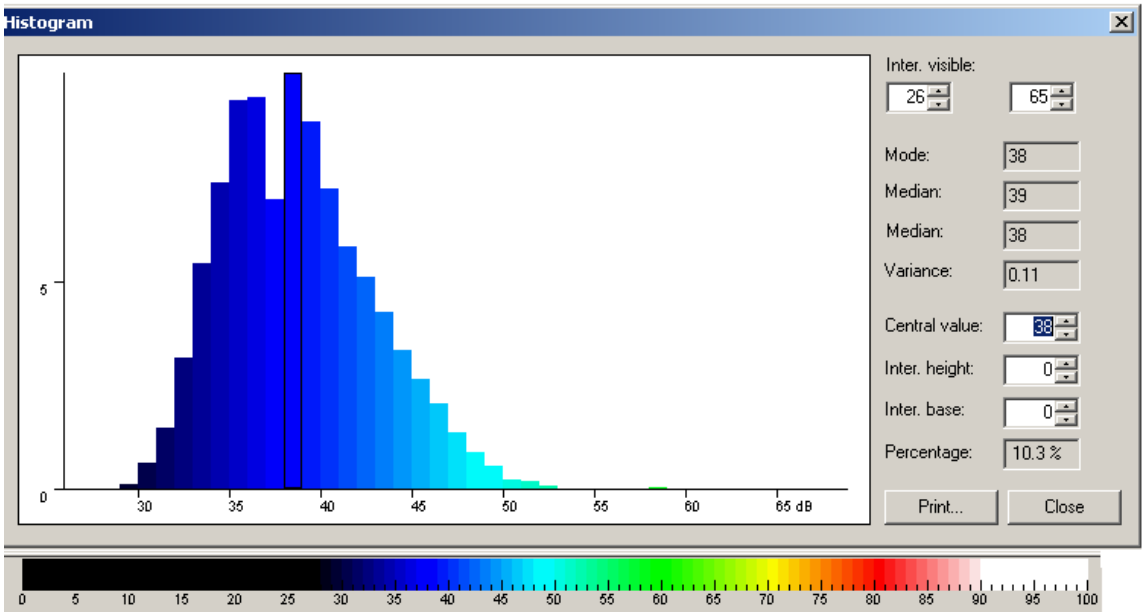


(b)

Figure 3.10 C-scan histograms showing dB loss percentages of the composite plates produced with a mold temperature of 60ºC, (a) with vacuum, and (b) without vacuum



(a)



(b)

Figure 3.11 C-scan histograms showing dB loss percentages of the composite plates produced with a mold temperature of 120ºC, (a) with vacuum, and (b) without vacuum

Percentage of these dB losses (≥ 42 dB), which can be also referred as percentage of "defects", for all composite plates were determined and compared in Figure 3.12.

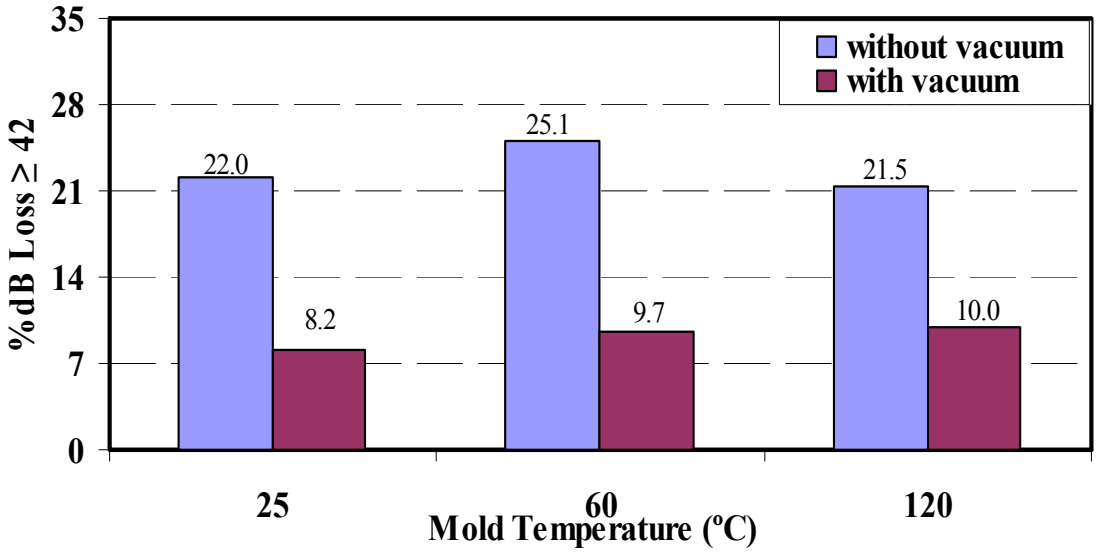


Figure 3.12 Percentage of dB losses (≥ 42 dB), referred as "defects", for all composite plates

Figure 3.12 shows that, when vacuum is applied during molding, amount of "defects" (which might be formed due to the bubbles in the resin or entrapped air at the fiber / matrix interface) decreases considerably. The decrease in the percentages of "defects" were 63, 61, and 54% for the mold temperatures of 25º, 60º, and 120ºC, respectively.

3.2.2 Mechanical Properties

Just like in the previous part of this study, three mechanical tests: tension, Charpy impact and flexural tests were conducted for each plate to investigate the effects of vacuum. Their results are given below.

(i) Tensile Strength

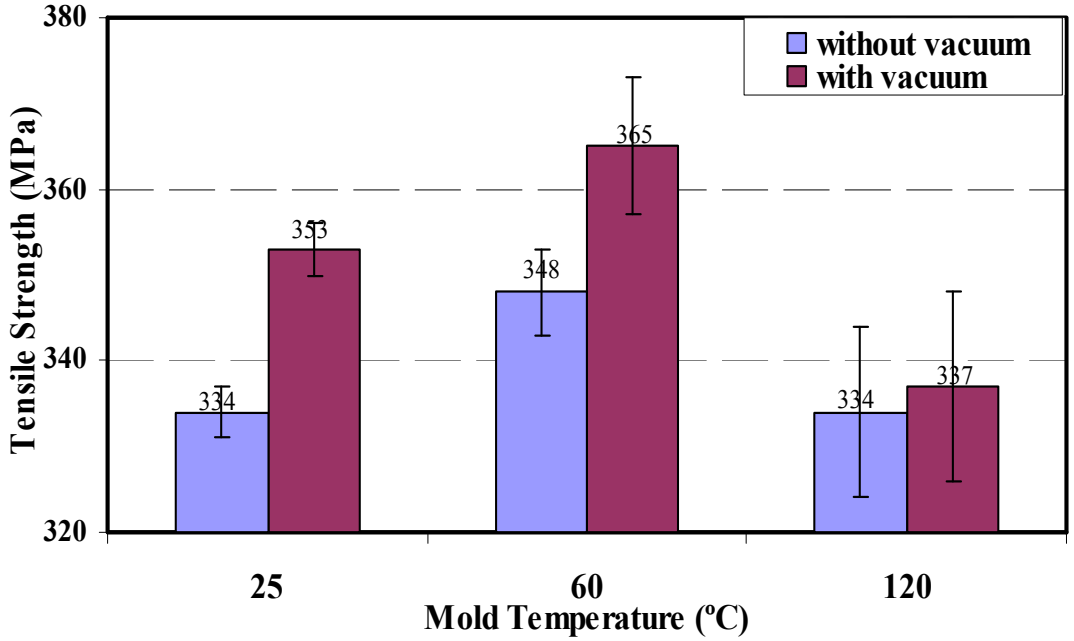
After obtaining stress versus strain curves of four specimens for each condition (one example for each is given in Appendix C), their tensile strength were determined by taking the mean values. These data are tabulated in Table 3.4 and compared in Figure 3.13(a). It is seen that, use of vacuum increases the tensile strength of the specimens 6 and 5% for the mold temperatures 25º and 60ºC, respectively.

Table 3.4 Tensile Strength and Charpy Impact Toughness of the Specimens Produced with Vacuum and without Vacuum

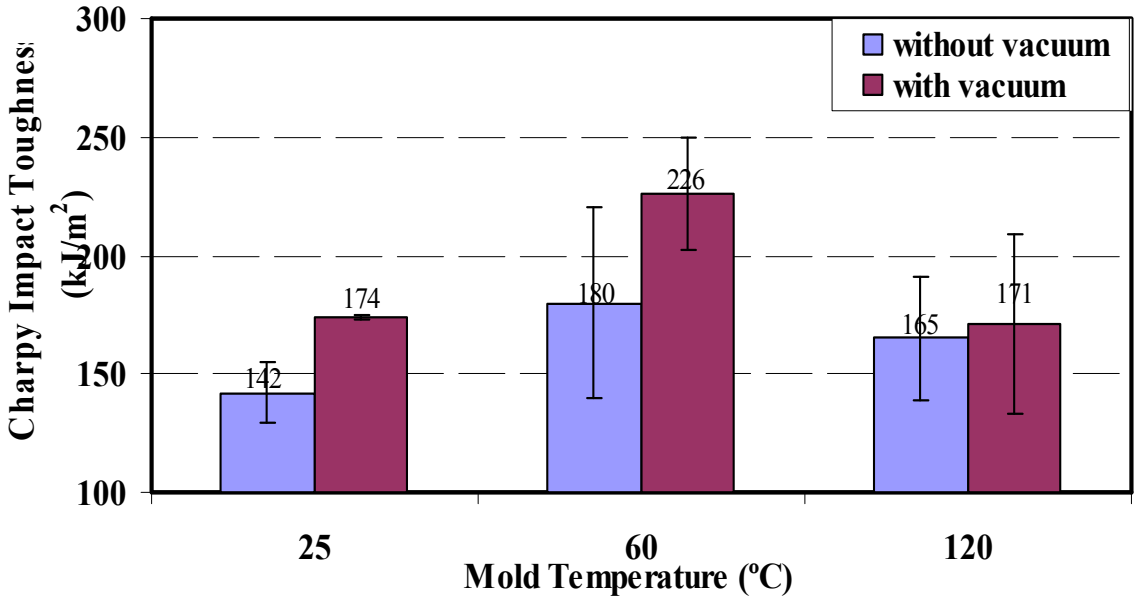
Mold Temperature (ºC)	**Tensile Strength (MPa)**		**Charpy Impact Toughness (kJ/m²)**	
	Without vacuum	**With vacuum**	**Without vacuum**	**With vacuum**
25	334 ± 3	353 ± 3	174 ± 1	142 ± 13
60	348 ± 5	365 ± 8	226 ± 24	180 ± 40
120	334 ± 10	337 ± 11	171 ± 38	165 ± 26

(ii) Charpy Impact Toughness

Mean values of the five Charpy impact test data are tabulated in Table 3.4 and compared with each other in Figure 3.13(b). This figure indicates that when vacuum is applied, Charpy impact toughness of the specimens increases as much as 23 and 26% for the mold temperatures of 25º and 60ºC, respectively, while it is only 4% for the 120ºC mold temperature.



(a)



(b)

Figure 3.13 (a) Tensile Strength and (b) Charpy Impact Toughness of the specimens produced with vacuum and without vacuum

(iii) Flexural Properties

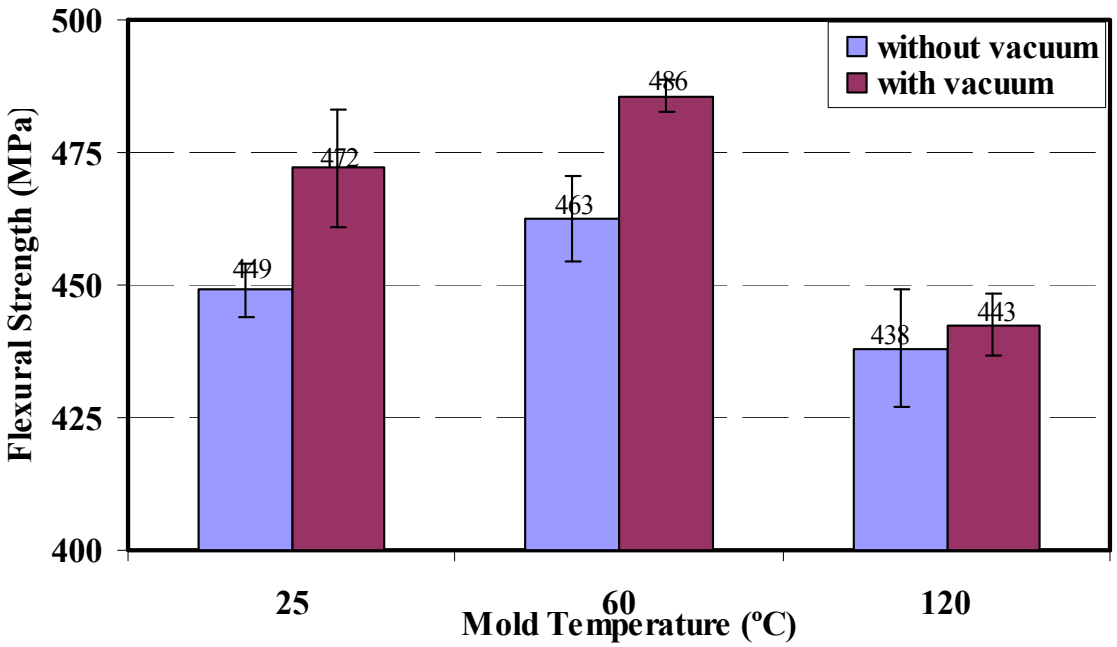
After obtaining flexural stress versus flexural strain curves of five specimens for each condition (one example for each is given in Appendix D), their flexural strength, flexural modulus, and flexural strain at break data were determined by taking the mean values. These properties are first tabulated in Table 3.5 and compared in Figure 3.14. These data indicates that, just like in the case of tensile strength, use of vacuum increases both flexural strength and flexural modulus of the specimens around 5% for the mold temperatures of both 25º and 60 ºC.

