A Novel Method for the Manufacturing of Thick Composites

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ABSTRACT

A Novel Method for the Manufacturing of Thick Composites

Yijun jiang

Due to the nature of exothermic reaction and high thermal resistance, processing thick-sectioned composites can be very difficult. Instead of expensive and time consuming trial and error methods, pre-catalyzing fabric technique applied to the hand lay-up process is very effective to decrease exothermal peak dramatically. By applying the peroxide catalyst to the fabric, this technique can slow down the polymerization reaction rate and subsequently reduce the internal temperature during curing. In this study, two kinds of pre-catalyzing methods were developed: one used polystyrene as the catalyst binder; another used epoxy resin as the binder. The experimental results indicate that the pre-catalyzing method using polystyrene as the binder can control the peak exothermic temperature to be under 30°C, and the method using epoxy binder can limit that temperature to be below 39°C. Latter method has shorter curing time than former one. Both methods can reduce the temperature gradient greatly. The degree of cure for both methods can be more than 87% with low exothermic temperature after the cure, and the laminate is rigid enough with this degree of cure to be used for further post cure. The degree of cure can be improved to be higher than 97% by leaving the samples for more than five weeks in ambient temperature. Compared with polystyrene binder which made the interlaminar shear strength decrease by 12.8%, the epoxy resin binder has the better

characteristic not to exhibit this decrease, and the short beam shear tests show no degradation of ILSS.

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Chapter 1

Introduction

Reinforced thermosetting resin matrix composite materials have been widely used in aerospace, military and construction applications because of their high specific modulus and strength. Fabrication of these composite materials is accomplished using techniques such as autoclave, resin transfer molding (RTM), filament winding, pultrusion and hand lay-up. However, conventional cure cycles recommended by the material suppliers are only used for fabricating thin laminates. Now more and more applications, such as lightweight submarines or ship hulls and bridge decking, pylons, I-beams etc., require composites with thicker sections. The conventional processing techniques could not satisfy the needs of the high quality and performance of thick-section composites, and their fabrication requires costly processing procedures or expensive equipment.

Recent technological improvements for thick-sectioned composites have made some progress in some aspects ([1] ~ [6]). However, final product qualities, application difficulties, processing time and processing of complicated geometry parts are still important concerns. In this research, we attempt not only to reduce the exothermic temperature, but also to improve the processing time of thick-section composites using hand lay-up. A new technique - pre-catalyzing fabric - is developed. The qualities of final products are also evaluated.

1.1 Problem Statement

Due to the highly exothermic nature of the polymer matrix during cross-linking reaction and low thermal conductivity of composites, the successful manufacturing of thick-sectioned composites can be a great challenge to existent manufacturing processes. Generally, once the thickness of composite parts exceeds12.5 cm (1/2 inch) [6], the processing of composite laminates becomes difficult.

In conventional **pre-mixing method**, catalysts are always mixed into bulk resin system before use. Since catalysts are distributed in the resin system evenly, the free radical crosslinking reaction should happen simultaneously at all points in the bulk resin. As we know, thermoset reaction is an exothermic process, especially for styrene-based thermoset. In this process, the double bonds break when the reaction occurs, and the energy which stored in these bonds within chemical compounds is released. Due to a large amount of heat produced at the same time during the reaction, the reactions that follow can be accelerated by this heat. As a result, more heat is generated again. Generally, this cure cycle with high exothermic energy does not influence the qualities of thin composite laminates because the heat can escape from parts easily. On the contrary, because of the low thermal conductivity of composites, the heat can not escape form the center of thick composites in a short time. This creates temperature overshoot at the center, and may lead to uneven cure, uneven shrinkage and variations in resin viscosity resulting in non-uniform consolidation. Figure 1-1 is an example of cure profile of a laminate fabricated with conventional pre-mixing method. It can be observed that the

center peak temperature is about 104°C which is 18°C higher than the edge. This large temperature gradient can induce internal stresses or resin cracks.

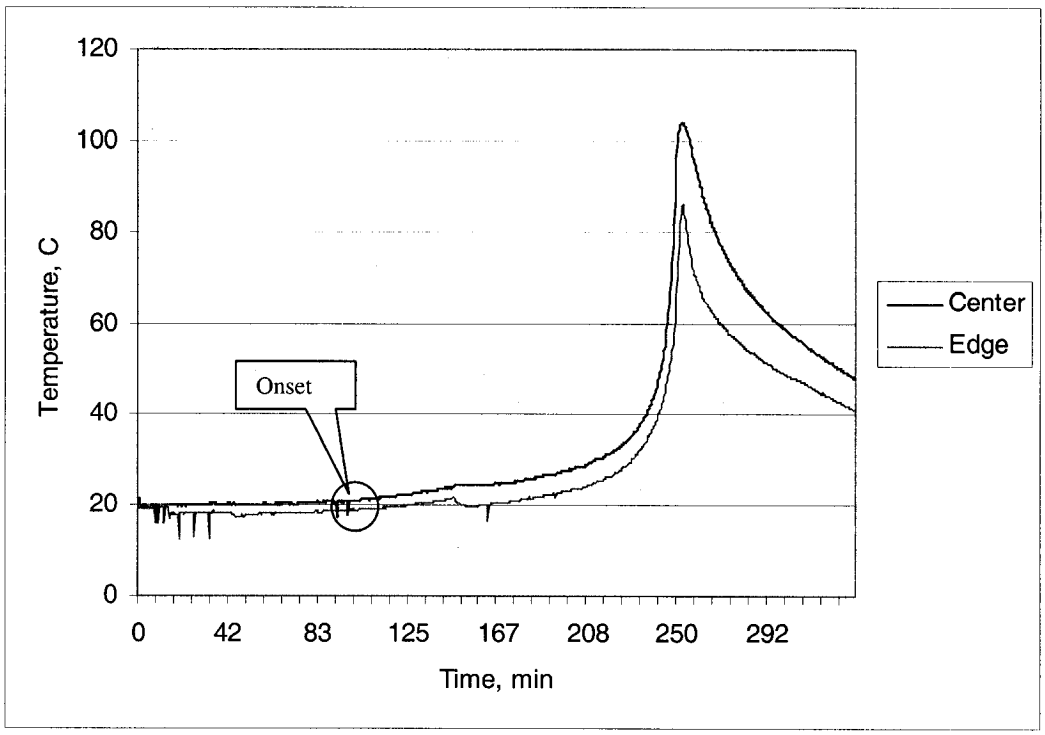


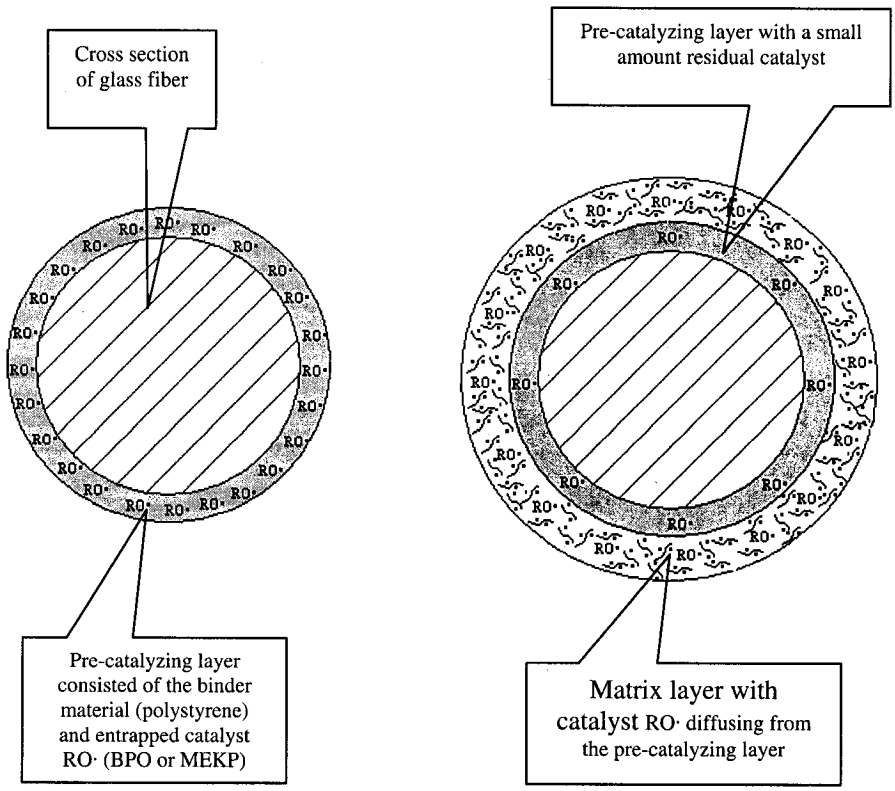
Figure1-1: Temperature profile of exothermic reaction with conventional pre-mixing method

The typical industrial approach is to use an empirical trial and error procedure, which mainly focuses on increasing the cure time for the purpose of decreasing the peak temperature of reaction heat by adjusting the process parameters and ingredients of resin systems. The commonly used method in industry is stage curing process. This method allows the operation to be divided into several steps. During each step, only a small number of layers are applied, and time is allowed between steps. Each step is begun after

the laminate made in previous steps reaches a partial cure from which most exothermic energy has come out. Obviously, this process leads to long process time, and may likely lead to more waste of materials. Another disadvantage is that molds used to make the composite structures are tied up during the waiting period. Recent methods of optimization use trail and error methods with simulation or expert system ([27]-[30]). For model based optimization, it requires an accurate numerical model of the geometry, and it has computational difficulties for a complex geometry. Expert systems, which can avoid computational difficulty, do not use mathematical model, but they rely on direct measurement of critical system properties. Only for flat composites, expert systems can have good comparison to those of conventionally manufactured composite. Cure simulation and expert system methods can be applied in Injection Molding of Composites (IMC), Pultrusion and Resin Transfer Molding (RTM), but in Laminated Object Fabrication (LOF) [51] [52], the two methods are applied only when prepregs are used. Besides, there has been recent attention given to alternate curing techniques such as e-beam [7] and microwave cure [8], which use high-energy electrons as ionizing radiation at controlled rates to cure polymer matrix composites. However, the investment on facilities and equipment to house and control the radiation is very large. Again, more development work is needed before this technique will be accepted.