Table 3.5 Flexural Properties of the Specimens Produced with Vacuum and without Vacuum

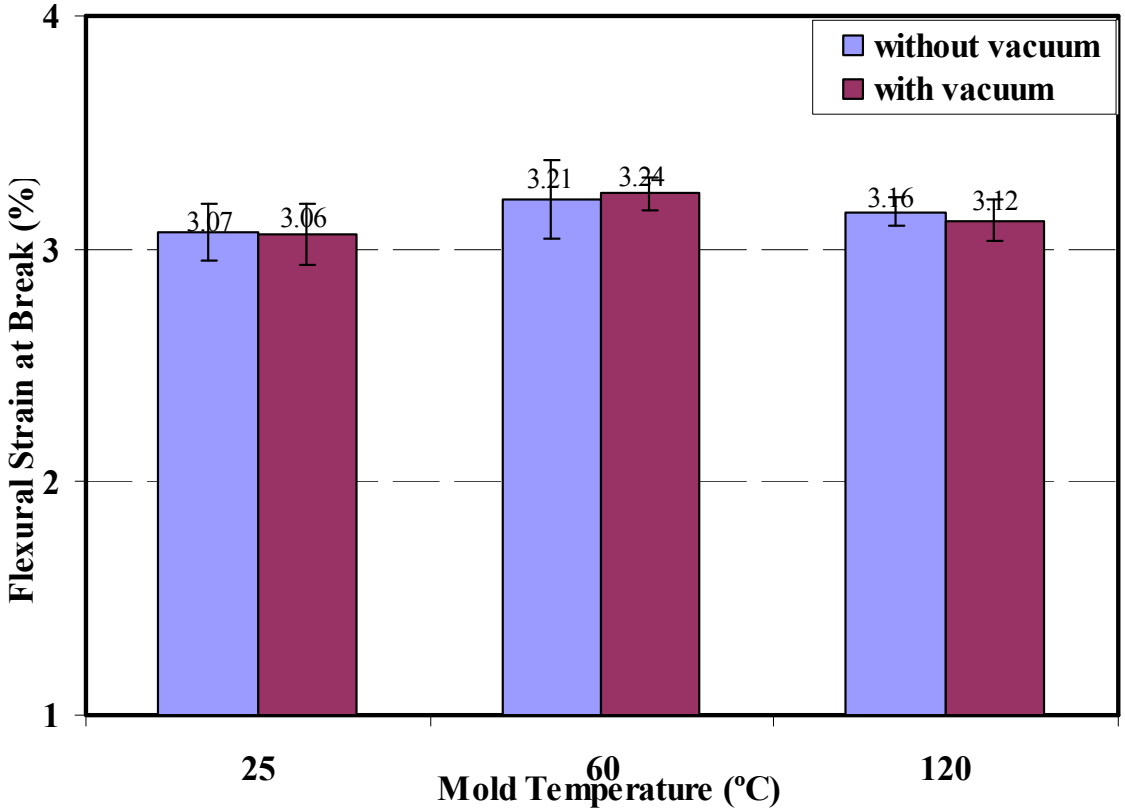
Mold Temp. (ºC)	**Flexural Strength (MPa)**		**Flexural Modulus (GPa)**		**Flexural Strain at Break (%)**	
	Without vacuum	**With vacuum**	**Without vacuum**	**With vacuum**	**Without vacuum**	**With vacuum**
25	449 ± 5	472 ± 11	14.6 ± 0.7	15.4 ± 0.8	3.07 ± 0.12	3.06 ± 0.13
60	463 ± 8	486 ± 3	14.5 ± 0.9	15.0 ± 0.3	3.21 ± 0.17	3.24 ± 0.07
120	438 ± 11	443 ± 6	13.9 ± 0.3	14.2 ± 0.5	3.16 ± 0.06	3.12 ± 0.09

(iv) Discussion

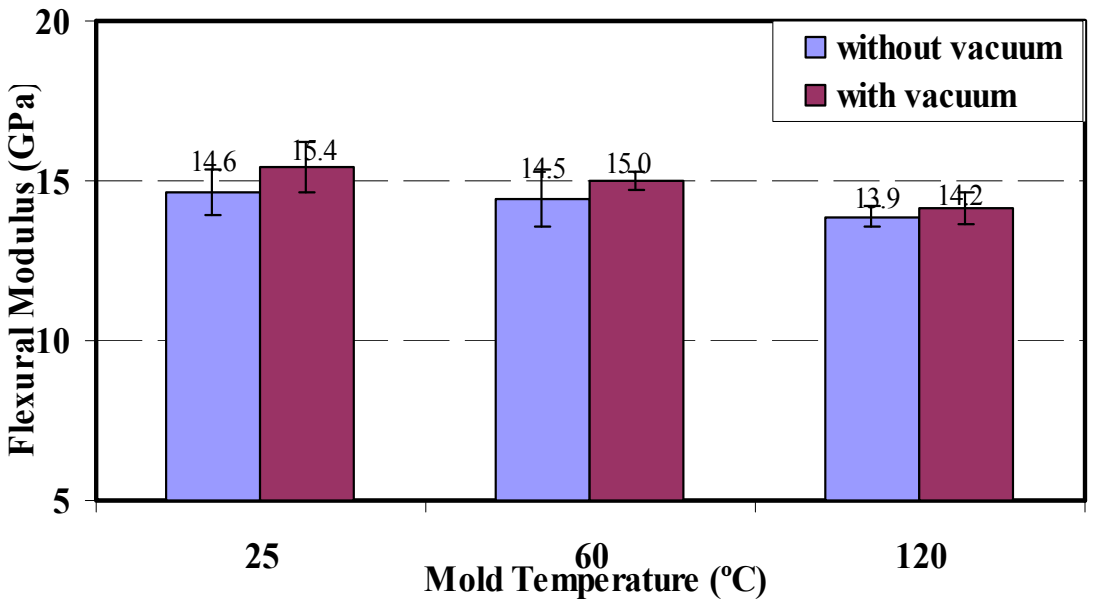
As shown in the above sections, mechanical properties of the specimens are higher when they are produced under vacuum which was expected. The increase in the tensile strength, flexural strength, and flexural modulus was around 5%, while in the Charpy impact toughness value it was as much as around 25% for the mold temperatures of 25º and 60 ºC.


without vacuum
with vacuum
Flexural Strength (MPa)
500
475
450
425
400
449
472
463
486
438
443
25
60
120
Mold Temperature (ºC)

(a)


without vacuum
with vacuum
Flexural Strain at Break (%)
4
3
2
1
3.07
3.06
3.21
3.24
3.16
3.12
25
60
120
Mold Temperature (ºC)

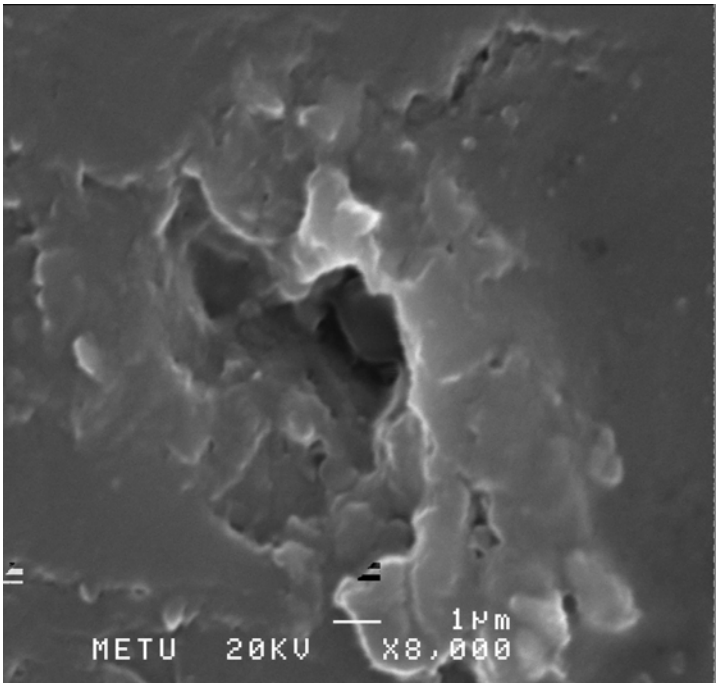
(b)



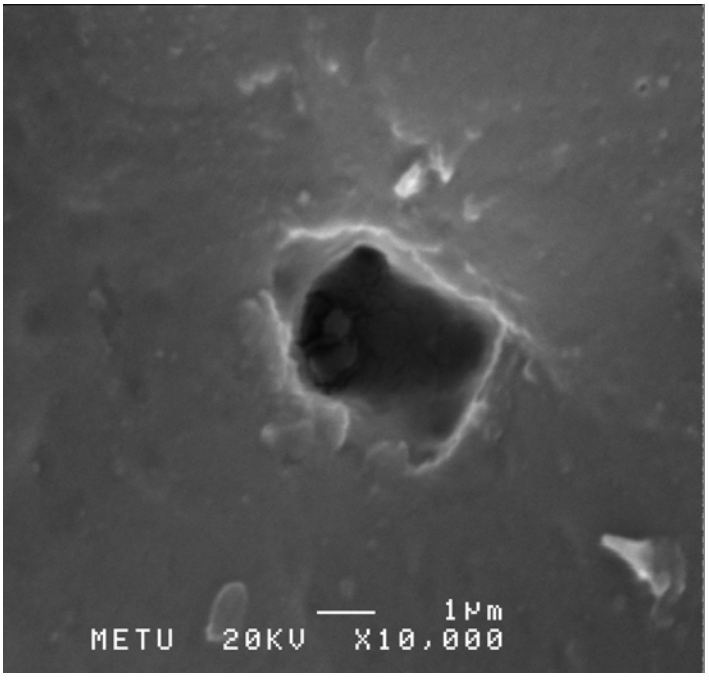
(c)

Figure 3.14 Flexural properties of the specimens produced with vacuum and without vacuum (a) Flexural Strength, (b) Flexural Modulus, and (c) Flexural Strain at Break

Of course, these higher values were due to the reduction in the percentages of the "defects" or "voids" under vacuum, in which reductions were more than 60% for the mold temperatures 25º and 60ºC. SEM analysis also indicated that there were more "micro defects" or "microvoids" formed in the structure when the specimens were produced without vacuum (Figure 3.15).



(a)



(b)

Figure 3.15 SEM fractographs showing microvoids formed in the structure when the specimens were produced without vacuum at the mold temperatures (a) 25º and (b) 60ºC

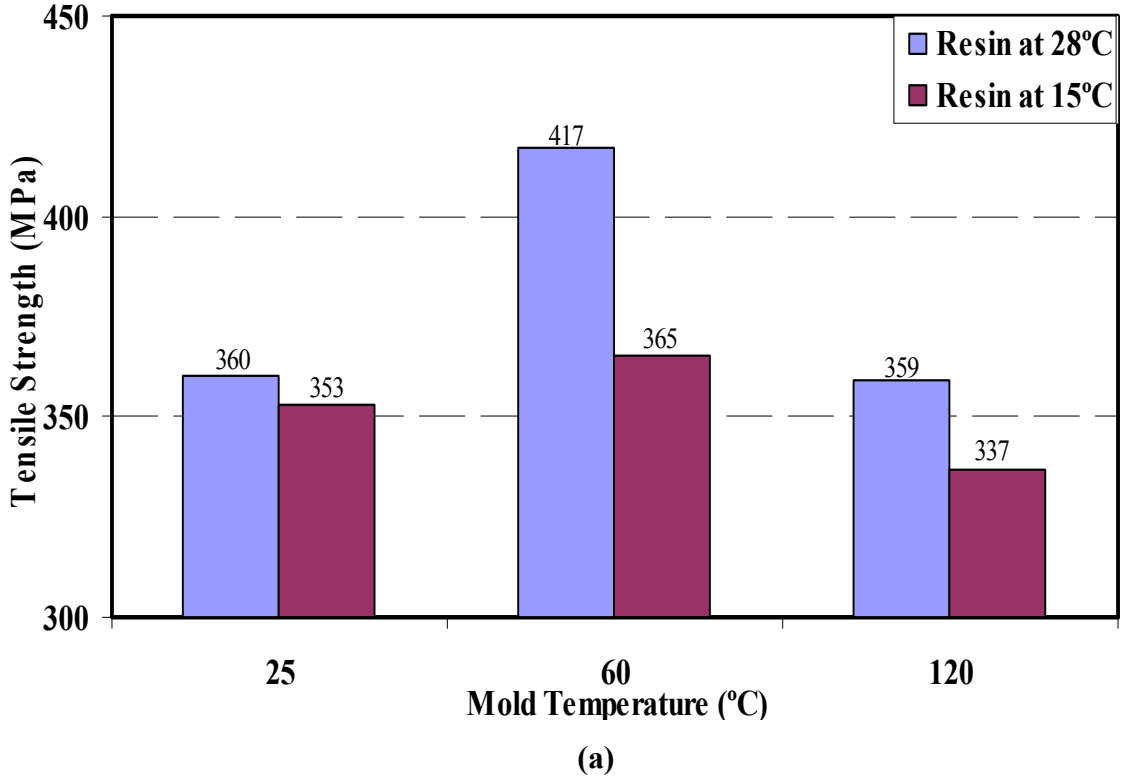
3.3 Effects of Initial Resin Temperature

As explained in the previous sections, the first set of composite plates for the effects of mold temperature were produced in summer (in June) with a room temperature of around 28ºC, while the second set of plates for the effects of vacuum were produced in winter (in November) with a room temperature of around 15ºC.

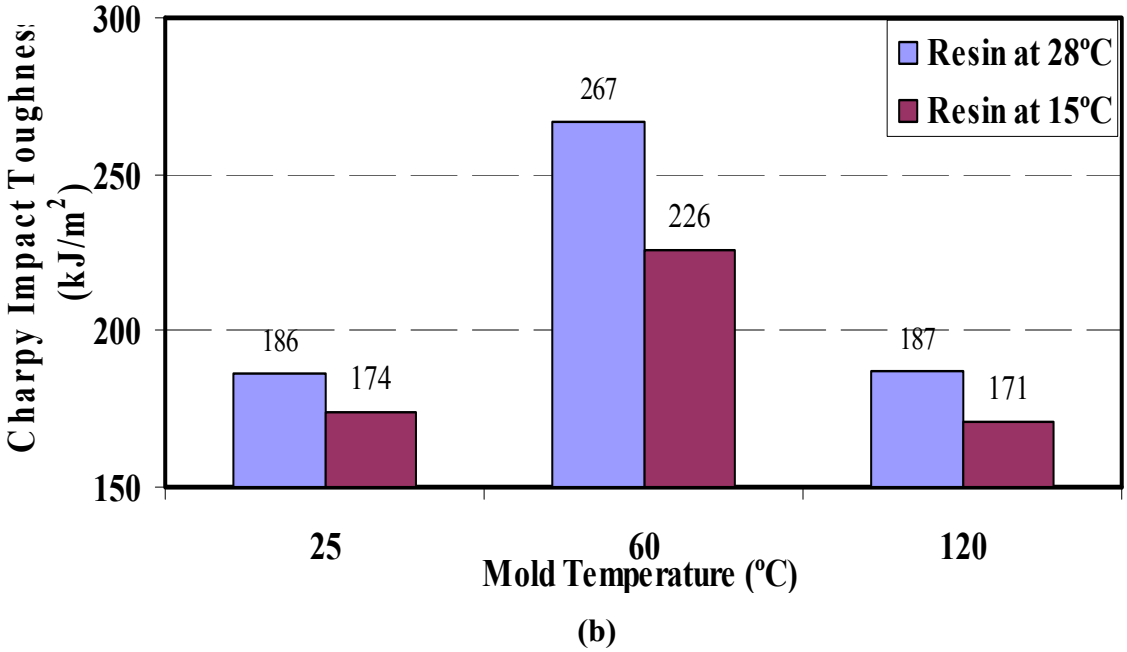
This large difference in the room temperature led to the opportunity to investigate the effects of initial resin temperature on the properties of the specimens. Therefore, the data of the specimens (only for three mold temperatures 25º, 60º, 120ºC under vacuum) were re-evaluated to compare their mechanical properties at two different initial resin temperatures 28º and 15ºC. These comparisons are given in Figure 3.16 only for tensile strength and Charpy impact toughness.

Figure 3.16 shows that, decreasing the initial resin temperature decreases the mechanical properties of the specimens. For instance, for the specimens produced with a mold temperatures of 60ºC, the decrease is 14% in tensile strength and 18% in Charpy impact toughness values.

The main reason for these decreases with decreasing initial resin temperature should be due to the increase in the viscosity of the resin. As shown in Table 2.2 (determined by the producer) resin viscosity is ~1250 mPa.s at 18ºC, while it is ~600 mPa.s at 25ºC. Thus, increasing resin viscosity leads to the difficulties in mold filling, fiber wetting, fiber impregnation, etc.