A new attractive technique of processing thick-section composite is developed recently in the University of Massachusetts at Dartmouth [9]. This technique uses glass fabric which is pre-catalyzed with the peroxide catalyst before resin is applied. The application of this technique consists of two main steps (figure 1-2): pre-catalyzing the fiber and applying the resin system to the fiber. In the first step, the fiber is "sized" with

the binder/catalyst/solvent solution. This solution contains the catalyst which can initiate the polymerization reaction by diffusing into the matrix, the binder which makes the catalyst adhere to the fiber surface. Normally, the catalyst may not mix well with the binder and a solvent is used to give good mixing. After the binder/catalyst/solvent solution has been applied on the fiber, the fiber has to be dried naturally in air for a certain time until the solvent evaporates completely. This process provides the glass fiber "sized" with the binder and entrapped catalyst (Figure 1-2 (a)) for the next step.



(a): First step (b): Second step

Figure 1-2: Sketch of pre-catalyzing technique

The second step (Figure 1-2 (b)) is the same as the conventional composite manufacturing process (pre-mixing) except here the resin matrix does not contain the catalyst (which has already existed in the pre-catalyzing layer of the fiber). In this step, after the resin is applied on the fiber, the monomer (styrene) in the resin system starts to dissolve the catalyst binder (polystyrene); then, the catalyst entrapped in the binder starts to diffuse from the pre-catalyzing layer and enter into the resin system to initiate the free radicals. Unlike the traditional cure process of which the polymerization reaction happens simultaneously, this cure process is in a gradual manner and depends on the rate of diffusion of the catalyst into the resin. So, the polymerization reaction is not as quick and violent as the traditional cure process.

This newly developed pre-catalyzing technique is very different from other techniques recently developed [1] [2] [3] [7] [17] [28](See Chapter 2). It does not need complicated operation and expensive equipment, and it is very simple and easy to perform.

The technique developed by Reuss [9] provides an interesting concept for the manufacturing of thick composites. However, due to the 80°C cure temperature and 86KPa pressure required by hot press, as well as large amount of toluene required in pre-catalyzing fabric process, which is very harmful to human's health and environments, the application of this technique can be difficult in manufacturing large and thick composites in ambient conditions.

1.2 Project objective

The primary objective of this project is focused on applying the pre-catalyzing technique to hand lay-up process of which the glass fiber/vinyl ester composites are cured at room temperature and under a very small pressure without using hot press machine. This thesis work uses another kind of solvent (acetone) instead of toluene in the pre-catalyzing fabric process by changing the catalyst binder. In order to achieve this objective, a few criteria should be satisfied to prove the feasibility of the pre-catalyzing technique

- Ensuring the degree of cure of laminates fabricated with pre-catalyzing technique to be more than 85% after the cure process and before further post cure.

- The interlaminar shear strength should not decrease more than 5% as compared to the value obtained by pre-mixing method. This was done by adjusting the ingredients of the catalyzing solution or by selecting the binder materials.

1.3 Thesis Outline

The organization of this thesis begins with literature review and experimental procedure, and ends in results discussion and analysis.

Chapter 2 presents the application background of thick-section composites and their manufacture difficulties. Then, the related manufacture techniques currently

developed are presented through the literature review. By analyzing the advantages and disadvantages of these techniques, the project is focused on the study of pre-catalyzing technique.

Chapter 3 gives a detailed description of experimental work including materials, processes and tests. Information about the materials used in the study can be found in this chapter. The detailed procedures of pre-catalyzing and hand lay-up process are listed. Finally, a brief introduction to all test methods and standards, including Resin Content Test, Differential Scanning Calorimetry (DSC), Atomic Force Microscopy (AFM) and Short Beam Shear (SBS) test, are presented.

Chapter 4 focuses on the discussion and analysis of experiment results. This chapter is divided into two sections. One section is for the pre-catalyzing method using polystyrene as the binder, another is for epoxy resin as the binder. The temperature profiles, DSC and SBS results are discussed and analyzed in both sections. Comparison of results from both pre-catalyzing and pre-mixing methods is done in this chapter.

Chapter 5 concludes with a summary of important contrubutions in this study. Recommendations for future work are also presented.

CHAPTER 2

REVIEW OF LITERATURE

AND DEFINITION OF THE PROJECT

2.1 Applications of Thick Composites

The unique characteristics of composite materials, such as high stiffness, strength, lightweight, high productivity, excellent process ability, corrosion resistance and cost effectiveness, offer opportunities to compete with conventional materials. Composites have primarily been used for thin, laminated plates or shells. This is characteristic of their use in the aerospace industry.

The new evolutionary step for composites is about the applications that require thick-sections. Thick composites have large number of demands in industry application, such as marine, aerospace, transportation and infrastructure application. Several examples are given below.

Raytheon System Company [10] predicted that the thickness of the glass/epoxy hull of Autonomous Underwater Vehicles (AUV) should be more than 0.5 inch in order to withstand the hydrostatic pressure at a water depth of 1700 feet.

DAMILIC [11] has been working with the US Army to develop next generation Composite Armored Vehicle (CAV). They reported the composite structures of CAV of several inches thick. Another example is that 50 mm thick multi-functional integral armor has been developed by Vaidya [12].

Thermoplastic composite pressure vessels for deep ocean applications are developed by Yousefpour and Nejhad [13]. The thickness of the wall is about 4.3 cm subjected to an external hydrostatic pressure of 71 MPa.

In 1997, Commission of the European Communities funded a project [14] where thick, strong pressure resistant carbon fiber composite structures were applied for housing the new generation of instrumentation.

Fiber glass/epoxy springs for heavy trucks and trailers became commercial in the U.S. in 1992. The Delco Chassis Division [15] of General Motors manufactured the single-leaf springs for heavy-duty trucks and trailers with unidirectional fiber/epoxy composites; the thickness of the spring is 3.5 inches.

NASA and Boeing today are turning to composite materials for commercial air travelers [16]. They predicted that thick composite structures could be used for heavily loaded wings.

Due to the inherent characteristics of thick section composites, such as low thermal conductivity and thermal spiking, some process techniques for addressing the processing difficulties have been developed.

2.2 Current Manufacturing Methods

The successful manufacture of thick-section composites can be very difficult due to the exothermic nature of the resin cross-link reaction and high thermal resistance. The most harmful behavior presented during thick composite curing is thermal spiking [2]. Due to the poor thermal conductivity, the heat generated from the exothermic curing reaction is trapped in the interior. This entrapped heat makes the interior temperature rise even further, and induces faster curing and more rapid heat release. This process may produce a thermal spike. The peak temperature of exothermal reaction can be quite high and may cause matrix degradation. Furthermore, large thermal and cure gradients induced by low thermal conductivity can lead to detrimental residual stresses which can cause delamination or crack of composites.

Conventional processes are unable to fabricate thick section composites due to the thermal spiking and large thermal gradients. The often-used methods to control thermal spiking are very slow heat-up rates and several intermediate dwells. This leads to the long processing time and high manufacture cost. Recently, some new processing techniques that address these problems for manufacturing thick composites have been developed.

Stage curing technique

S. R. White and Y. K. Kim developed the staged curing technique [17], as shown in Figure 2-1. This technique comprises two steps in curing incremental layers in a thick composite. In the first step, a relatively thin stack of material is built up either by hand lay-up or using automated method. This stack is then subjected to a partial cure cycle

(stage 1). During this cure cycle, the material is gelled, consolidated, and some of the exothermic energy is released. Subsequently, another incremental stack of material is placed on top of the first and the entire structure is again subjected to a stage-1 cure cycle. This procedure is repeated until the desired thickness is reached. After the entire structure has been built and subjected to a partial cure, the final cure occurs in stage 2. During the final curing, the remaining exothermic energy is released and a complete cure is reached throughout the entire part. Stage curing addresses two of the major problems in manufacturing of thick composites: non-uniform consolidation stage and thermal spiking. First, since the consolidation stage is carried out during stage 1 when the material thickness (incremental) is small, the consolidation is no more difficult than with any thin laminated composite. Second, since a portion of the exothermic energy is released during stage 1, there is less energy available for thermal spiking during stage 2. In addition, the amount of uncured material added at each increment during stage 1 curing is small and there is little chance of thermal spiking until stage 2. S. R. White et al [17] have shown success in applying this technique in manufacturing laminate panels composed of a total thickness of 24 plies. From their results, they found no degradation in the shear modulus and the interlaminar shear strength. The author concluded that this technique could be used to produce very thick section composites with a uniform fiber volume distribution.

Even though stage-curing technique has successfully eliminated the thermal spiking, long processing time can limit its application. Another disadvantage is that the molds are tied up during the dwell periods.

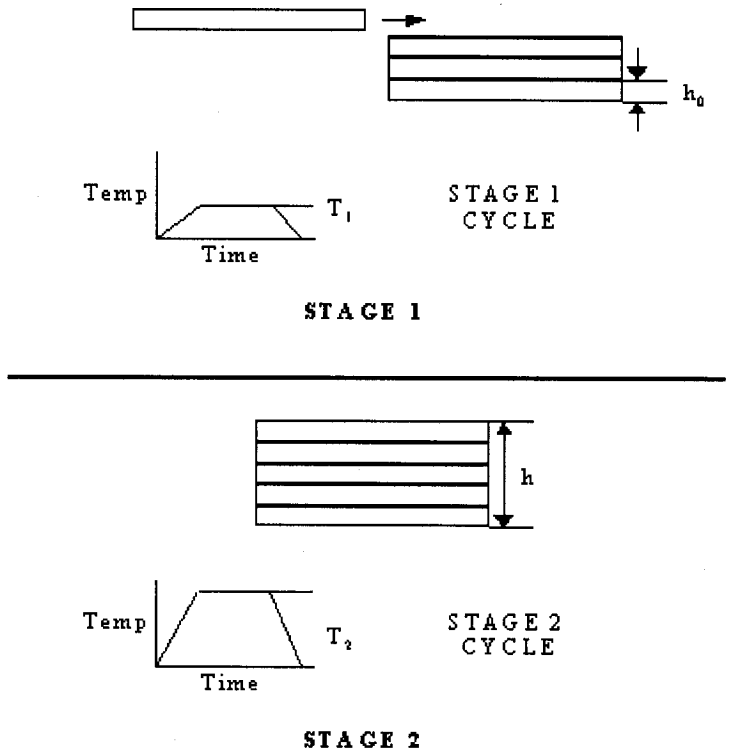


Figure 2-1: Schematics of staged curing process [17]

Continuous curing technique

A new manufacturing method, continuous curing, was introduced by Cheol Kim et al in 1995 ([2] [3]). In this process, layers of fresh composite material are supplied to the outer surface of the part at a steady rate. The inner surface is heated to initiate a cure front which propagates through the thickness of the part as in Figure 2-2. With the proper control of processing parameters such as material accretion rate (V), and temperature boundary conditions, the cure front speed (Vc) can be made to match the material accretion rate and thermal spiking inside the part can be avoided. A 100mm thick

laminate was cured by this method. The laminate was fully-cured after 13 hours. Compared with conventional autoclave curing, this process demonstrated no thermal spiking behavior and great reduction in total manufacturing time. Experimental results for a graphite/epoxy laminate with this process show some degradation of material strength compared with the conventional thin composites. This technique has also been applied into a thick filament wound composite cylinder by Kim et al [18].

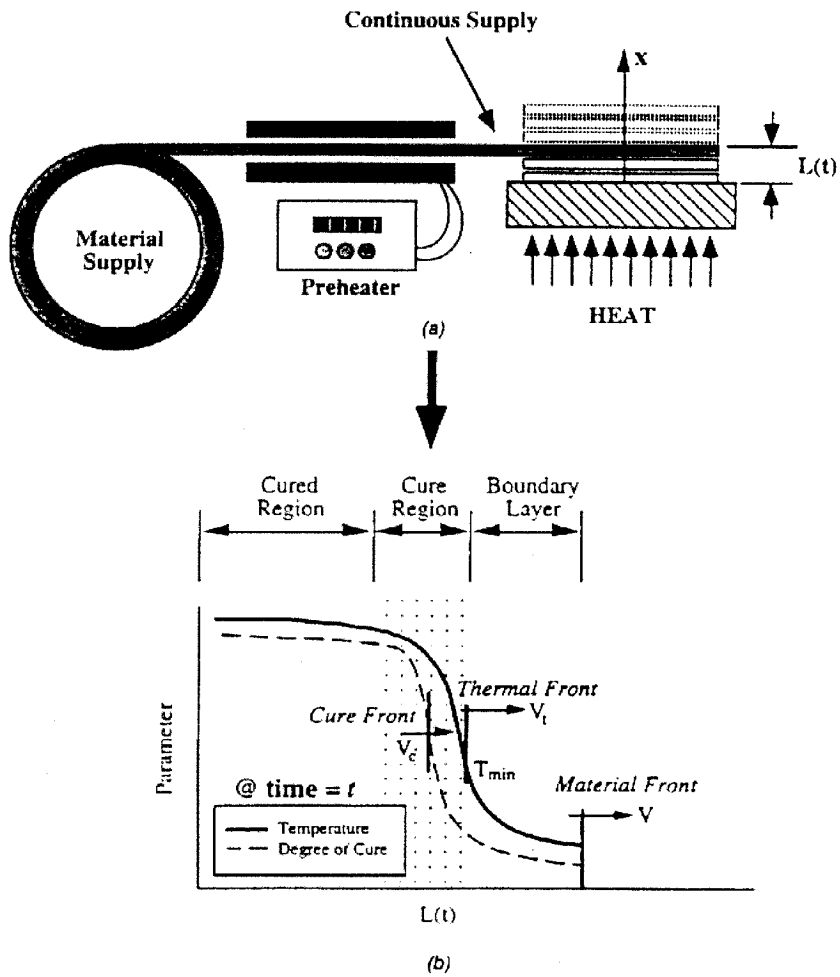


Figure 2-2: Continuous curing process: (a) Schematic and

(b) Thermochemical behavior[2]

Even this process shows advantages over the conventional one, the processing time is still long and the heat resource has to be provided. On the other hand, the material accretion rate needs to be controlled properly in order to comply with the cure front speed. This could make the operation complicated.

Pre-bleeding technique

Another technique called pre-bleeding was developed by Hojjati [53]. This technique was applied in autoclave process, and two stages were designed. Pre-bleeding is the first stage, in which sub-laminates were soaked under vacuum and pressure for 70 minutes; meanwhile, temperature was increased to 116^{o}C. In this stage, the extra resin moves out, and sub-laminates are partially cured. In the second stage, all the sub-laminates were piled up; then the vacuum, pressure and temperature were applied again to finally cure thick laminate. In this stage, since less resin remains inside the sub-laminates after the pre-bleeding stage, less heat is produced compared with all bleeding method which more resin is contained. Moreover, due to the release of some heat when sub-laminates undergo partial cure, the exothermic temperature is lower in this stage than in all bleeding method.

The laminate which thickness was 45mm was made with this technique, and the exothermic temperature was reduced approximately by 10^{o}C from 160^{o}C. This technique can not be applied in room temperature cure process because the high temperature is required for pre-bleeding process.

Proactive Control System

In autoclave, press molding, and repair processes, self-directed control systems have been widely used with knowledge of materials' properties to control the cure of composites combining with real-time sensor data [19]. Even through these systems have been shown to lead to shorter and higher quality cures, they can only respond to the data currently supplied by the sensors, and they are unable to control the cure of thick parts due to their inherent thermal characteristics. Buczek and Mason [20] developed a proactive control system. This system's control software has a predictive cure model set in it to allow making control decisions based on anticipated future cure states. Sensor inputs are not only used to determine the current cure state but also used to update the model predictions to minimize modeling error. This system was shown capable of controlling the cure reaction rate to avoid an undesirable exotherm of 128-ply glass/epoxy composite.

Cooling and Reheating Curing Steps

Kim [1] modified the conventional cure cycle using the simulated results. He introduced the steps of cooling and reheating which were determined by the cure rate and temperature at the midpoint of the laminate into the conventional cure cycle. In order to predict the temperature distribution of the thick laminate during cure, the heat transfer equation including the heat generation term was simulated by the finite difference method. Using the simulation results of the cure rate and temperature at the midpoint of the laminate, the steps of cooling and reheating were calculated by the trial and error method. The 15 and 30 mm thick laminates were cured using the developed cure cycle. It was

found that the developed cure cycle prevented effectively the temperature of the laminate from overshooting and cured the laminate uniformly during the exothermic reaction. Figure 2-3 shows the modified autoclave cure cycle for the 100 layers (15mm) composite determined from the simulation with cooling and reheating steps.

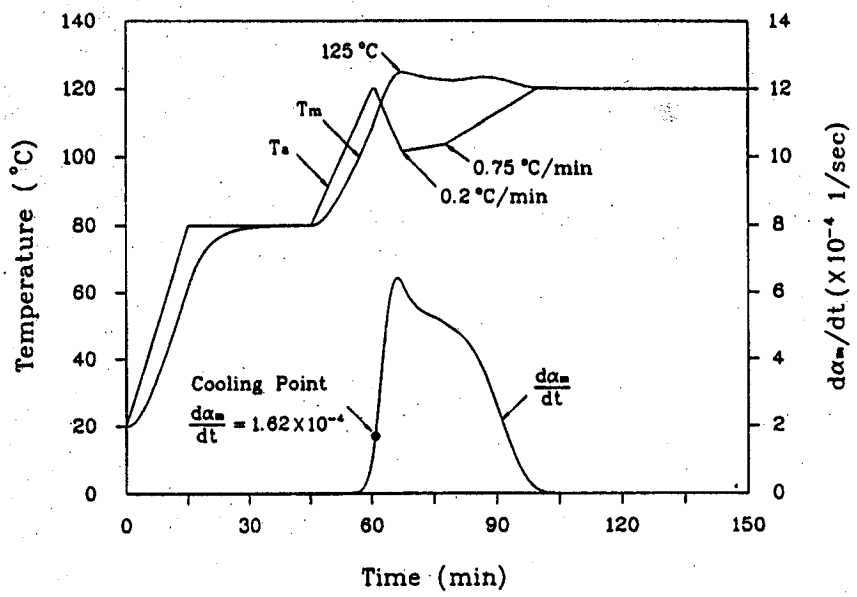


Figure 2-3 Autoclave cure cycle for the 100 ply thick laminate determined from the simulation with cooling and reheating steps [1]

Even though the uniform cure has been achieved, and the overshooting during the exothermic reaction has been overcome, there is still difference between the experimental and simulation results. This method is limited in autoclave process, and it is difficult to fabricate complex geometry thick composite part.

Electron Beam (EB) Curing

A new low-temperature-cure technique, Electron Beam (EB) curing, was reported by Goodman and Byrne [7]. This technique uses high–energy electrons to initiate polymerization and cross-linking reactions and allows curing at room temperature. The EB curing process greatly reduces the residual stresses and the time required to cross-link the polymer matrix compared to convention heat curing and without the release of volatile organics. Goodman and Byrne [7] used EB technique to cure vinyl ester resin. The result shows that EB curing can happen at very low temperature (near room temperature) with fast speed. This allows the use of low cost and temperature tooling and reduces the residual thermal stresses in low temperature curing. This method is able to cure thick section composites at low temperature by increasing the electron beam energy. The "thick behavior" can be eliminated because no exothermal processes are found.

However, due to the high cost of EB facilities, principally the electron accelerator and concrete radiation shielding, the capital costs of whole EB curing systems are large. Besides, there are many issues such as process, materials, equipment and safety which must be solved before composite curing becomes commercial reality [21].

Microwave-Accelerated Curing

In the manufacture of thick-section composites, the low thermal conductivity of most polymer systems and the exothermic nature of curing process induce complex temperature distributions. Thostenson ([8], [22]) achieved a significant result in reducing thermal gradients using microwave curing technique. Microwaves are able to penetrate materials and deliver energy through direct interaction of electromagnetic fields at

molecular level. The result is heat generation throughout the volume of the material. This "Volumetric" heating can reduce thermal gradients (Figure 2-4) and decrease processing times. Thus, microwave processing is a desirable technique for manufacturing thick-section composites.