(a)



(b)

Figure 3.16 Mechanical properties of the specimens produced with an initial resin temperature of 28º and 15ºC, (a) Tensile Strength and (b) Charpy Impact Toughness

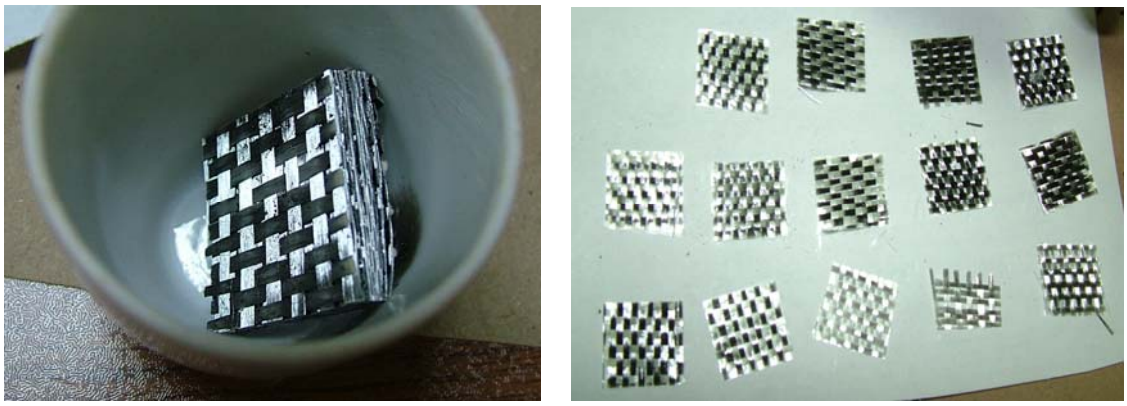
3.4 Thermal Analyses

Ignition loss and TGA were conducted to investigate resin content, fiber content, and thermal stability of the specimens. Three tests for ignition loss and one TGA were done for each condition.

3.4.1 Ignition Loss

Standard test method for "Ignition Loss of Cured and Reinforced Resins" (ASTM D-2584) was used to determine the amounts of epoxy matrix resin and woven glass fiber reinforcement by weighing the specimens before and after the ignition precisely. Figure 3.17 shows the appearance of the fiber layers without matrix after ignition loss.

After calculating the ignition loss (residue) of the specimens in weight percent (which can be also considered as the matrix resin content), it was also possible to determine the volume percent of the fiber reinforcement by using their densities. Mean values of these data determined are given in Table 3.6 as wt% resin content and vol% fiber content.



(a) **(b)**

Figure 3.17 Views of the fiber layers after ignition loss of the matrix resin, (a) Laminate specimen in the crucible, and (b) Separated 14 layers

This table indicates that resin content of the composite plates for each condition is very close to each other (38 – 40 wt%), i.e. under each condition the mold was filled with almost the same amount of matrix resin. This table also shows that, use of 14 layers of woven glass fiber led to 39 – 41 vol% reinforcement.

Table 3.6 Resin Content and Fiber Content of the Two Sets of Specimens Determined by Ignition Loss Analysis

(a) For the Specimens of First Set

Mold Temperature (ºC)	**Resin Content (wt%)**	**Fiber Content (vol %)**
25	40 ± 1	39 ± 1
40	40 ± 2	39 ± 2
60	38 ± 3	41 ± 1
80	39 ± 1	40 ± 1
100	40 ± 1	39 ± 1
120	40 ± 2	39 ± 2

(b) For the Specimens of Second Set

Mold Temp. (ºC)	**Vacuum Condition**	**Resin Content (wt%)**	**Fiber Content (vol %)**
25	With	39 ± 2	40 ± 2
25	Without	38 ± 1	41 ± 1
60	With	39 ± 1	40 ± 1
60	Without	36 ± 2	43 ± 2
120	With	38 ± 3	41 ± 3
120	Without	39 ± 1	40 ± 1

3.4.2 TGA

Thermogravimetric analysis was especially used to investigate the thermal stability of the specimens. For this purpose, first TGA curves of the specimens were obtained, as shown in Appendix E and F. Then, TGA curves were used to determine the Decomposition Temperatures and Total Weight Loss of the specimens. In order to compare Decomposition Start Temperatures, an initial weight loss of 5% was used as shown in Figure 3.18. Decomposition End Temperatures and Total Weight Loss of the specimens were taken directly from their TGA curves. These data for all specimens are tabulated in Table 3.7.

Table 3.7 shows that in the composite specimens, thermal decomposition starts between 302º – 361ºC and reaches a maximum decomposition level between 649º – 723ºC, leading to a total weight loss between 34 – 50%.

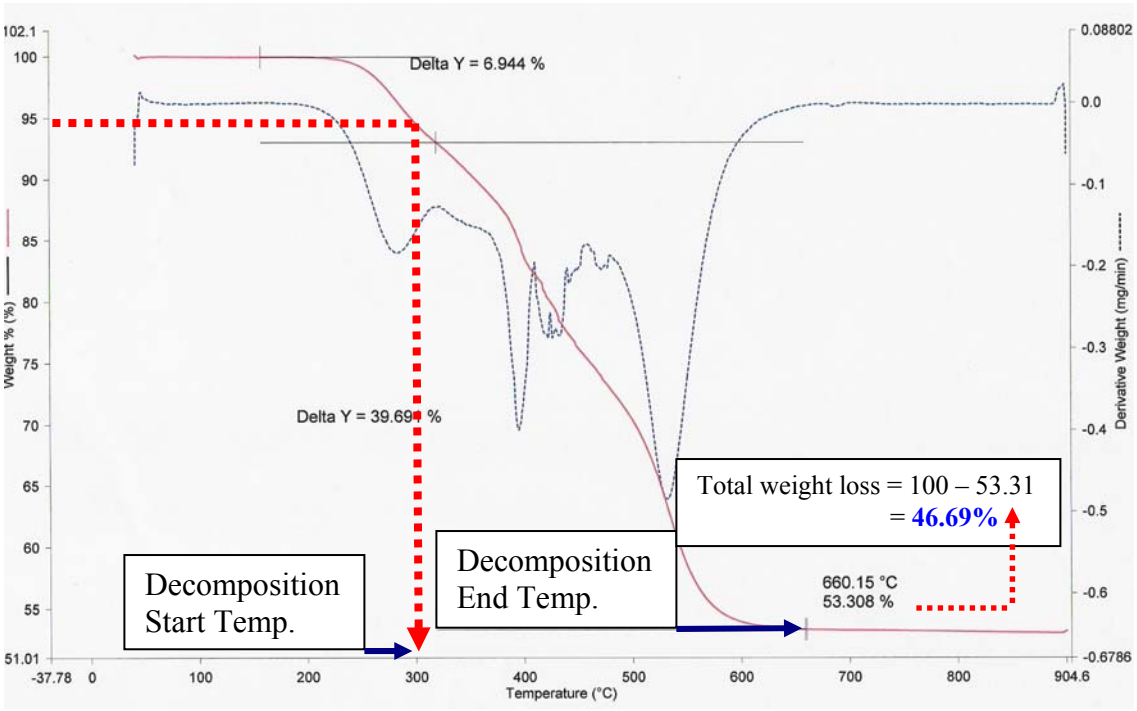


Figure 3.18 An example of TGA curve showing Decomposition Start and End Temperatures and Total Weight Loss

Table 3.7 Decomposition Temperatures and Weigh Loss of the Two Sets of Specimens Determined by TGA

(a) For the Specimens of First Set

Mold Temperature (ºC)	**Decomposition Start Temperature (ºC)**	**Decomposition End Temperature (ºC)**	**Total Weight Loss (%)**
25	341	666	45
40	361	649	50
60	359	654	34
80	327	665	41
100	346	723	46
120	323	694	47

(b) For the Specimens of Second Set

Mold Temperature (ºC)	**Vacuum Condition**	**Decomposition Start Temp. (ºC)**	**Decomposition End Temp. (ºC)**	**Total Weight Loss (%)**
25	With	304	660	47
25	Without	306	699	42
60	With	346	685	49
60	Without	302	683	42
120	With	313	684	49
120	Without	338	671	42

3.5 Failure Modes and SEM Fractography

During tension tests specimens were fractured into two pieces. In the flexural and Charpy impact tests there were basically two failure modes: “complete break” or “hinge break”. In the hinge break, specimens are held together by a few fiber layers in the form of a hinge.

Since during three point bending loading, tensile loads develop on the central lower part of the specimen, and compressive loads on the central upper part of the specimen, and shear loads along the neutral axis of the specimen, all these types of failure modes were observed. This is shown in Figure 3.20.

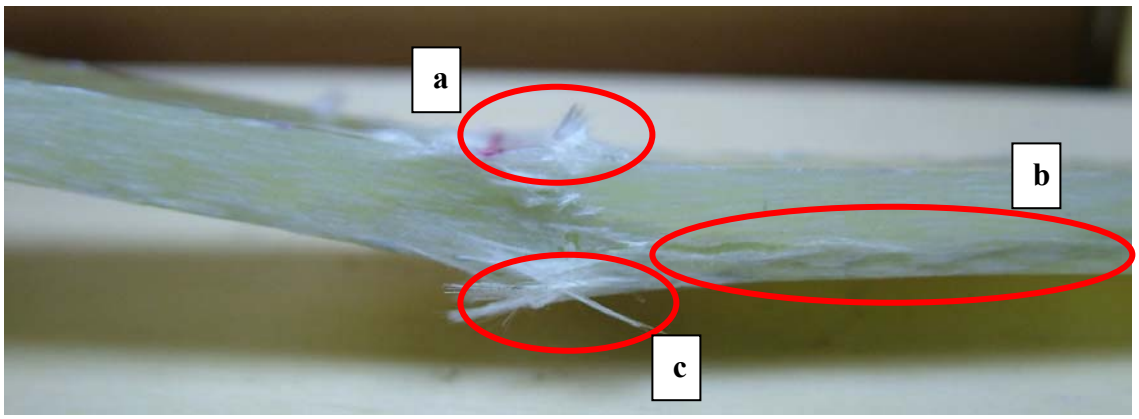
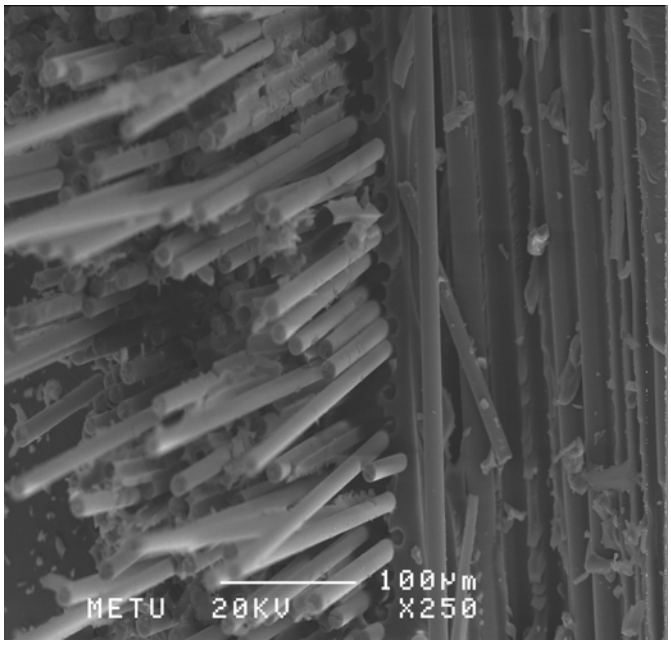
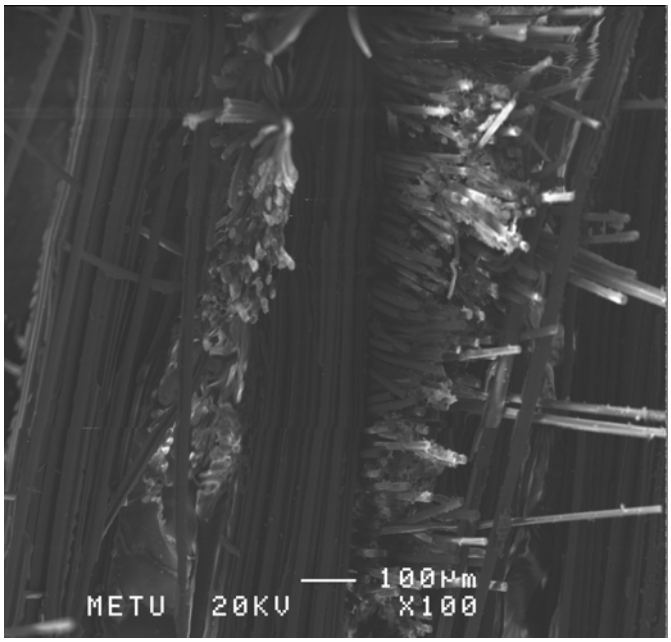


Figure 3.19 An example of an hinge break impact specimen showing three modes of failure: (a) compressive, (b) interlaminar shear, and (c) tensile

Apart from investigation of microvoids in the specimens, SEM was also used for the fractographic analysis of the specimens. Figure 3.20 shows general views of the fracture surface of the specimens indicating the woven form of the fibers with their vertical and horizontal alignment. Three main stages of the composite fracture mechanisms; *debonding* at the matrix/fiber interface, *fiber fracture* with increased loading, and *fiber pull-out* holes left in the matrix were observed. These stages are shown in Figure 3.21.

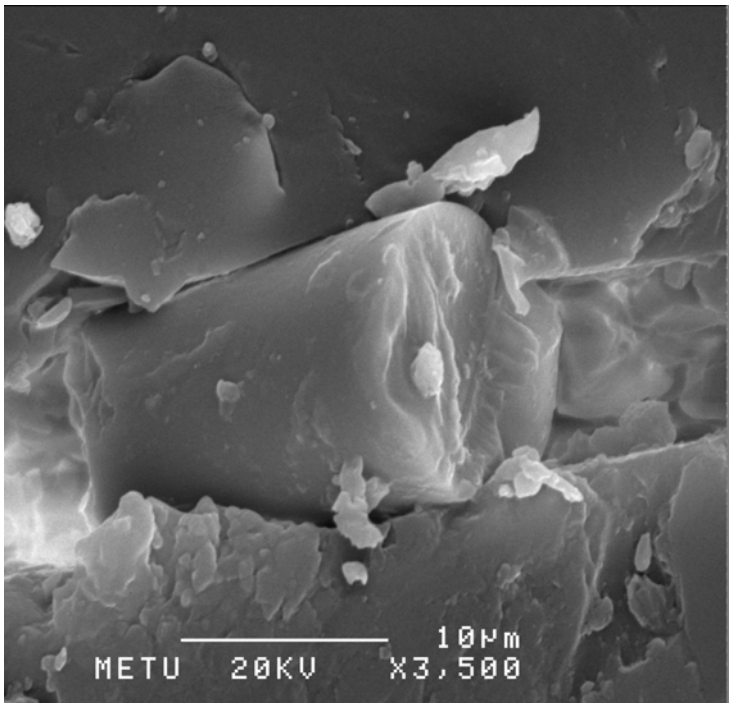


(a)

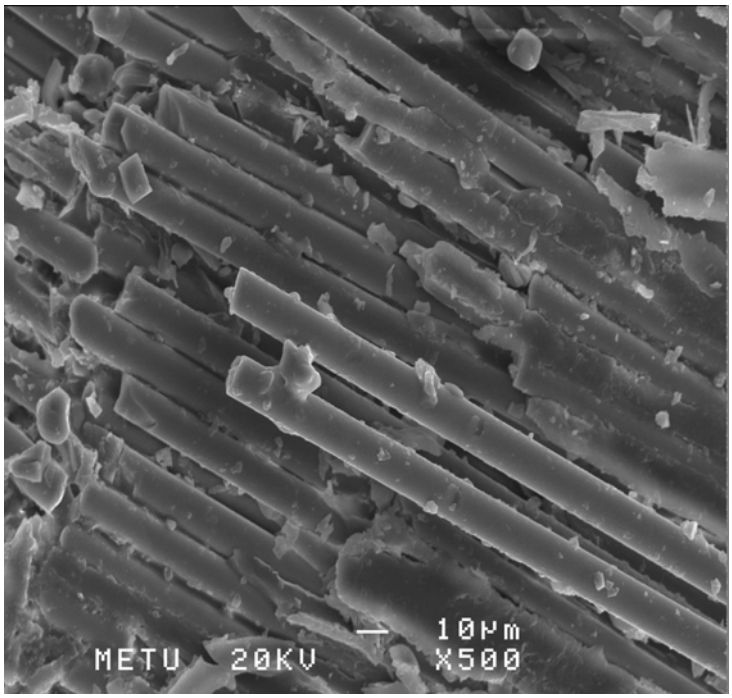


(b)