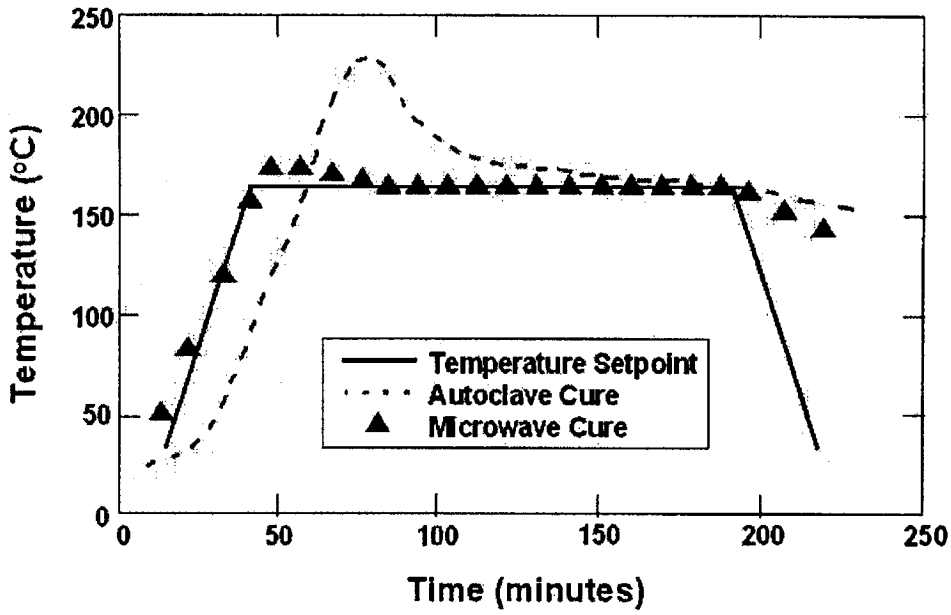


Figure 2-4: Numerical results for microwave and autoclave curing of a 2.54 cm (1 inch) thick composite laminate [22]

Because of the costly investment for the microwave facilities, which consist of a cylindrical multi-mode resonant cavity, it is difficult to apply microwave-curing technique in industry. Moreover, microwaves are harmful to human health, so protection measures should be taken.

Different Resin Formulations Used in One Composite Part

Boukhili and Gauvin [5] investigated the cure of thick glass/polyester composites with varying thickness between 25 and 76mm. The processing temperatures were varied across the thickness between 80°C and 140°C. In order to lower this large temperature gradient which can lead to crack formation in composites, different resin formulations were used. In their study, the main idea was established by introducing two kinds of catalysts which have same total heat of reaction and different reaction initiation temperatures and exothermal peaks. One resin formulation with one of the catalysts was used in the outer region and another formulation with the other catalyst in inner region. In this case, the outer region starts curing before the inner region. However, even though the cure of the inner region is delayed, its rate of cure is fast enough to compensate for the delay, and when the surface region reaches 50% cure, the outer and the inner region almost cure at the same rate. With this technique the temperature gradient decreased significantly, and large cracks disappeared.

Since the optimal combination by changing the catalyst concentration and type largely depends on the specifics of the experiments, this work can be costly and time consuming. Also, this method is not suitable for complex geometry composite parts, and it is difficult to apply in industry.

Curing of Composites Using Internal Resistive Heating

Ramakrishnan *et al* [23] found another method which is different from the way of Boukhili and Gauvin to provide a uniform curing through the thickness of composites. Due to the fast cure of outer layers of the laminate, which are subject to external heating,

the cure rates are very different between outer and inner layers. This could lead to structurally poor products. Ramakrishnan et al explored the use of conductive carbon mats embedded inside the composite as a means of providing internal volumetric resistance heating during the cure process. The passage of electric current through the conductive fibers causes resistive internal heating which provides for a uniform curing through the cross sections of parts. This approach reduces to effectively dividing the thick composite section into a number of thinner sections, each of which is cured uniformly by resistance heating form the conduction fiber. However, because the conductive fibers are left embedded in the composite after cure has finished, the parts with electric isolation function cannot be fabricated with this method.

Cure Simulation of Thick Thermosetting Composites

Before the introduction of computers, the cure cycle recommended by the manufacturer for thicker composites was often used during curing thick section composites. It has been found that this cure cycle would lead to spatial variations in fiber volume fraction and thickness, and hence affects the final quality of the part ([24], [25], [26]). Computer could provide a much more systematic and hopefully improved means of modifying cure cycles to successfully produce thick section composite parts.

Twardowski et al [27] developed a computer simulation system which recovers much of the thermal behavior of a 5 cm thick part. This simulation is used to investigate important processing variables and changes in chemorheology and temperature in a thick section laminate during cure. It can be found that initial extent of reaction is relatively unimportant; consolidation is an important processing variable; the peak temperature

originates near the surface of the laminate and propagates to the center; viscosity never reaches low values simultaneously through the thickness in laminates in excess of 10 cm thickness.

In Bogetti's study [28], an investigation into the two-dimensional cure simulation of thick thermosetting composites was presented. Complex gradients in temperature and degree of cure were predicted as a function of the autoclave temperature history, and the influence of the tool on the curing process was demonstrated. Spatial gradients in degree of cure are shown to be strongly dependent on part geometry, thermal anisotropy, cure kinetics and the autoclave temperature cure cycle.

The development of numerical simulations for the composite processes has provided a less expensive and less time-consuming means of investigating different cure cycles, and many researchers have relied on simulation results to determine cure cycles [6]. However, simulation approach is still non-optimal and not accurate because the physical parameters of a composite system can be difficult to predict. Also, it has computational difficulties for a complex geometry.

Expert System Strategies

Expert system approach to developing a successful cure cycle has been to use sensor information from the process to guide modifications to the cure cycle. This system uses current temperature, laminate top and middle layer temperatures, and the viscosity of the resin to evaluate the state of cure and make control decisions. Although

the system was not provided with a preset cure cycle, the resulting cure cycle generated during processing can successfully cure laminate with low thermal gradients [6].

Pillai et al developed an expert-system-based tool in order to operate the autoclave cure of a thick section composite laminate in an optimal manner [29]. The purpose of this tool is to minimize the total cure time, reduce the temperature excursions during an exotherm and minimization of process-induced residual stresses in the laminate. It can be found that the whole strategy is easy to implement and is expected to be very flexible with regard to changes in material, geometry, etc.

Another rule-based expert system was developed by Ciriscioli *et al* [30] for controlling the autoclave temperature and pressure. The inputs to the expert system are the measured instantaneous autoclave temperature and pressure, the composite midpoint and surface temperatures, composite thickness, and ionic conductivity. These inputs are examined by pre-established rules and, on the basis of decisions dictated by the rules, the autoclave heater, cooler and pressure controllers are adjusted to the appropriate settings. This system can cure laminates ranging in thickness from 0.1 to 6.5 inches, and produced laminates whose mechanical properties are as good as those cured by conventional methods.

Because the cure cycle is very dependent on the quality of sensor data from the process, and incorrect or missing sensor data could lead to poor control decisions, it can not accurately control the cure cycle. In addition, expert systems can have good comparison to those of conventionally manufactured composite only for flat composites,

and it has not yet been demonstrated that expert systems will work well for parts with complex geometries.

Pre-Catalyzed Fabric Technique

A new attractive technique of processing thick-sectioned composite was developed recently at the University of Massachusetts at Dartmouth [9]. Reuss successfully made high quality thick composite by using glass fabric pre-catalyzed with benzoyl peroxide (BPO) catalyst instead of conventional pre-mixed catalyst and polyester resin compounds. This method can slow down the polymerization reaction rate by applying the peroxide catalyst to the fabric and subsequently reduce the internal temperature during curing. Polyester/styrene resin cures by a process of free radical polymerization. Free radicals are initiated by the catalyst and diffused throughout the bulk resin system. This diffusion-limited reaction is extremely fast in conventional systems since the catalyst is spread throughout the resin. By localizing the initialization sites for free radical generation to the fiber surface, the rate of curing in the bulk resin can be slowed. Figure 2-5 shows that at 80°C cure temperature, the maximum temperature is reduced to 119°C from 165°C with full pre-catalyzing method; and the peak temperature is reduced to 110°C with alternate ply pre-catalyzed method. The results of mechanical testing shows that thick composites manufactured using pre-catalyzed fabric are as strong as thin conventionally manufactured composites, but stronger than those of conventionally prepared composites of the same thickness. Some important information and data in this study is summarized in table 2-1.

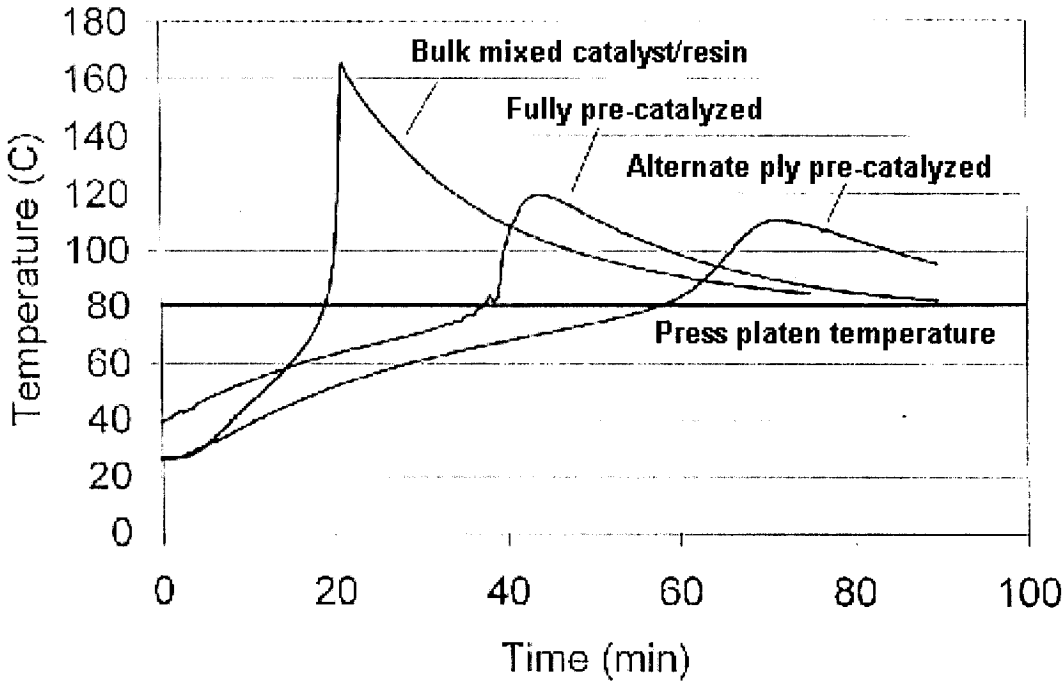


Figure 2-5: Cure temperature profile of conventional and fiber pre-catalyzing process at 80°C [9]

The pre-catalyzing fabric technique not only can decrease the exothermal peak temperatures, but also has the potential to fabricate complex geometry parts and solve the problem in which the pot life of conventional resin system is very short. The latter advantage is very unique in manufacturing large and thick composite parts such as submarine and scrubber. It eliminates the waste of the resin and reduced the times of mixing the resin. However, even though the hand lay-up process was used, the cure process was carried out at 80°C cure temperature and 86KPa pressure by using hot platen press. This would limit its application from extending to large complex geometry parts. Next, the peak exothermic temperature was reduced by 46°C, but it was still 119°C which

is high and may cause mold deformation. Moreover, in their study, the cure degree at lower cure temperature by pre-catalyzed fabric method was not considered. The influences of ingredients on the polymerization reaction and mechanical properties were not mentioned.

Table 2-1: Summary from Reuss's study [9]

Process	Method	Hand lay-up
	Cure temperature	80°C
	Pressure	86KPa
	Facility	Platen press providing temperature and pressure
Materials	Fiber	E-glass, 7 oz/yd^2
	Resin	Polyester
	Catalyst	Benzoyl Peroxide
	Catalyst binder	Polystyrene
Peak exothermic temperature		Conventional pre-mixing method: 165°C Pre-catalyzing method: 119°C Exothermic temperature reduction: ΔT= 46°C
Mechanical properties compared with pre-mixing method	Tension strength	+80%
	Compression	+25%
	Shear	+35%

2.3 Definition of the Project

In previous section, current development of thick composite manufacturing techniques was discussed. It is resumed that even through some techniques can successfully fabricate good quality composite parts with thick cross-section, some inherent problems in these techniques still could not be solved. For example, long process time is required to process thick-section composites using stage or continuous curing technique; electron beam and microwave-accelerated curing need large investment on their facilities; the cure simulation is computationally difficult for a complex geometry part; and expert system also could not make an optimum cycle for curing parts with complex geometry. A novel pre-catalyzed fabric technique can overcome these disadvantages due to the character of which the reaction rate can be controlled by catalyst diffusion from pre-catalyzing layer into matrix layer.

As we know, composites have been widely applied in aerospace, automobile, ship and construction fields. Some composite parts are very large and have thick cross-section, such as submarine hull, armored vehicle and scrubber. Hand lay-up process is commonly used for manufacturing these parts. Usually, it takes a very long time to finish a part. For example, in fabricating submarine hull, it needs more than one month. In order to avoid high exothermal temperature, the operation has to stop until the resin system reaches partial cure. This long operation period runs into conflict with the limited pot life of the resin system. Polyester and vinyl ester resin system which cure at room temperature are always chosen in manufacturing large and thick composite parts using hand lay-up process. Even though the retardant is added into the resin system to delay the gel time,

the gel time is still not long enough. As a result, the labor work is increased by manifold, or materials have to be thrown away because resin has gelled before finishing.

Pre-catalyzed fabric technique is unique and may overcome difficulties of thick-section composite manufacturing. First, because no additional equipment is required by this method, it is easy for this technique to be accepted by industry. Second, because the reaction rate is controlled by free radical diffusion to the resin from the fiber surface, this characteristic is superior for the complex geometry composite parts. Third, this technique eliminates the pot life issue; as the result, the material waste can be avoided, and operation time can be reduced. This advantage is very important for manufacturing large composite parts. Fourth, the waiting period in molds can be greatly reduced as compared to stage curing. Finally, successful application of pre-catalyzed fabric technique on hand lay-up process may be extended to other composite manufacturing processes.

Compared with other techniques, pre-catalyzed fabric technique has potential priority for further investigation. In Reuss's study [9], only reaction temperatures are undertaken. However, the cure degree at low exothermic temperature and the influence of pre-catalyzing materials to the interlaminar shear strength have not been discussed. Also, because the cure temperature and pressure are provided by hot platen press, it is difficult to extend this technique to thick-section composites with large size and complicated geometry when they are cured at room temperature. Moreover, the large amount of toluene consumed in pre-catalyzing process may constrain the application of this technique due to its toxicity. In this thesis, the pre-catalyzed fabric technique is chosen for further study to fulfill the manufacture of large and thick-section composites with complicated geometry when they are cured at room temperature.

CHAPTER 3

EXPERIMENTAL WORK

The study of thick-section composite manufacturing with pre-catalyzed-fabric technique is based on the hand lay-up process. Glass fiber and vinyl ester resin, which are commonly used in hand lay-up, are chosen as main raw materials in this project. In this experiment, in order to compare two methods, conventional bulk mixing and pre-catalyzing, 50-layer and 100-layer laminates were fabricated with these two methods. Differential Scanning Calorimetry (DSC) tests and Short Beam Shear tests were also performed for evaluating the quality of these thick-section composites.

3.1 Hand Lay-up Process

The hand lay-up technique is one of the oldest, simplest and most commonly used methods for manufacture of composite products. In this process, the reinforcements which are in the form of woven, knitted, stitched or bonded fabrics, are placed in or on a mould by hand. The resin is manually applied by pouring, brushing, or spraying over the reinforcements. Entrapped air is removed with rollers or brushes. Gel coat is usually applied for improving surface finish. Finally curing occurs at ambient temperature with or without pressure. Figure 3-1 shows the sketch of hand lay-up process. Catalyst, accelerator or retardant may be added to the resin system in order to achieve a desired curing rate.

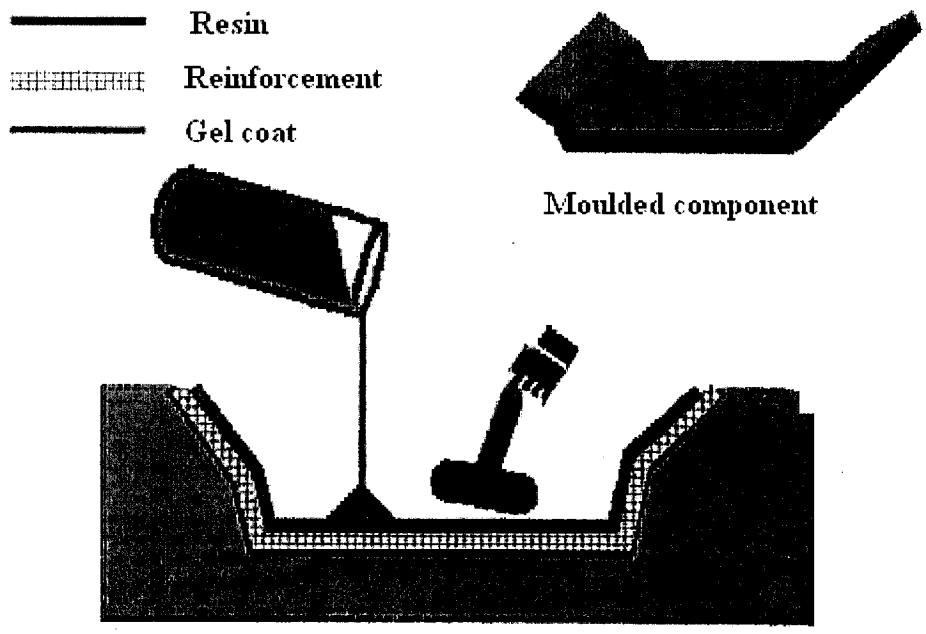


Figure 3-1: Sketch of hand lay-up process

The application of the hand lay-up process in the boat building industry has made great success. It also has been employed in other applications including radomes, ducts, pools, tanks, corrosive environment equipment and automotive components. The advantages of hand lay-up process can be summarized as follows:

- Complex geometry and large parts can be fabricated.
- Large equipment and tooling investment is not required.
- The preparation time and cost are low.
- The design is flexible.

The hand lay-up process also has its disadvantages, such as a low volume, intensive labor work, variable quality and high material waste. During operation the environmental issue can be a concern because the low molecular weights of the resin required by hand lay-up have the potential to be more harmful than higher molecular weight products. The extraction system is necessary for limiting airborne styrene concentrations.

3.2 Raw Materials

The main raw materials for composite manufacture are reinforcement and resin matrix. Any kind of fiber used in composite industry can be used in hand lay-up process, but glass fiber is the most commonly used reinforcing material. The thermosetting resin such as epoxy, polyester and vinyl ester are often used in hand lay-up, but polyester and vinyl ester resins are favored because of low cost and ease of handling.

Reinforcement

Glass fibers exhibit superior thermal and impact resistance, high tensile strength, excellent chemical resistance and outstanding insulation properties. E-glass, which accounts for more than 90 percent of all glass fiber reinforcements, offers good electrical resistance and good strength properties at a low cost. E-glass is particularly well-suited to applications where radio-signal transparency is desired.

Woven fabrics are more pliable and conform more easily to curved surface. Woven roving is a thick fabric that is used for heavy reinforcement, especially in hand

lay-up operation. Due to its relatively coarse weave, woven roving wets quickly and is relatively inexpensive.

E-glass woven roving fabric (18 oz/yd^2) is chosen as the reinforcement in the experiments of this project. The typical properties of E-glass fiber are given below (Table 3-1):

Table 3-1: Typical properties of E-glass fiber

Property	Value
Modulus, (GPa)	72
Strength, (MPa)	3448
Maximum Strain, (%)	4.8
Density (g/mm^3)	2.54

Resin

Matrix resins for glass-reinforced composites bind the reinforcing fibers together and to a certain extent protect the fibers from impact and environmental assault. Variety of polymer matrix resins is available for engineers to design and fabricate glass-reinforced composites. In thermoset resin, the most commonly used resins are epoxy, polyester and vinyl ester. Among them polyester and vinyl ester have been commonly used in glass-reinforced composites.