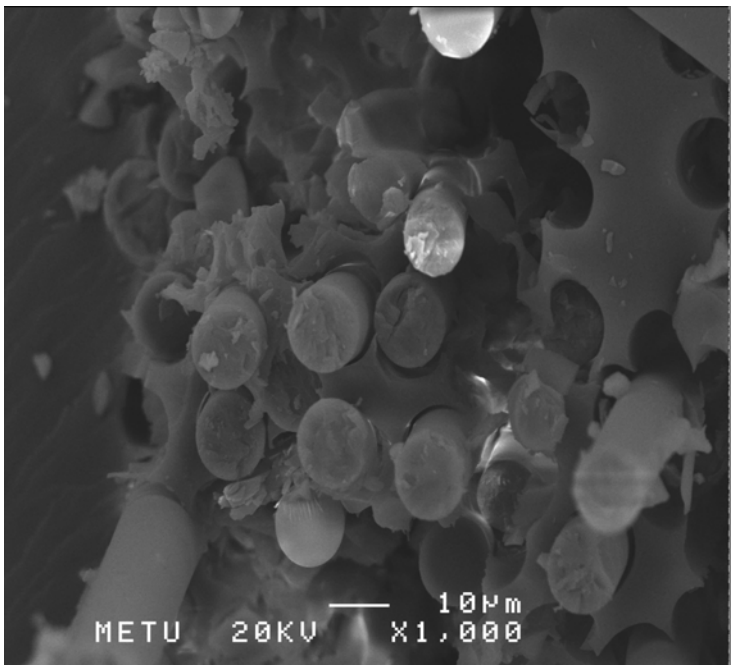
Figure 3.20 (a) and (b) Two general views of the fracture surfaces of the Charpy Impact specimens



(a)



(b)



(c)

Figure 3.21 Three main stages of the composite fracture mechanisms: (a) Debonding, (b) Fiber Fracture, and (c) Fiber Pull-out

CHAPTER 4

CONCLUSIONS

After characterizing two different sets (12 different conditions) of composite specimens produced by RTM with different mold temperatures, initial resin temperatures, and vacuum, the following conclusions were drawn;

(i) Effects of Mold Temperature

- Increasing mold temperature decreased the mold filling time due to the decrease in resin viscosity.
- Generally, mechanical properties of specimens had an increasing trend from 25º to 60ºC mold temperatures, while a decreasing trend from 60º to 120ºC.

- Specimens produced with a mold temperature of 60ºC had 16% higher tensile strength, 43% higher Charpy impact toughness, 26% higher flexural strength and modulus than the specimens produced at 25º and 120ºC mold temperatures.

- Therefore, the optimum mold temperature was determined as 60ºC.

- Because, use of 60ºC mold temperature led to an optimum resin viscosity and optimum resin gel time to ventilate micro bubbles or "micro voids" out of the mold properly.

(ii) Effects of Vacuum

- C-scan inspection indicated that when vacuum was applied during molding, percentage of dB loss above a certain level which can be referred as "defects" decreased more than 60% compared to without vacuum condition.

- Under vacuum condition, specimens had higher mechanical properties, for instance 5% higher tensile strength, flexural strength and modulus, and 26% higher Charpy impact toughness compared to without vacuum condition.

- Because, use of a vacuum level of 0.03 bar was sufficient to ventilate micro bubbles or "microvoids" out of the mold properly.

(iii) Effects of Initial Resin Temperature

- Decreasing the initial resin temperature from 28º to 15ºC also decreased mechanical properties, for example, for the specimens produced with the mold temperatures of 60ºC, this decrease was 14% in tensile strength and 18% in Charpy impact toughness values.

- Because, decreasing initial resin temperature increased viscosity of the resin leading to the difficulties in mold filling, fiber wetting, fiber impregnation, etc.

(iv) Ignition Loss and Thermal Stability

- Matrix resin content of the specimens were 38 – 40 wt%, while all of 14 glass fiber layers led to 39 – 41 vol% reinforcement.

- Thermal decomposition of the specimens started between 302º – 361ºC and reached a maximum level between 649º – 723ºC leading to a total weight loss between 34 – 50%.

(v) Failure Modes and Mechanisms

- Flexural and impact specimens had failure modes of "complete break" or "hinge break". SEM fractography indicated three main stages of the composite fracture mechanisms; debonding, fiber fracture, and fiber pull-out.

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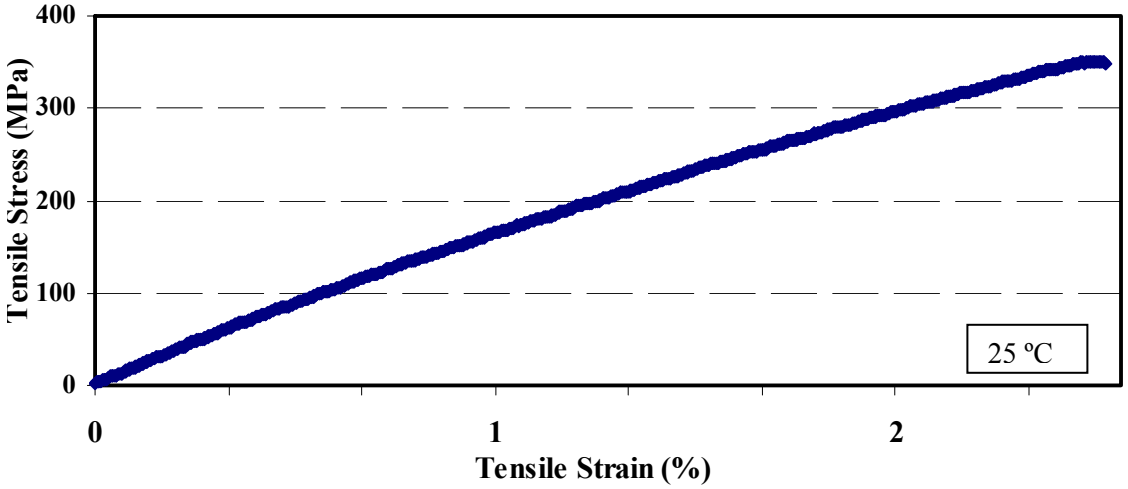
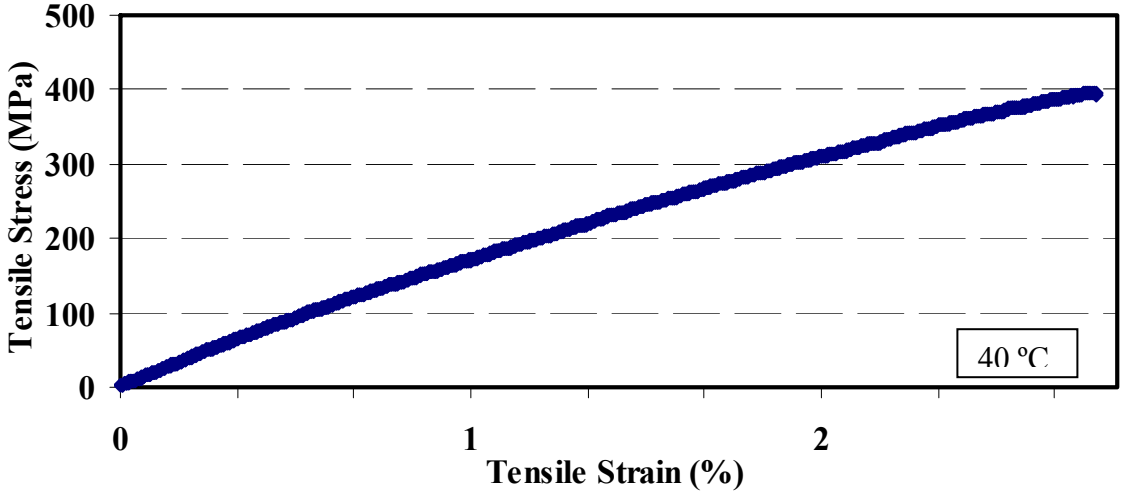
[30] ISO 11358 Thermogravimetry (TG) of Polymers: General Principles

APPENDIX A

Examples of Tensile Stress versus Tensile Strain Curves of the Specimens Produced with different Mold Temperatures



(a)



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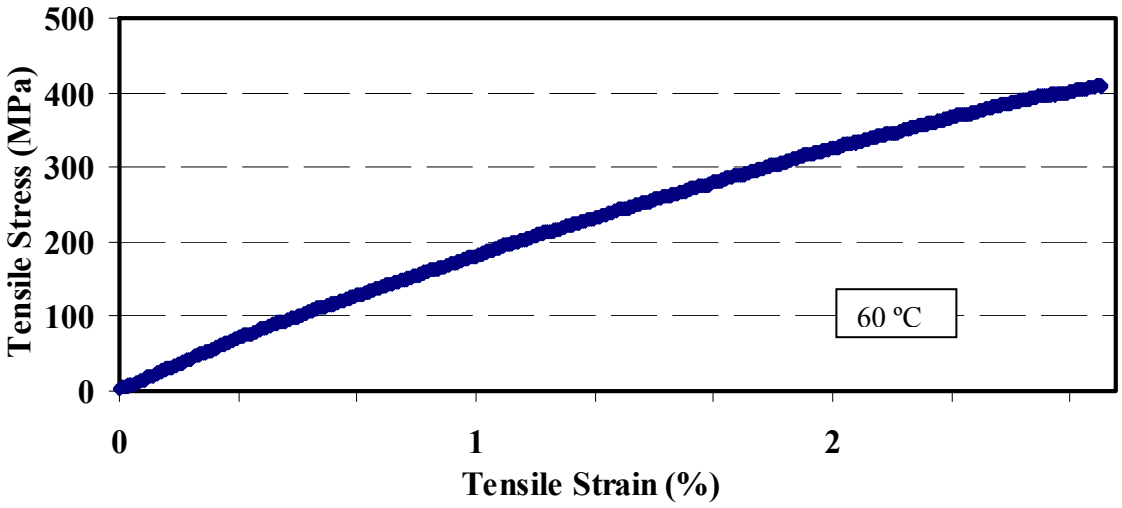
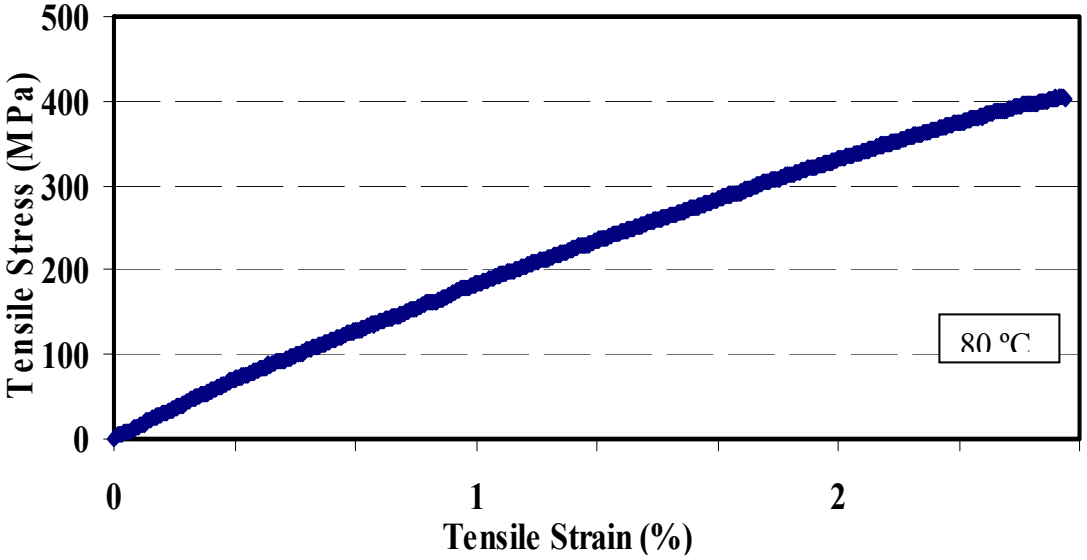
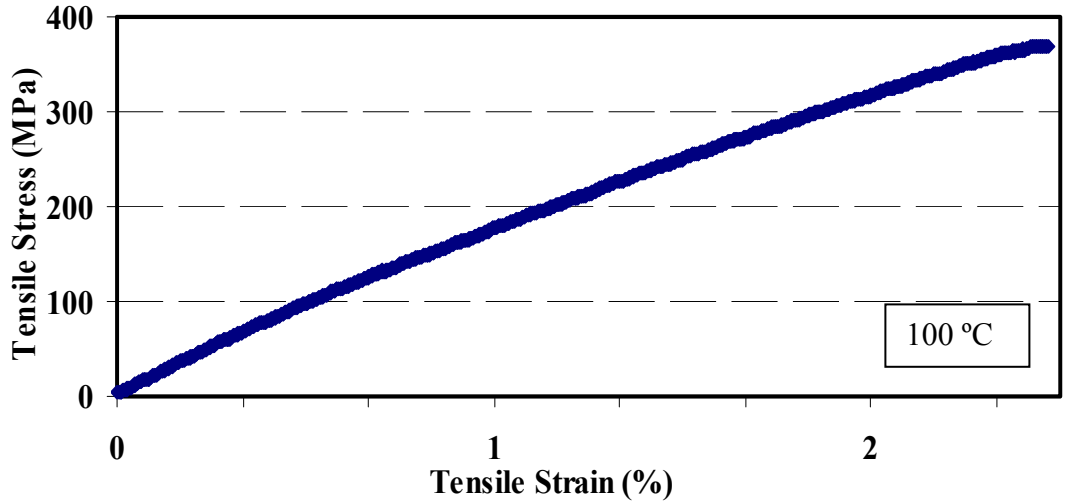

500
400
300
200
100
0
Tensile Stress (MPa)
60 ºC
0
1
2
Tensile Strain (%)

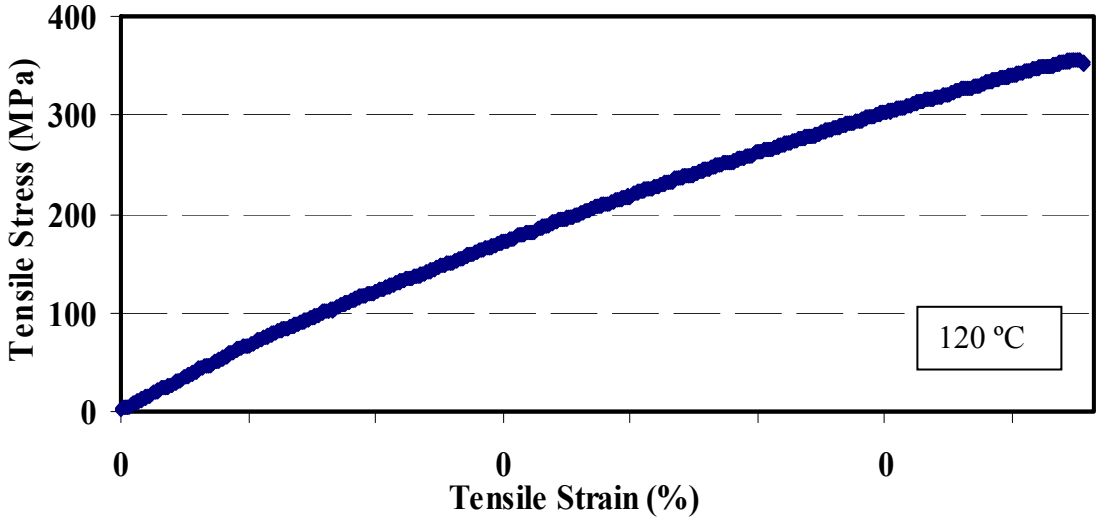
(c)