Vinyl esters are chemically similar to both unsaturated polyesters and epoxy resins. They were developed as a compromise between the two materials. A vinyl ester

resin consists of an epoxy backbone for chemical resistance and high strength, vinyl groups for high reactivity, and styrene monomer for low viscosity. Figure 3-2 gives the chemical formula of a vinyl ester resin.

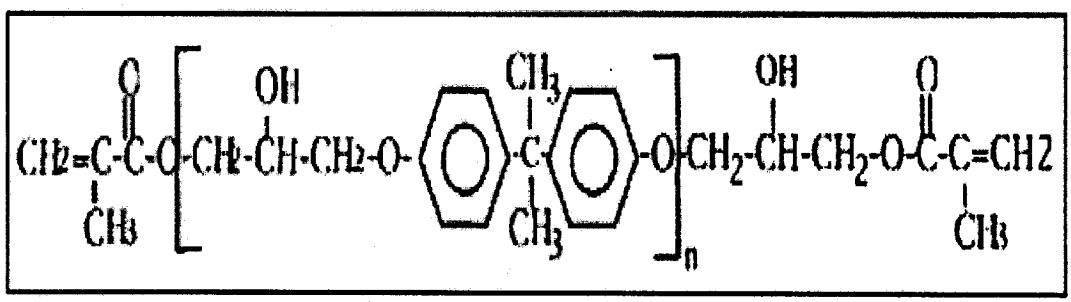


Figure 3-2: Chemical formula of a vinyl ester resin

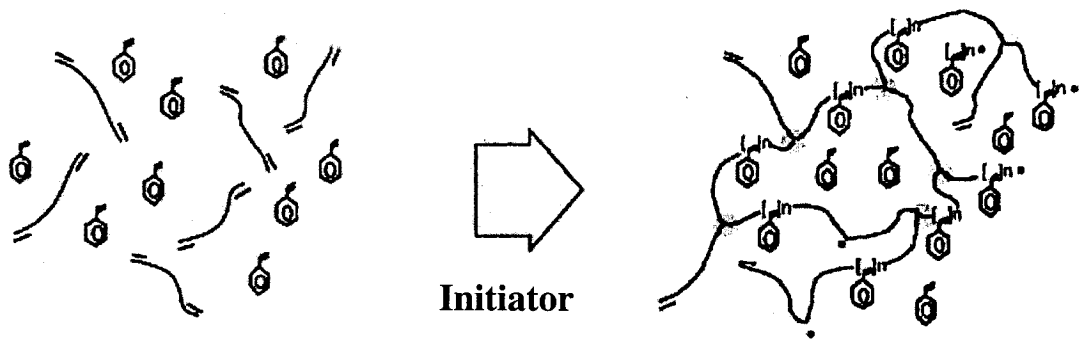


Figure 3-3: Crosslinking process

Vinyl esters, like unsaturated polyesters, contain double bonds. It reacts with the styrene diluents under the initiation of catalyst. The crosslinked network is formed via free radical chain reaction (See Figure 3-3).

Vinyl esters have better chemical resistance than polyesters. They also have high level moisture resistance. During polymerization, they produce low peak exothermal temperatures, and shrinkage upon cure is very low. In addition, because of the hydroxyl groups, they bond well to glass. Thus, Vinyl esters are often used in hand lay-up process to fabricate chemical tanks and boat.

A commercial vinyl ester resin, Dow Derakane 411-350 obtained from Dow Chemical Co., was chosen as matrix material. This resin is designed for ease of fabrication using hand lay-up. Derakane 411-350 is a mixture of 55 wt% of epoxy based vinyl ester resins, and 45 wt% of styrene monomers. The two kinds of catalyst, methyl ethyl ketone peroxides (MEKP) and benzoyl peroxide (BPO), can be used in this resin to initiate the reaction. Table 3-2 gives typical properties of Derakane 411-350 resin.

Table 3-2: Typical properties of Derakane 411-350 resin

Property	Value
Density, (g/mm^3), 25°C /77°F	1.046
Viscosity, cps at 25°C /77°F	350
Styrene content (by weight)	45%
Shelf life at 25°C /77°F	7 months

Table 3-3 gives the ingredients and their proportions of the resin system used in this experiment. In this resin system, cobalt napthenate (CONAP) is used as a promoter to activate Derakane 411-350 vinyl ester resin from its dormant state; dimethyl aniline (DMA) is added as an accelerator to accelerate the cure reaction; 2,4-pentanedione (2,4-P)

is added as a gel time retardant; in addition, methyl ethyl ketone peroxide (MEKP) is used as the catalyst that actually starts the curing process.

Hardener 3046 was used in the improved pre-catalyzing method (refer to Section 3.3.1) for curing the epoxy resin between the layers of glass fiber and vinyl ester resin system. It should be noted that the hardener could not be mixed in the pre-catalyzing solution; instead, it should be mixed with the bulk vinyl ester resin system.

Table 3-3: Ingredients of Derakane 411-350 resin system

Ingredient	Ratio(phr*)
Derakane 411-350 resin	100
CONAP	0.17
DMA	0.03
2,4_p	0.07
MEKP**	1.18
Hardener 3046***	0.28

*: phr: per hundred part of resin

**: Only for pre-mixing method

***: Only for Exp-11 and Exp-12

2,4-P may be mixed into the master batch prior to adding MEKP, and it must be cautious that explosion can happen if MEKP is mixed directly with DMA or CONAP apart from the base resin.

3.3 Pre-Catalyzing Fabric Procedure

Pre-catalyzing fabric is a critical procedure in pre-catalyzing technique. It involves two steps: mixing pre-catalyzing solution and sizing fabric with catalyst solution.

3.3.1 Mixture of Catalyst/Binder/Solvent Solution

Two different compositions of catalyst/binder/solvent solution were used in this study.

Composition No. 1

In this composition, the catalyst solution consists of methyl ethyl ketone peroxide (MEKP), polystyrene and toluene.

Polystyrene is a kind of hard crystal pellet. Catalyst MEKP is in liquid state. Polystyrene here serves as an agent to bind the catalyst MEKP to the fiber surface. Toluene is used to dissolve the solid polystyrene and dilute the catalyst solution. The amounts of ingredients of pre-catalyzing solution for pre-catalyzing **1kg** glass fabric are shown in table 3-4. Two formulas are used in the experiments.

The mixing procedure is described as follows:

- Weigh proper amount of MEKP according to the fabric weight to be used and Table 3-4
- Weigh proper amount of polystyrene and toluene according to the proportion in table 3-4

- Mix MEKP, polystyrene and toluene together in a container and stir them using a stirring machine for at least 40 minutes until all the polystyrene pellets dissolve in the toluene.

It should be cautious that toluene can evaporate fast during stirring operation, so the container must be covered to prevent toluene from evaporation. In addition, this operation should be done under the fume hood

Table 3-4: Amounts of ingredients in Composition No.1 for pre-catalyzing **1kg** fabric

Ingredient	Formula I (for Exp-2,3,5,6)	Formula II (for Exp-4)
Toluene	550 g	550 g
Polystyrene	27 g Molecular weight: unknown	14 g Molecular weight: 250,000 (g/mol)
MEKP	27 g	27 g

Composition No. 2

Another composition of the catalyst/binder/solvent solution used for improving pre-catalyzing method consists of MEKP, epoxy resin Epon 828 and acetone.

Epon 828 is a medium viscosity resin. Like polystyrene, it is used as the binder to make MEKP adhere to the surface of glass fiber. Acetone, like toluene, is used to dissolve the Epon 828 and dilute the catalyst solution, but it is less toxic than toluene.

Table 3-5 gives the amounts of ingredients for pre-catalyzing **1kg** glass fabric. Three formulas are used in the experiments.

Because acetone can dissolve the resin and MEKP very easily (only several minutes stirring manually), the mixing operation can be performed just before the pre-catalyzing procedure begins.

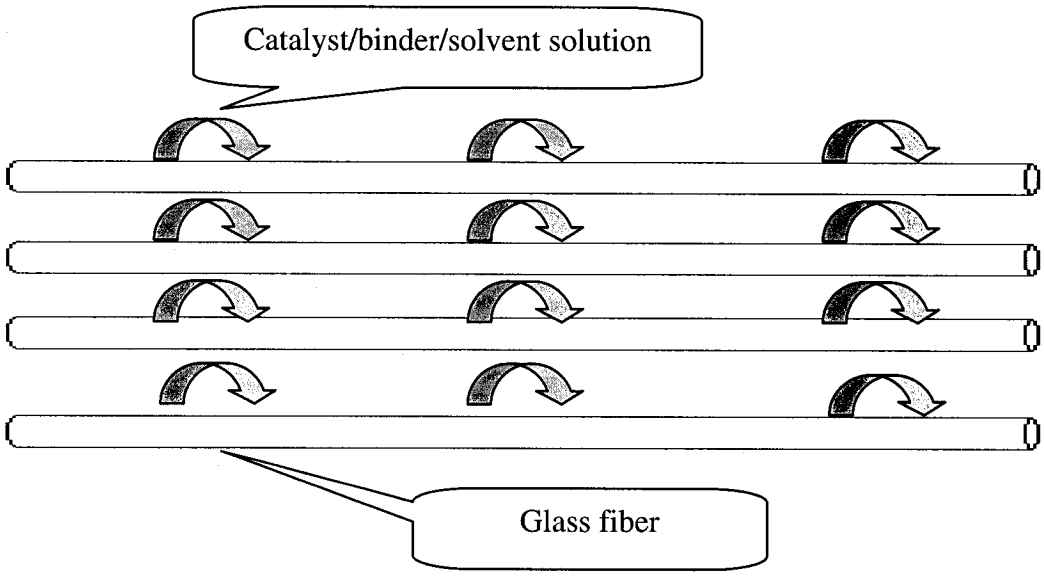
Table 3-5: Amount of ingredients in composition No. 2 for pre-catalyzing **1kg** fabric

Ingredient	Formula I (for Exp-8)	Formula II (For Exp-9,11,12)	Formula III (for Exp-10)
Acetone	550g	550g	550g
Epon 828	27g	20.25g	14g
MEKP	27g	27g	14g

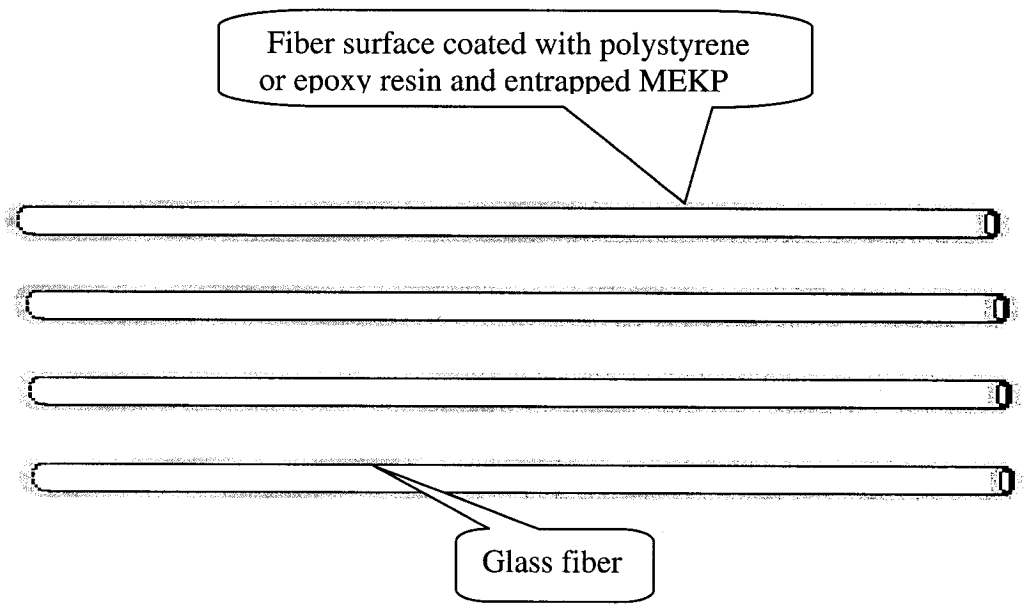
3.3.2 Procedure of Pre-catalyzing glass fiber

Figure 3-4 gives a sketch of pre-catalyzing fiber procedure. This procedure can be described as follows:

- Measure the required glass fabric and cut it from the roll
- Weigh the fabric
- Put a sheet of plastic on the operation table which is under the fume hood, and lay the fabric on it.
- Mix the catalyst/binder/solvent solution (refer to § 3.3.1)



(a): Pre-catalyzing fabric



(b): Sized glass fiber

Figure 3-4: Sketch of pre-catalyzing fiber procedure

- Apply the catalyst/binder/solvent solution on the fabric with a brush. Be cautious that the fabric could not be removed from the fume hood until 24 hours after the fabric is pre-catalyzed.

After completely drying, all the solvent (toluene or acetone) has evaporated to the air, and only polystyrene or epoxy resin with entrapped MEKP remain on the fiber surface (See figure 3-4 (b)). The pre-catalyzed fabric becomes stiffer than its original status.

3.4 Preparation for Hand Lay-up Experiments with Pre-catalyzing Method

Composite lay-up materials and equipment

- Pre-catalyzed glass fabric sheets which have been cut into the required size
- Derakane 411-350 vinyl ester resin system according to table 3-3
- Nylon bagging film
- 2 pieces of metal mold plates for bottom and top of the laminate respectively
- Thin thermocouples (TT-K-40-SLE)
- Containers for mixing resin system
- Scale for weighing ingredients of resin system
- A brush or roller for applying resin on the fabric
- Computer 386 stored with data acquisition software GEN200
- Data acquisition device: System 200, Model: 293, manufactured by Sciemetric Instruments Inc.

Figure 3-5 is a photo to show the set-up.

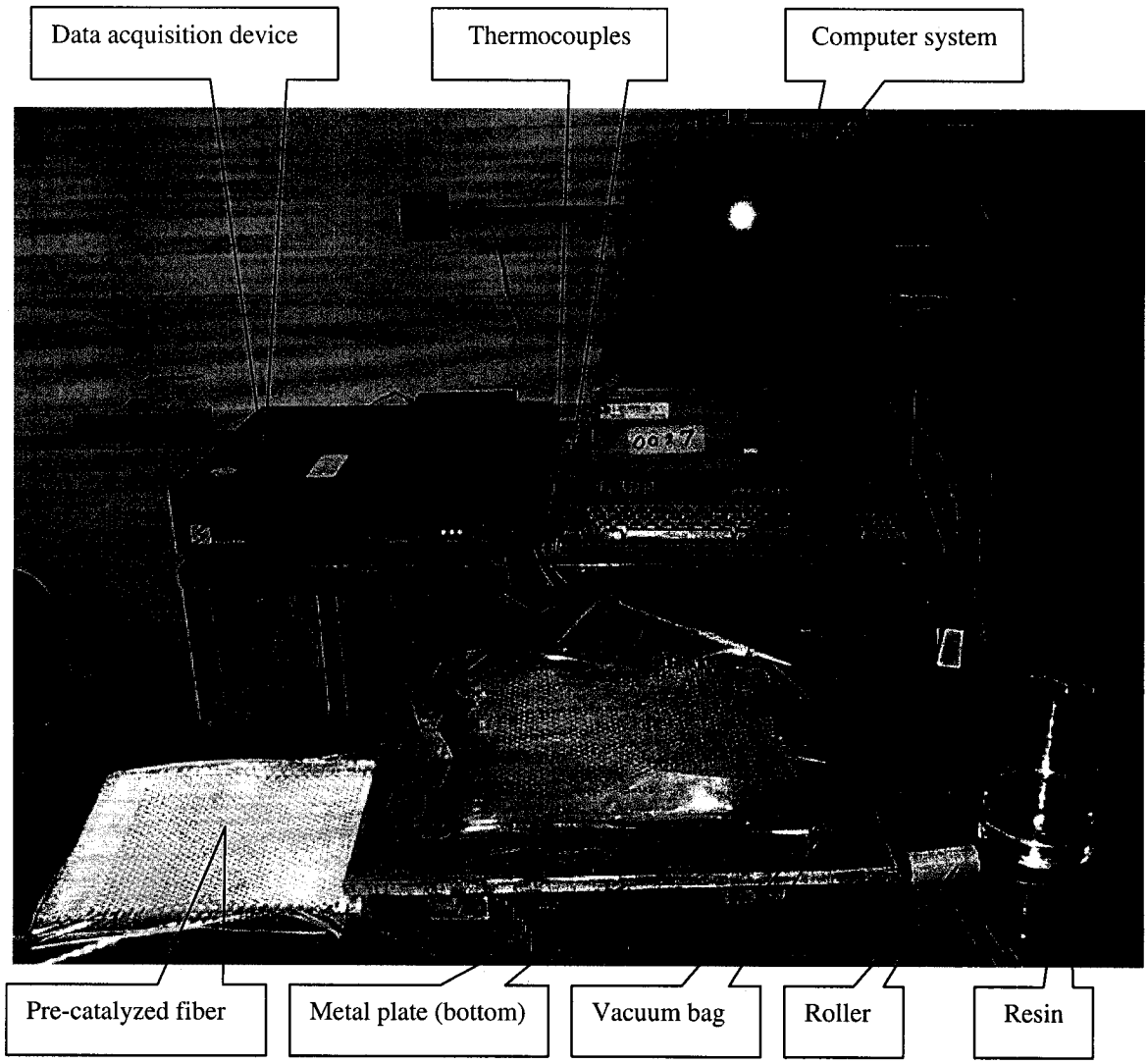


Figure 3-5: Set-up picture of hand lay-up process

Thermocouple location in the laminates

Because the tips of thermocouples will be embedded in the composite after cure is finished, very fine thermocouples which normal dimension is 0,015"X 0.024" were selected in the experiments. One end of each thermocouple was connected to Data Acquisition System 200. The yellow wire (chromega) was connected to the "Positive", and the red one (alomega) was connected to the "Negative". The other end of the thermocouple should be welded together by thermocouple welder 116SRL. During welding operation, argon is used for preventing fire which might be caused by high welding temperature.

Figures 3-6, 3-7 and 3-8 show the thermocouple distributions in the laminates. Table 3-6 gives detail description about them.

Table 3-6: Description for figures 3-6, 3-7 and 3-8

Figure No.	Layers	Size of laminates (length X width)	Experiment No.	Total number of thermocouples	Thermocouple No. at center layer
Figure 3-6	50	280 X 280 mm	Exp-1, 2, 3	6	T3
Figure 3-7	100	280 X 280 mm	Exp-5, 6	6	T4
Figure 3-8	50	170 X 170 mm	Exp-4, 7, 8, 9, 10, 11, 12	3	T2