500
400
300
200
100
0
Tensile Stress (MPa)
80 ºC
0
1
2
Tensile Strain (%)

(d)



(e)

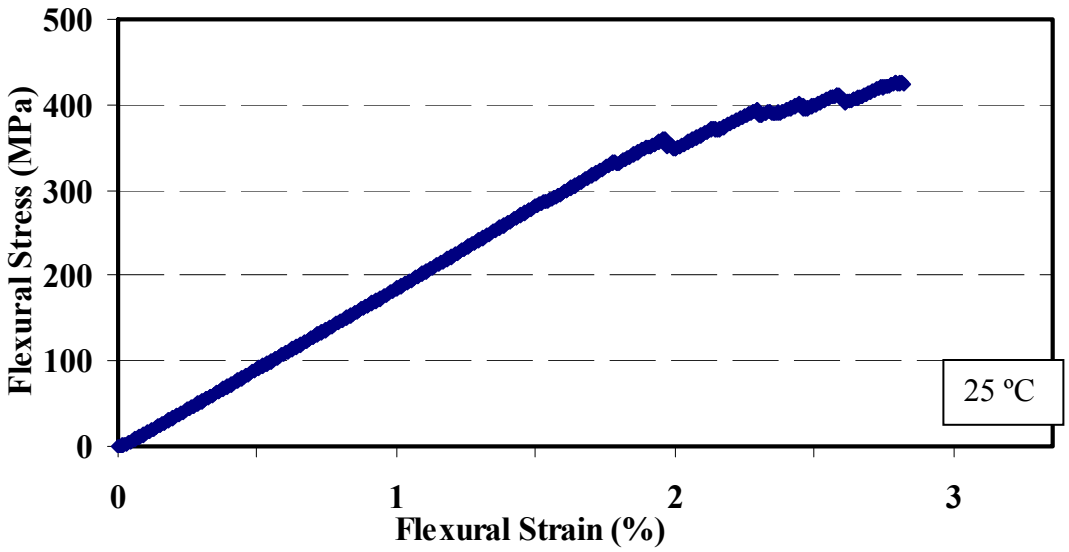


(f)

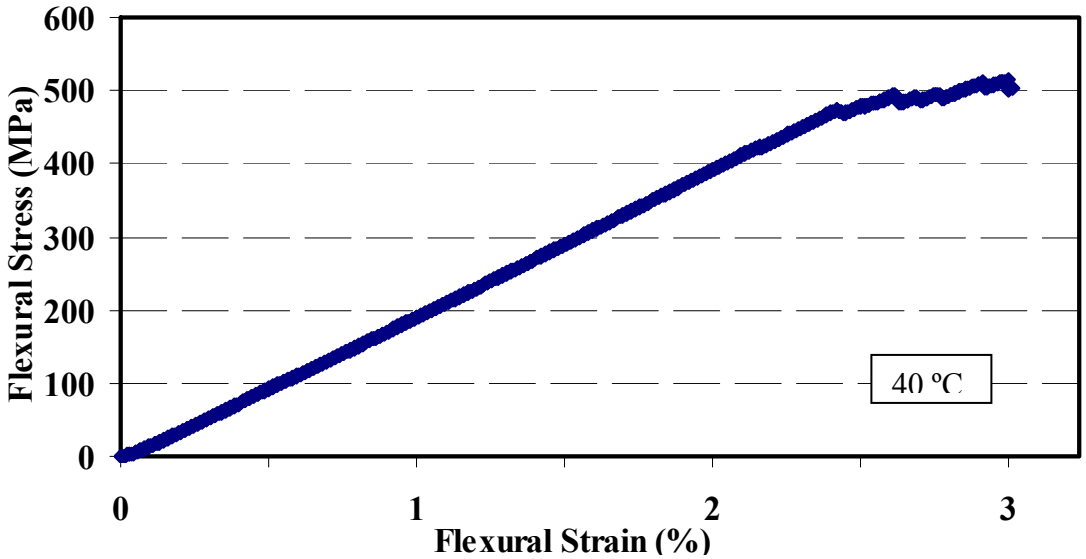
Figure A Examples of Tensile Stress versus Tensile Strain Curves of the Specimens Produced with Mold Temperatures of (a) 25, (b) 40, (c) 60, (d) 80, (e) 100, and (f) 120ºC

APPENDIX B

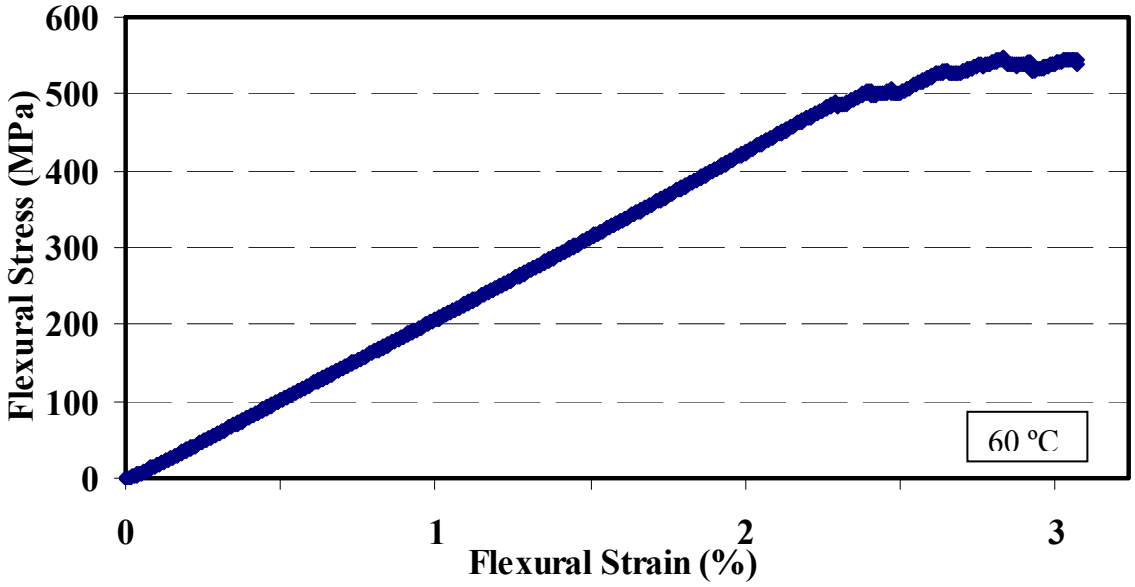
Examples of Flexural Stress versus Flexural Strain Curves of the Specimens Produced with different Mold Temperatures



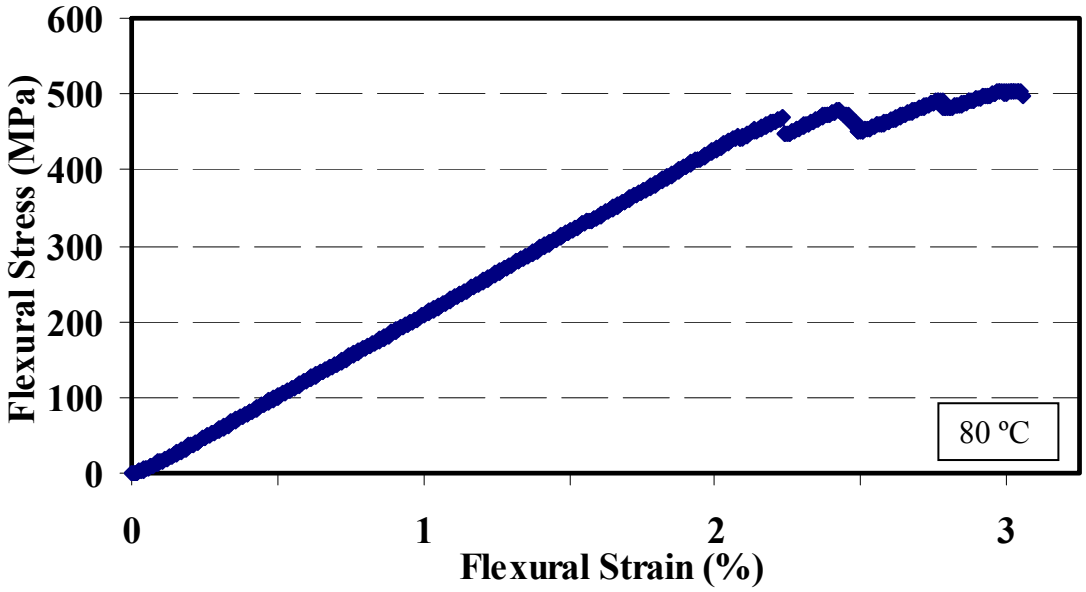
(a)



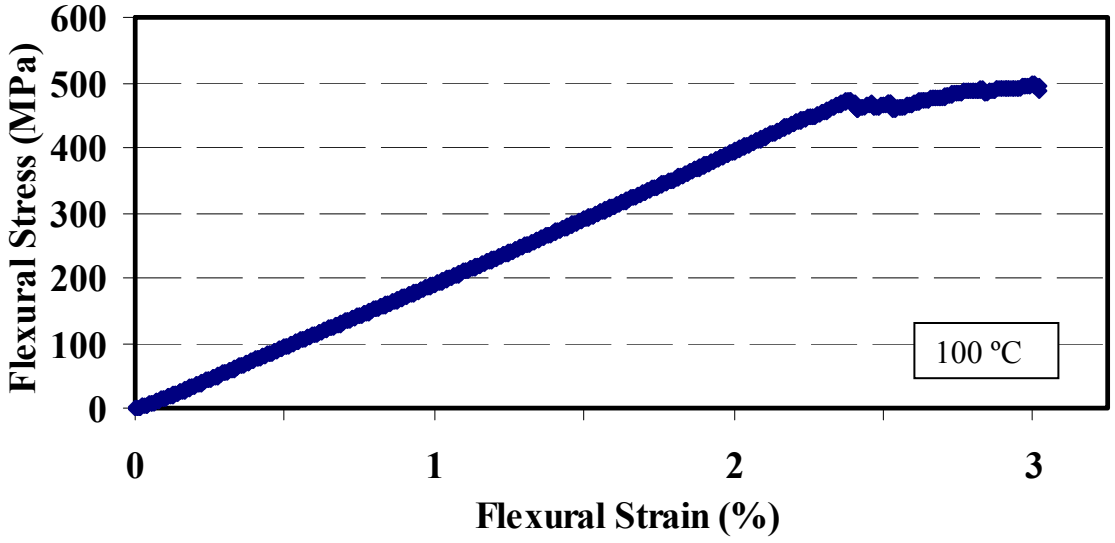
(b)


600
500
400
300
200
100
0
Flexural Stress (MPa)
0
1
2
3
Flexural Strain (%)
60 ºC

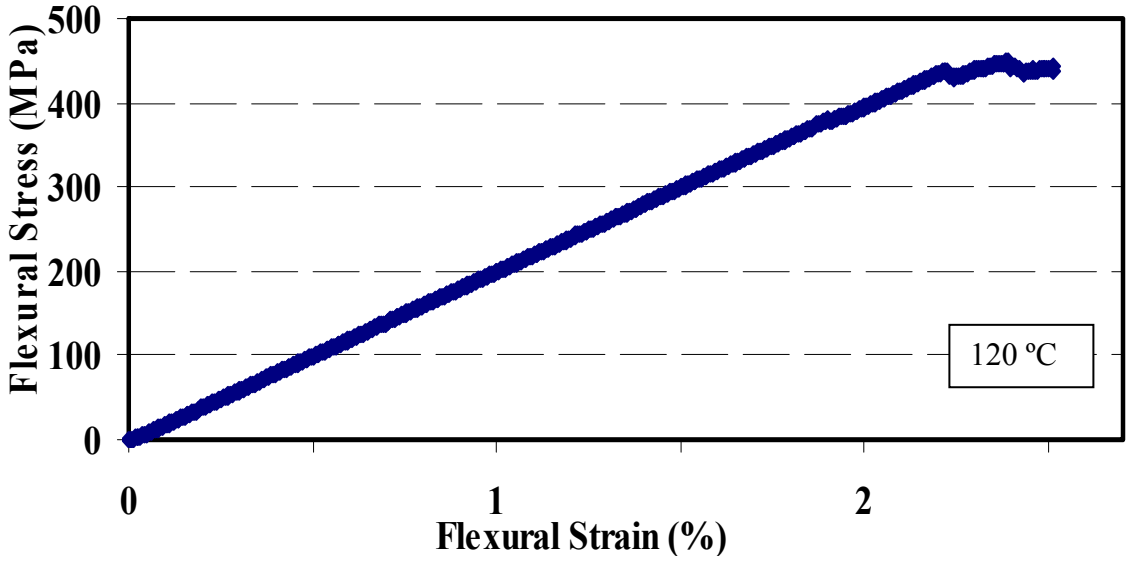
(c)


600
500
400
300
200
100
0
Flexural Stress (MPa)
0
1
2
3
Flexural Strain (%)
80 ºC

(d)



(e)

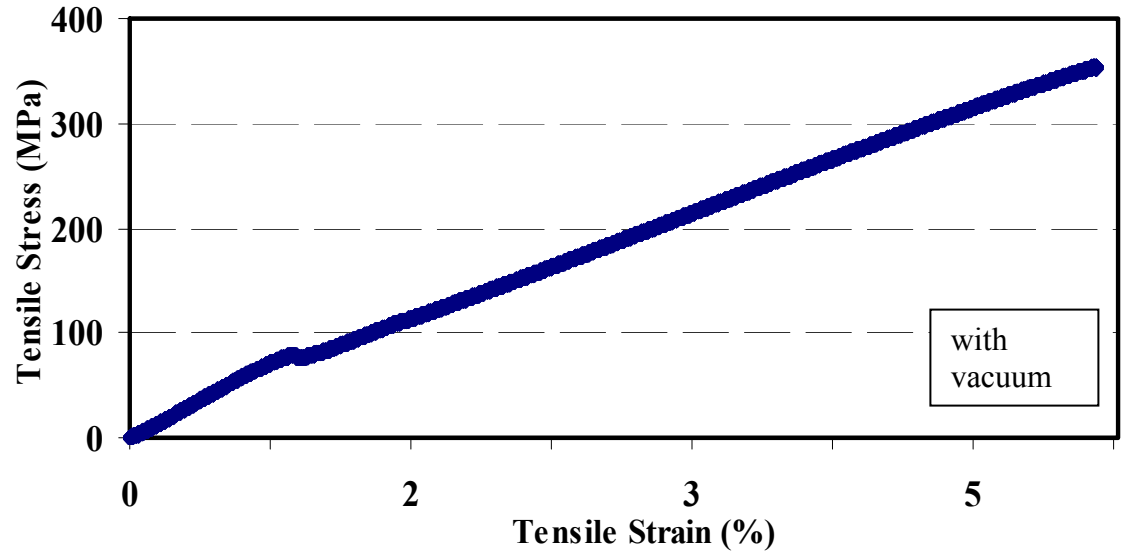


(f)

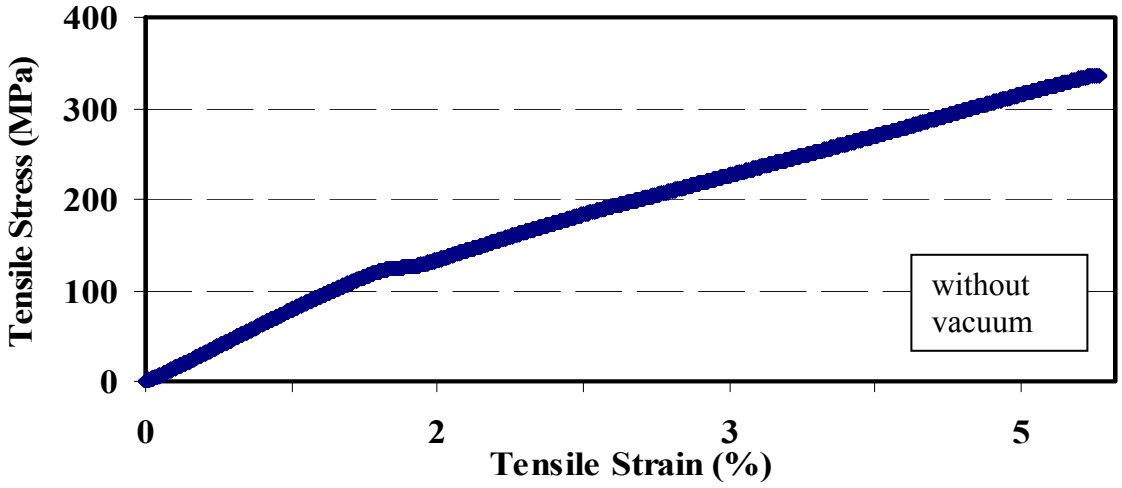
Figure B Examples of Flexural Stress versus Flexural Strain of the specimens Produced with Mold Temperatures of (a) 25º, (b) 40º, (c) 60º, (d) 80º, (e) 100º, and (f) 120ºC

APPENDIX C

Examples of Tensile Stress versus Tensile Strain Curves of the Specimens Produced with Vacuum and without Vacuum

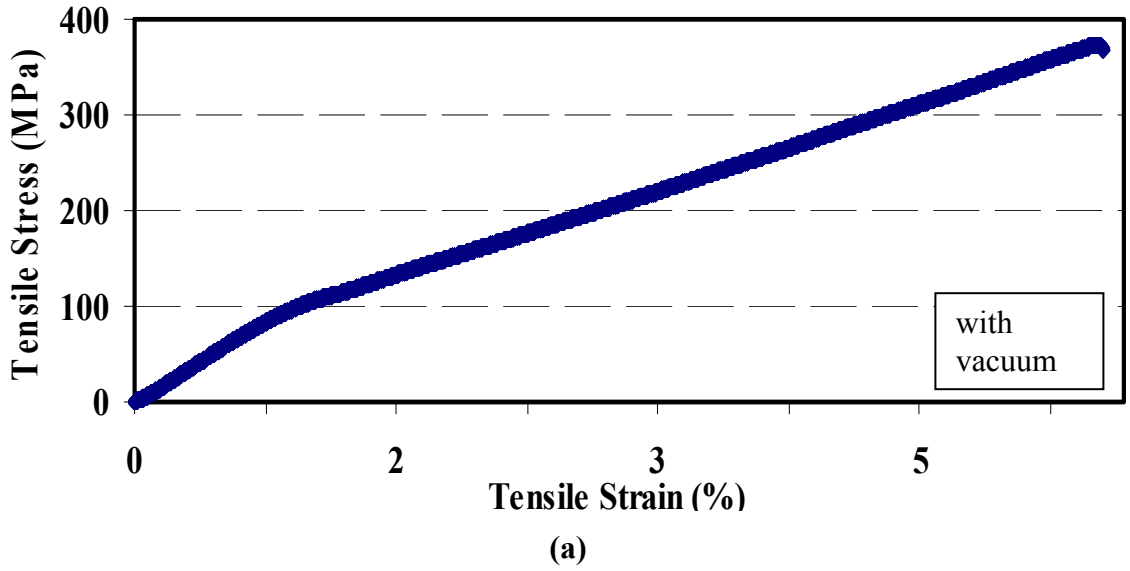


(a)

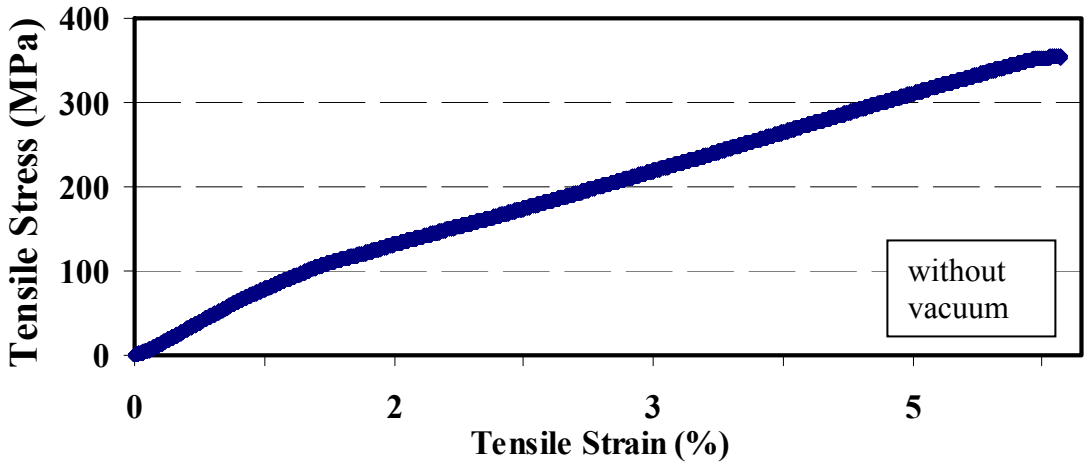


(b)

Figure C.1 Examples Tensile Stress versus Tensile Strain Curves of the Specimens Produced with a Mold of Temperature of 25ºC, (a) with vacuum, (b) without vacuum

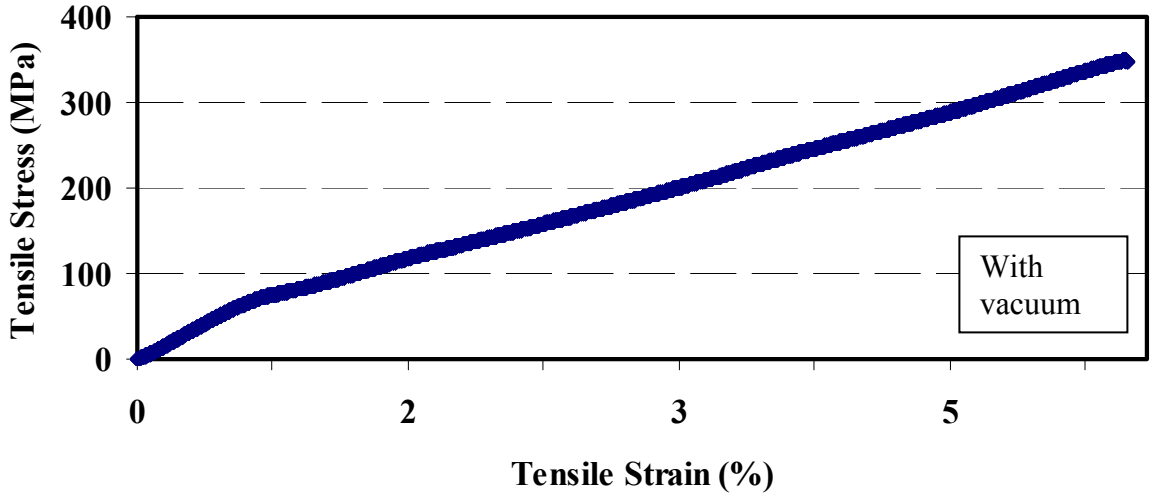


(a)

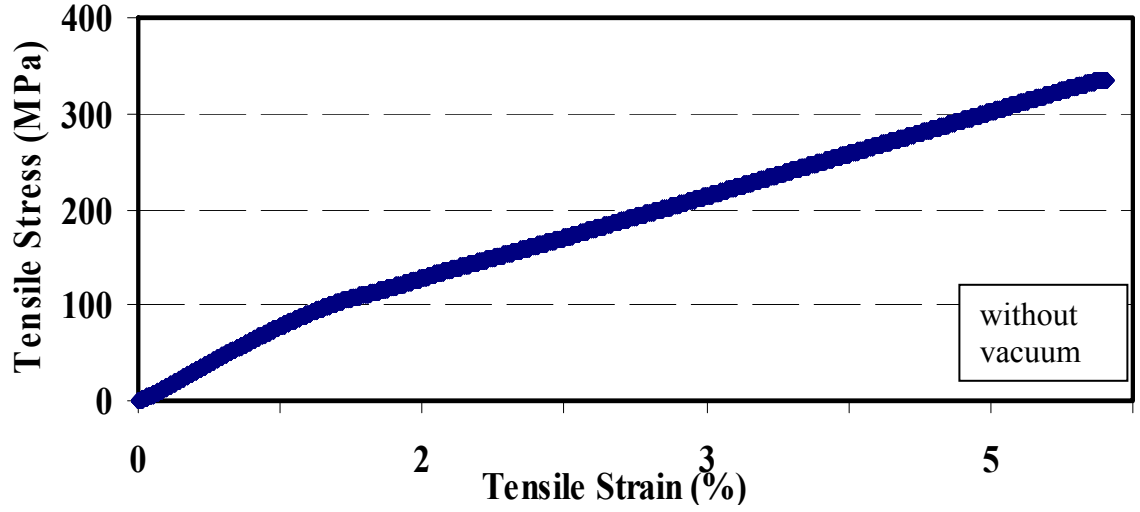


(b)

Figure C.2 Examples Tensile Stress versus Tensile Strain Curves of the Specimens Produced with a Mold of Temperature of 60ºC, (a) with vacuum, (b) without vacuum



(a)

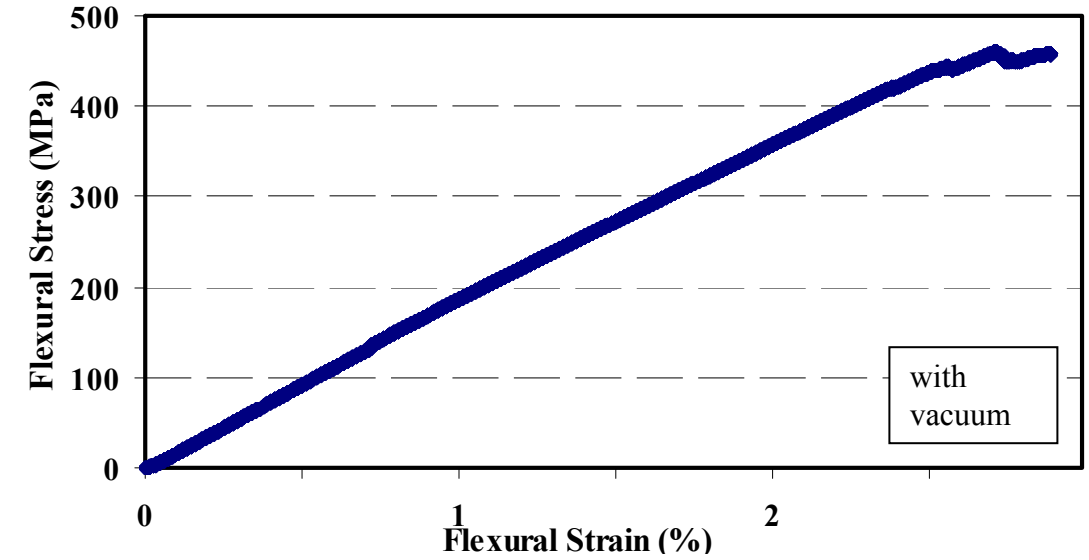


(b)

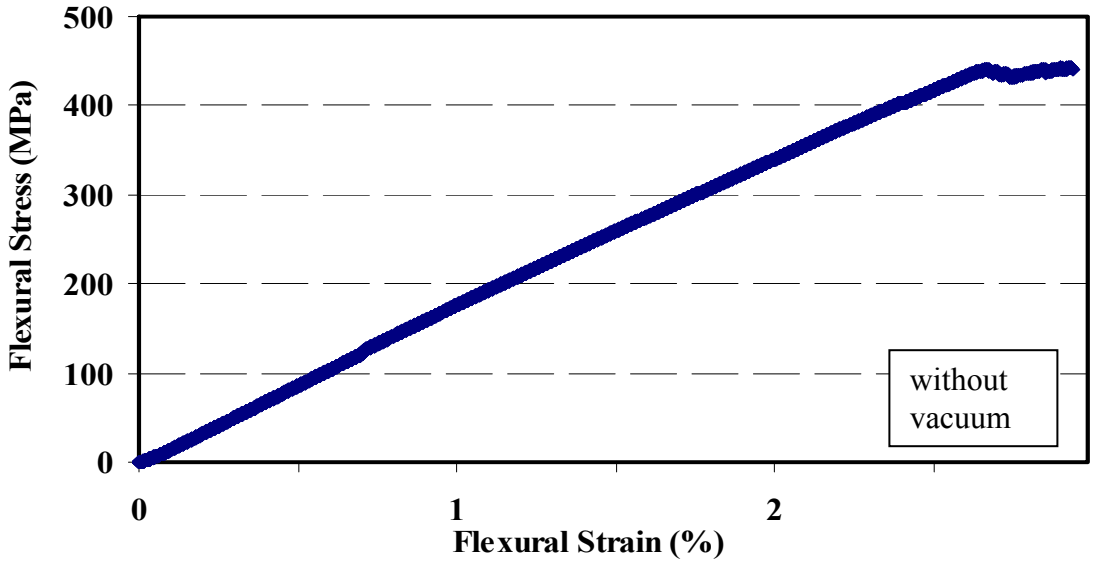
Figure C.3 Examples Tensile Stress versus Tensile Strain Curves of the Specimens Produced with a Mold of Temperature of 120ºC, (a) with vacuum, (b) without vacuum

APPENDIX D

Examples of Flexural Stress versus Flexural Strain Curves of the Specimens Produced with Vacuum and without Vacuum

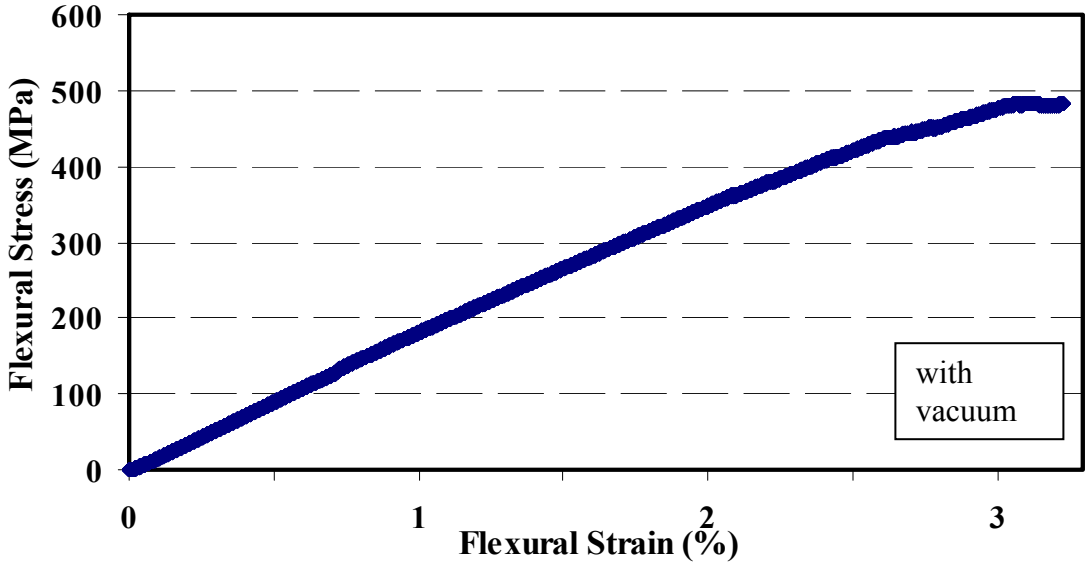


(a)

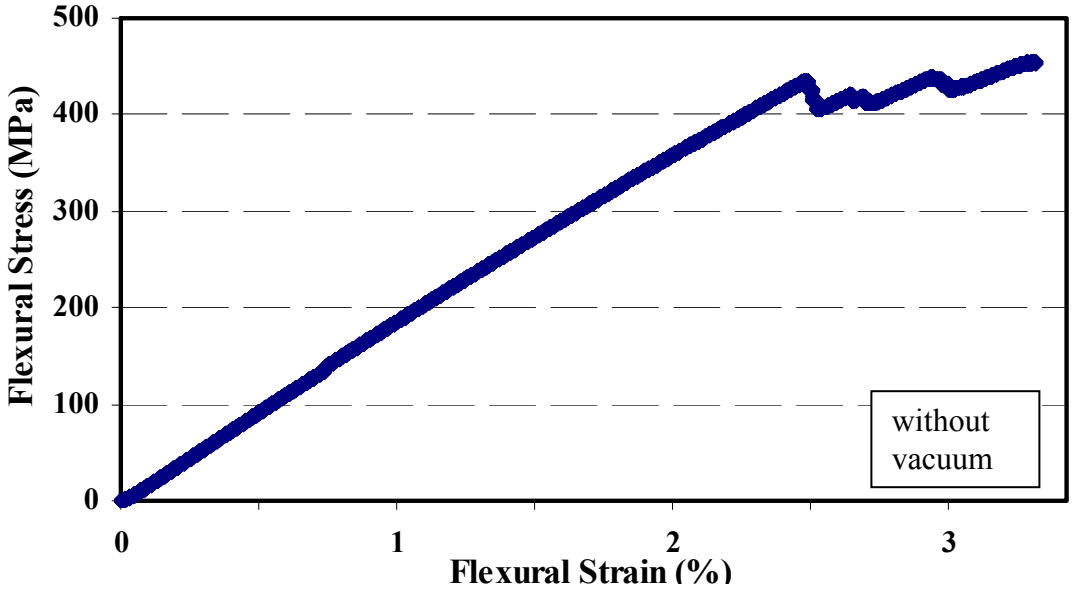


(b)

Figure D.1 Examples Flexural Stress versus Flexural Strain Curves of the Specimens Produced with a Mold of Temperature of 25ºC, (a) with vacuum, (b) without vacuum

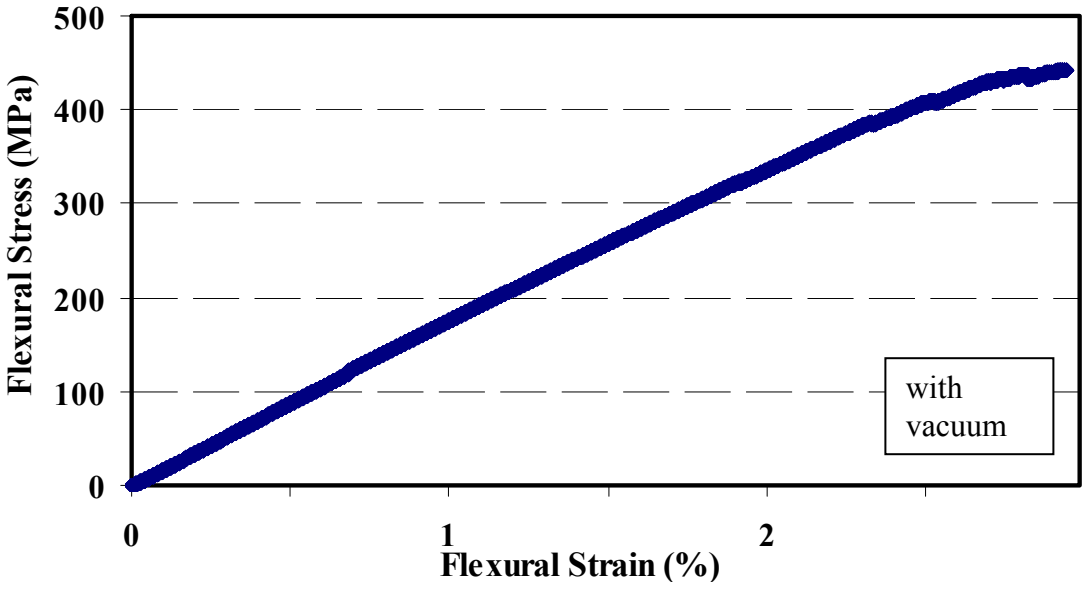


(a)

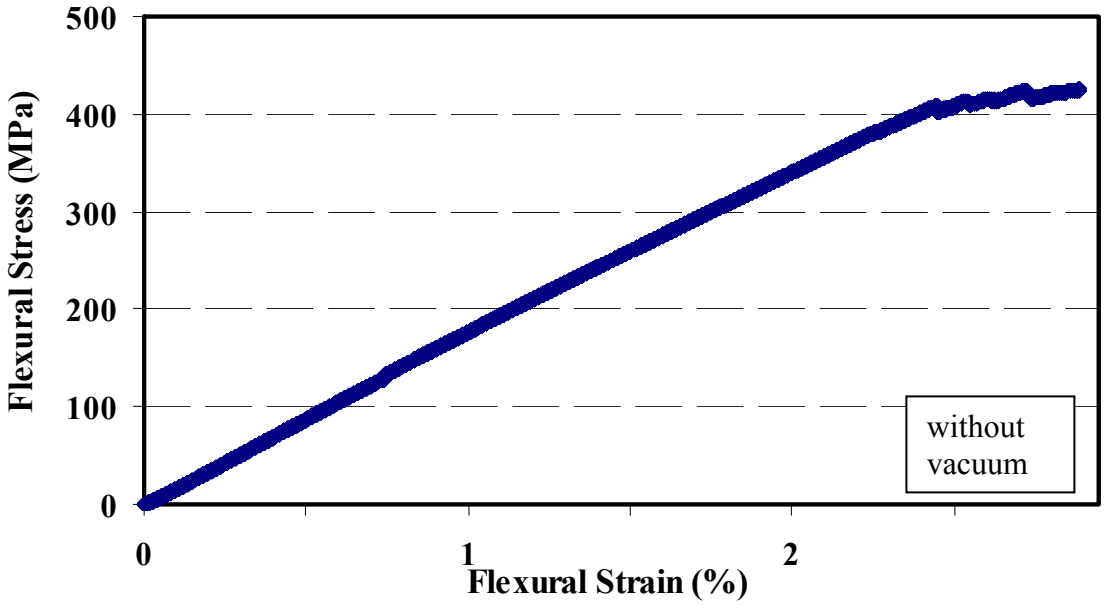


(b)

Figure D.2 Examples Flexural Stress versus Flexural Strain Curves of the Specimens Produced with a Mold of Temperature of 60ºC, (a) with vacuum, (b) without vacuum



(a)

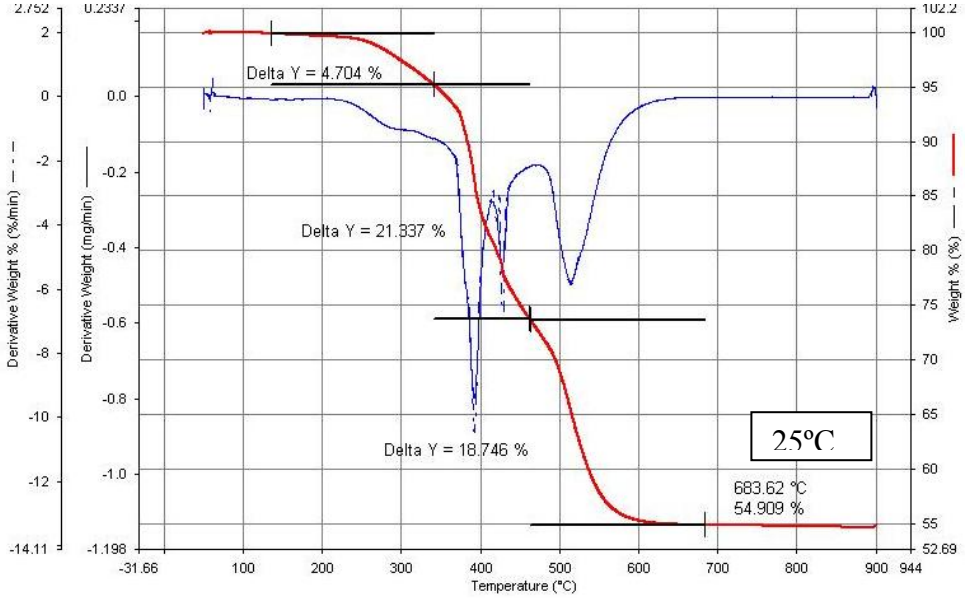


(b)

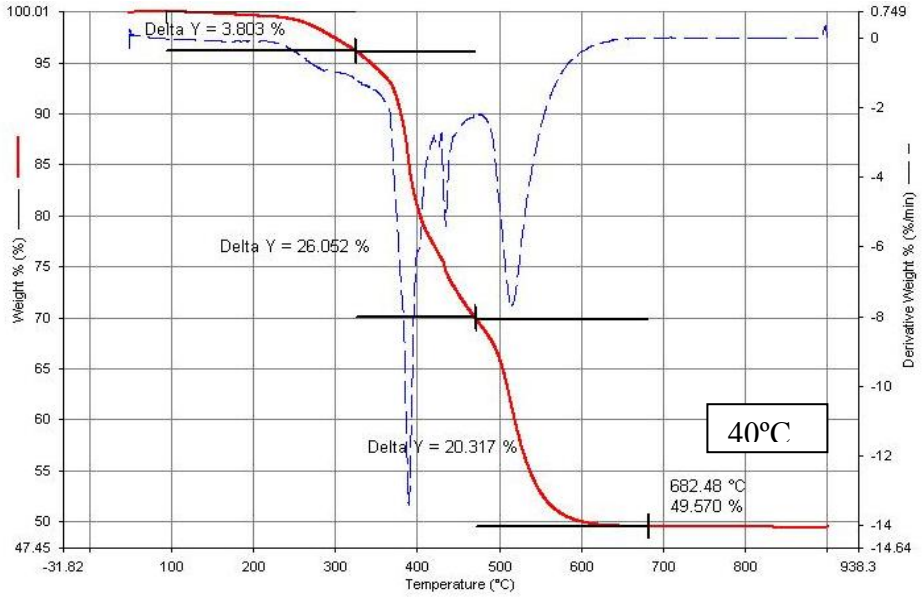
Figure D.3 Examples Flexural Stress versus Flexural Strain Curves of the Specimens Produced with a Mold of Temperature of 120ºC, (a) with vacuum, (b) without vacuum

APPENDIX E

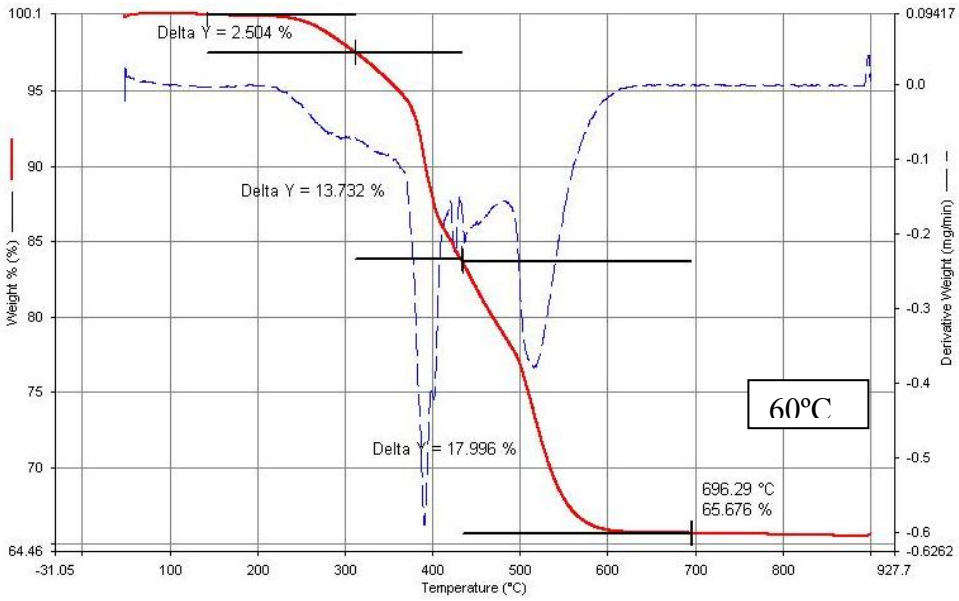
Examples of TGA Curves of the Specimens Produced with different Mold Temperatures



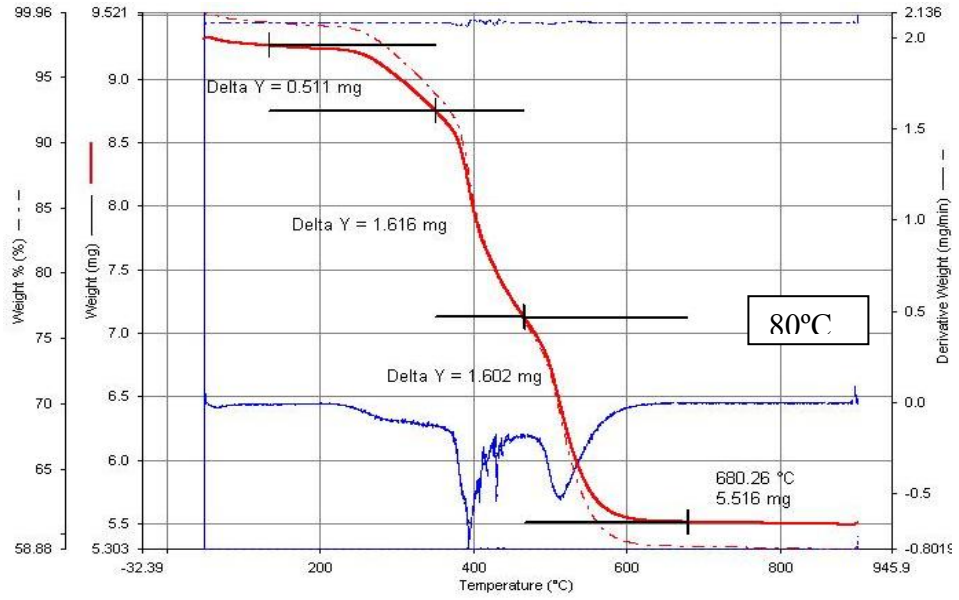
(a)



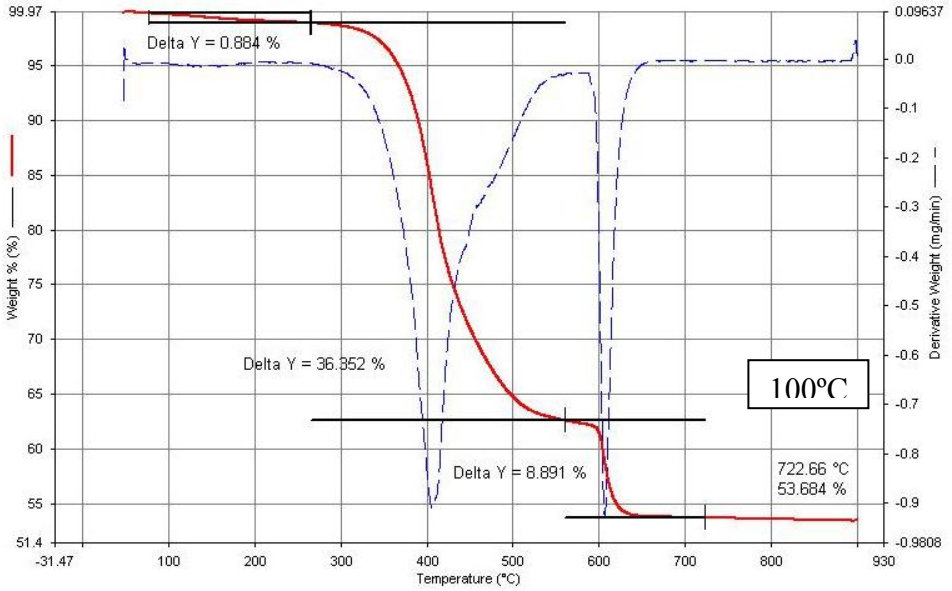
(b)


Delta Y = 2.504 %
Delta Y = 13.732 %
Delta Y = 17.996 %
696.29 °C
65.676 %
60ºC
Weight % (%)
Derivative Weight (mg/min)
Temperature (°C)
100.1
95
90
85
80
75
70
64.46
-31.05
100
200
300
400
500
600
700
800
927.7
0.09417
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.6262

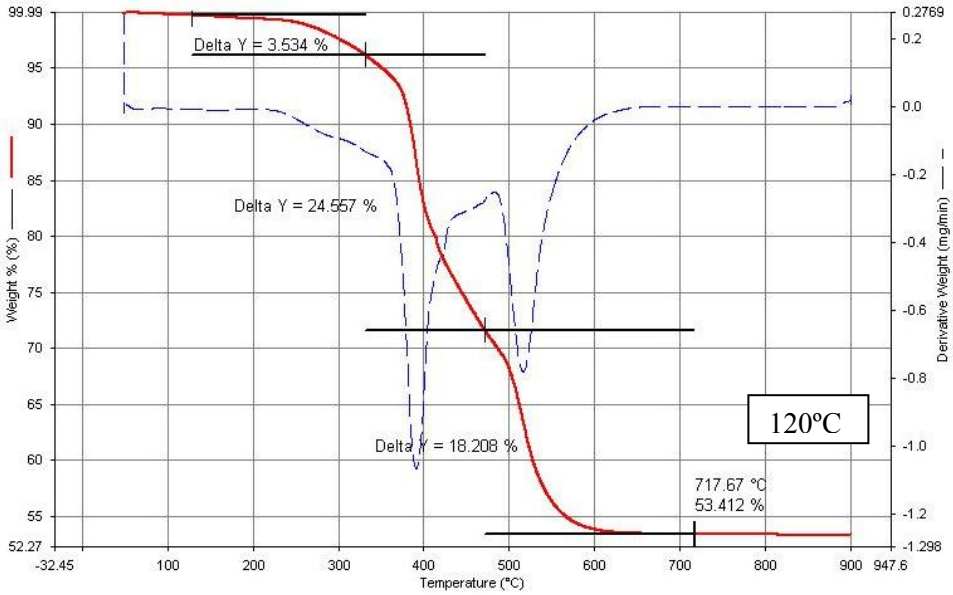
(c)


Delta Y = 0.511 mg
Delta Y = 1.616 mg
Delta Y = 1.602 mg
680.26 °C
5.516 mg
80ºC
Weight % (%)
Weight (mg)
Derivative Weight (mg/min)
Temperature (°C)
99.96
95
90
85
80
75
70
65
58.88
9.521
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.303
-32.39
200
400
600
800
945.9
2.136
2.0
1.5
1.0
0.5
0.0
-0.5
-0.8019

(d)



(e)

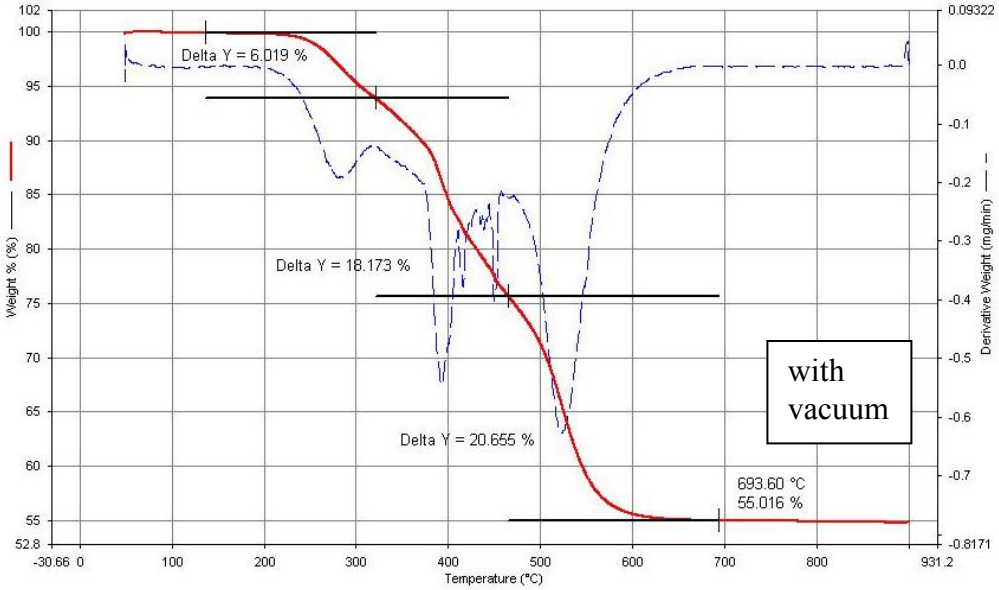


(f)

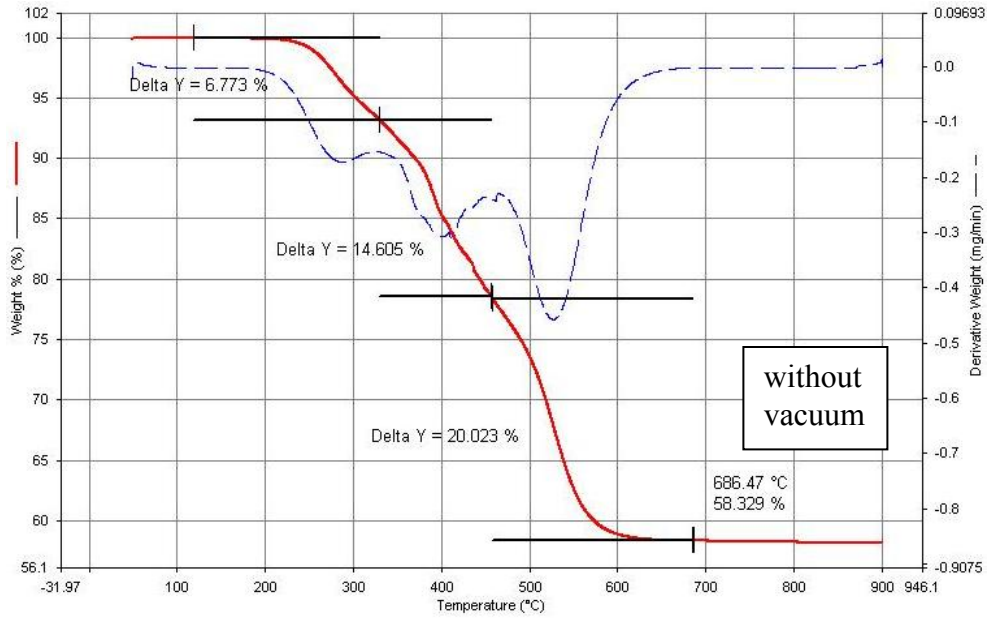
Figure E Examples of TGA Curves of the Specimens Produced with Mold Temperatures of (a) 25º, (b) 40º, (c) 60º, (d) 80º, (e) 100º, and (f) 120ºC

APPENDIX F

Examples of TGA Curves of the Specimens Produced with Vacuum and without Vacuum

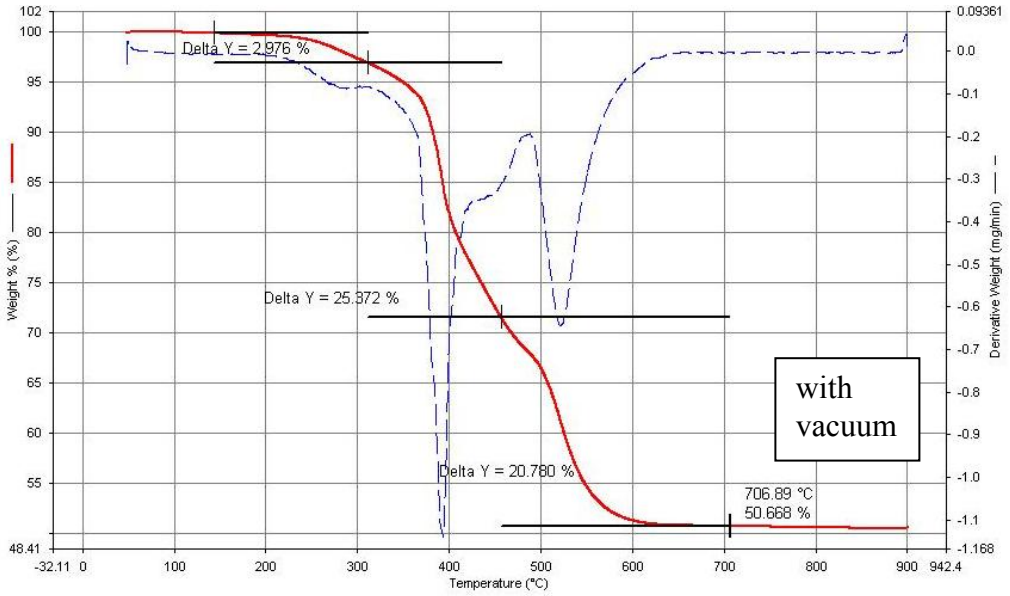


(a)

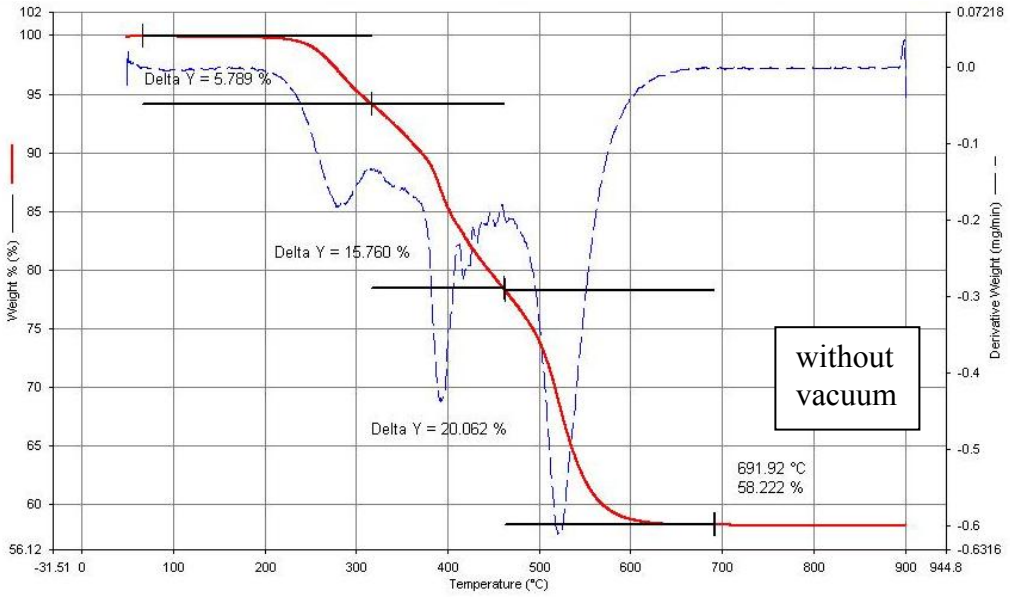


(b)

Figure F.1 Examples of TGA Curves of the Specimens Produced with a Mold Temperature of 25ºC, (a) with vacuum and (b) without vacuum

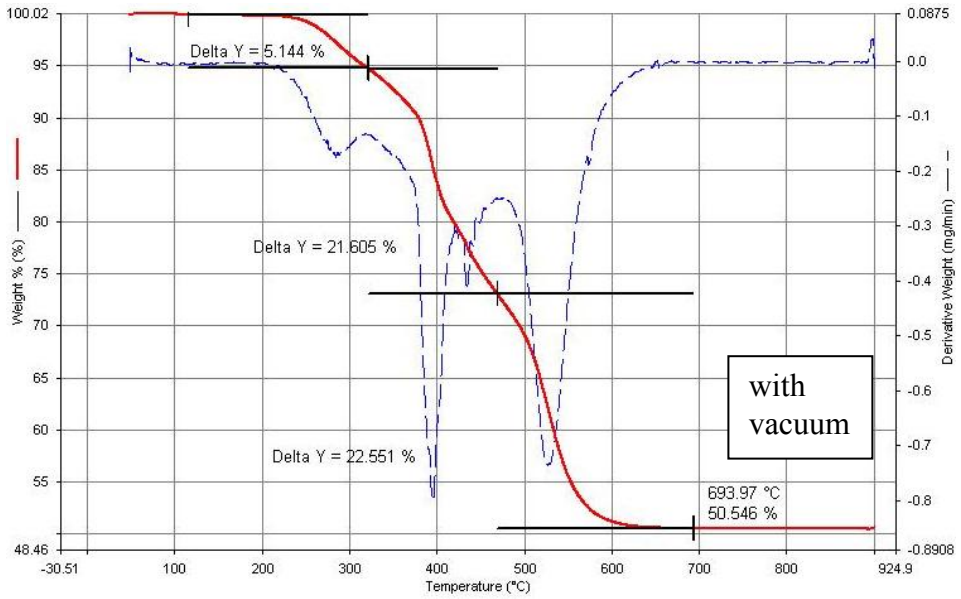


(a)

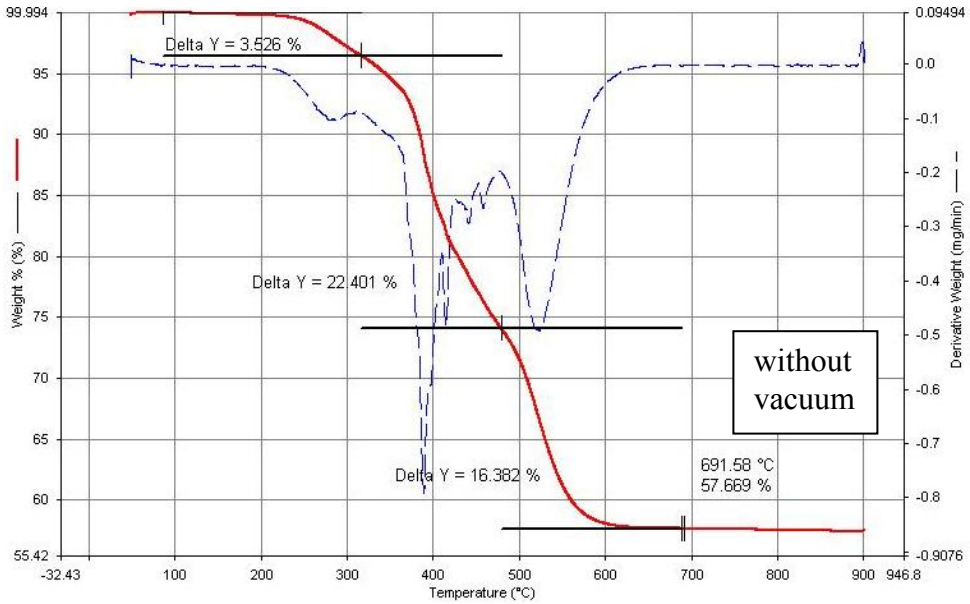


(b)

Figure F.2 Examples of TGA Curves of the Specimens Produced with a Mold Temperature of 60ºC, (a) with vacuum and (b) without vacuum



(a)



(b)

Figure F.3 Examples of TGA Curves of the Specimens Produced with a Mold Temperature of 120ºC, (a) with vacuum and (b) without vacuum