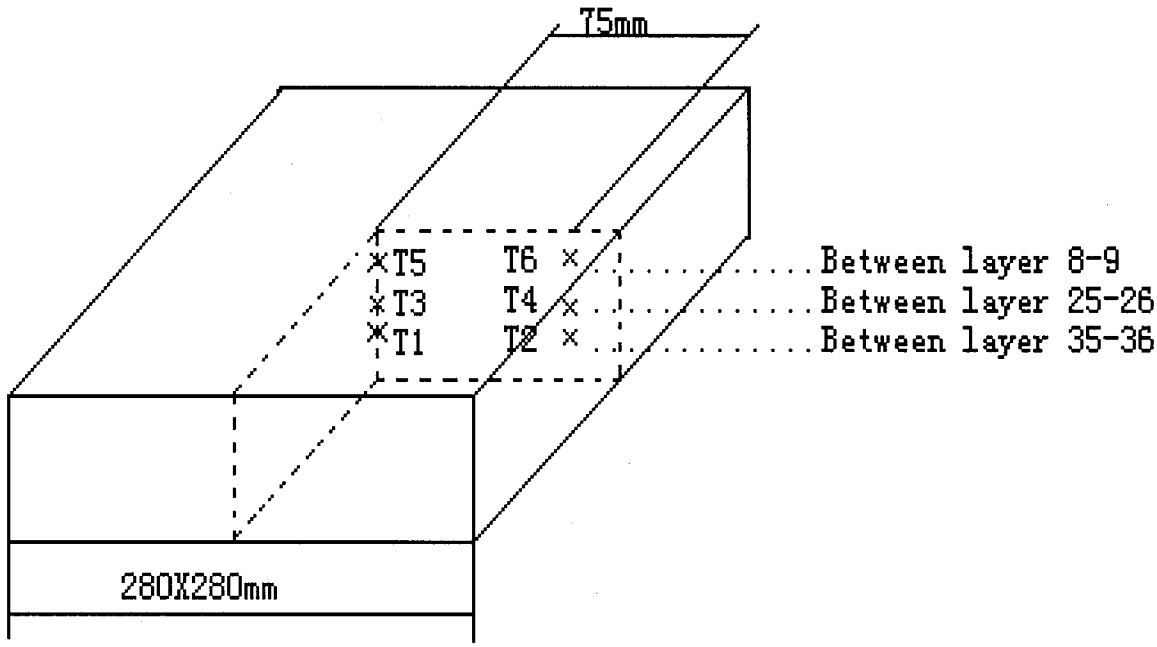


Figure 3-6: Thermocouple distribution of Exp-1, 2 and 3

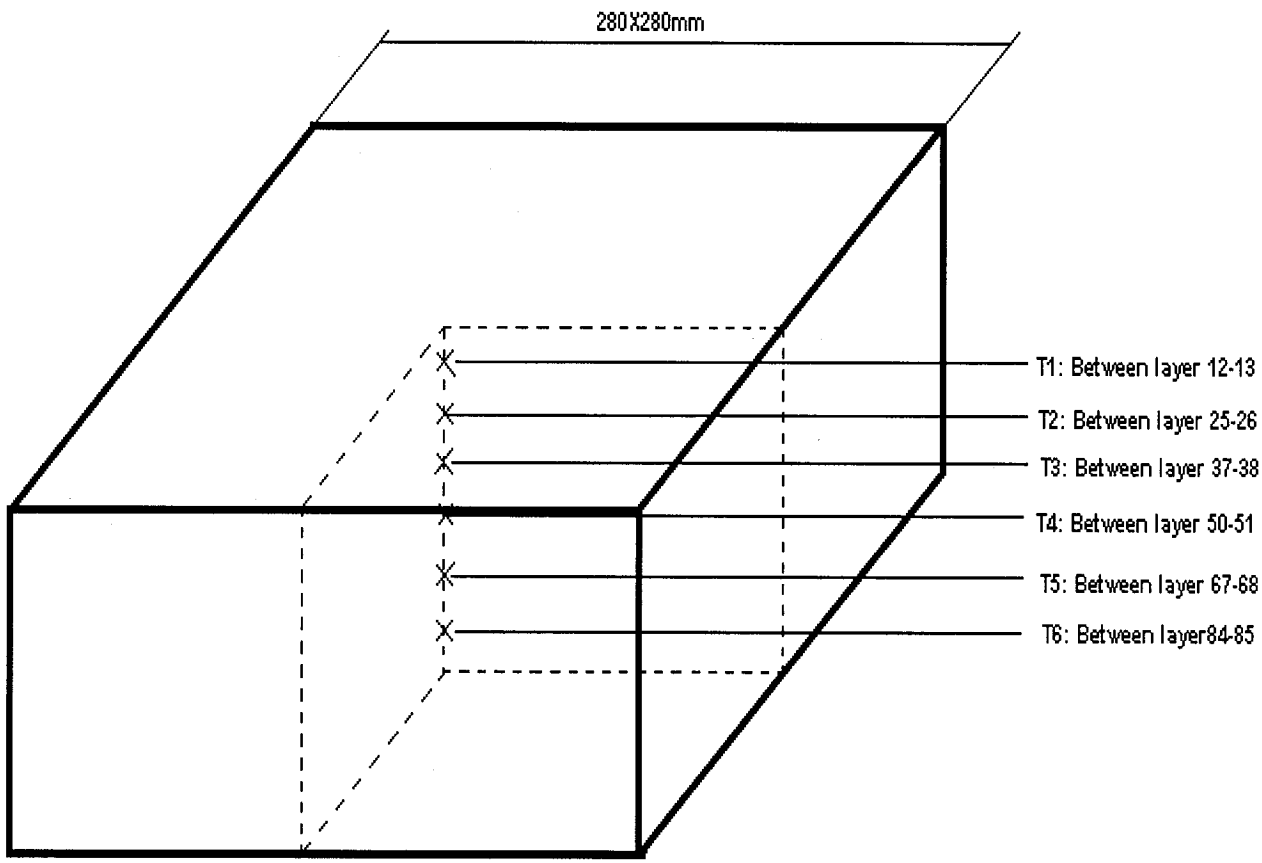


Figure 3-7: Thermocouple distribution in the 100-layer laminate (Exp-5, Exp-6)

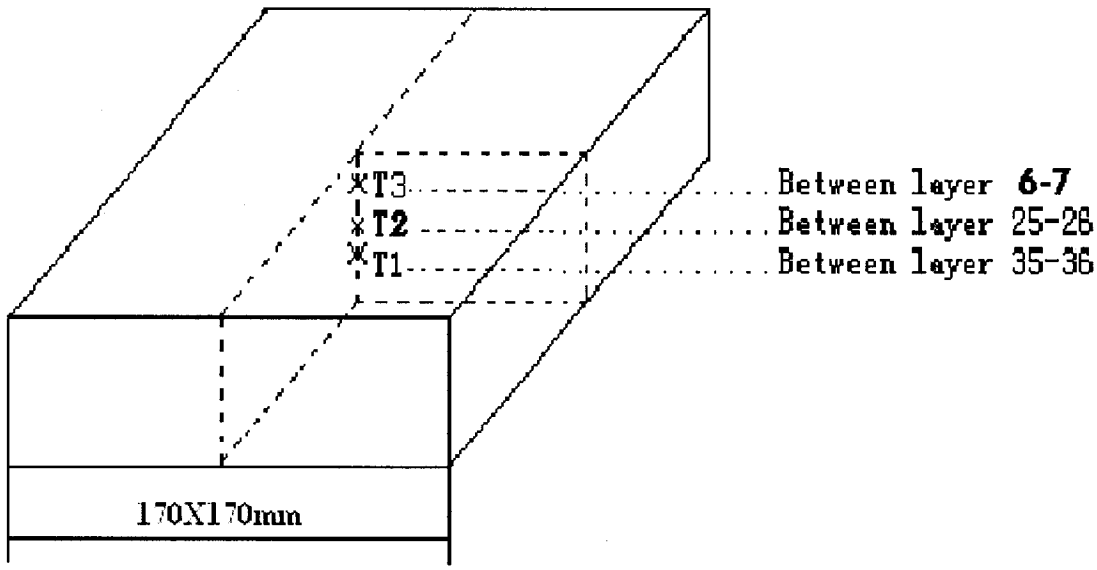


Figure 3-8: Thermocouple distribution for exp-4, 7, 8, 9, 10, 11 and 12

3.5 Curing of thick-section composites

The methods of preparing and curing the thick composites with conventional and pre-catalyzing technique are same, but no catalyst is mixed with resin when pre-catalyzing method is used. Figure 3-9 gives general view of curing.

The metal template with 15mm thickness is placed onto wood or concrete supports. A square piece of vacuum bag film is cut, and the four corners are folded to avoid resin from flowing out; then, the vacuum bag film is laid on the bottom template. It should be cautious that plastic film can not be used instead of vacuum bag film because it can be dissolved by styrene in vinyl ester resin.

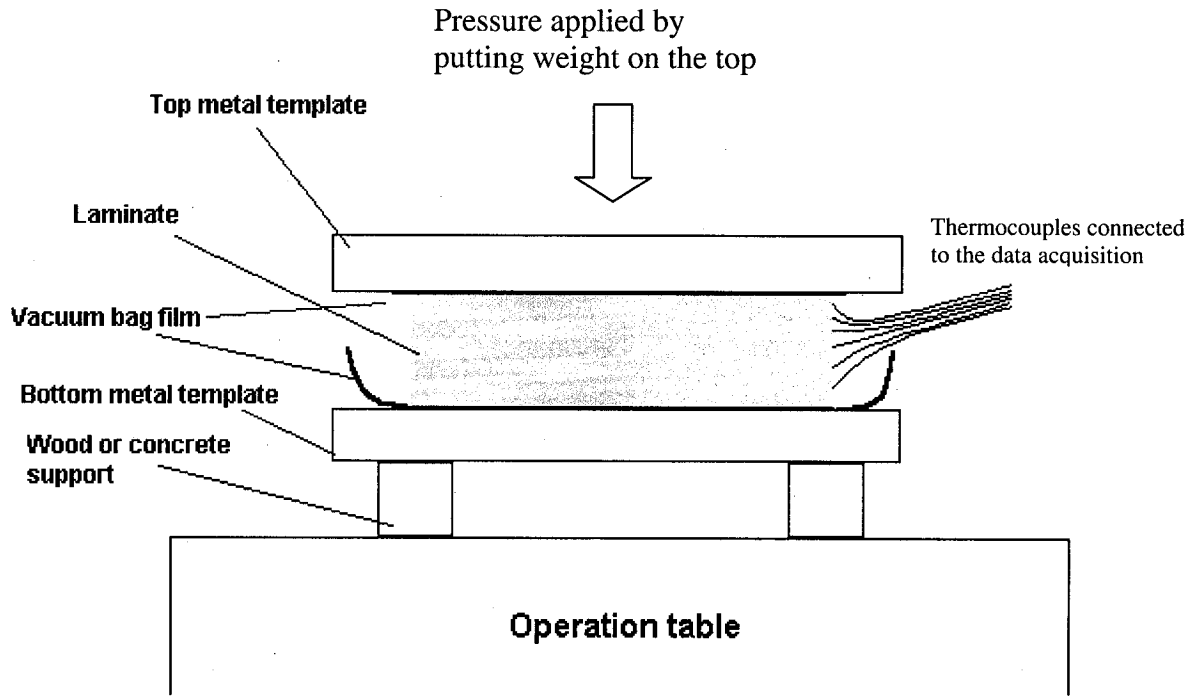


Figure 3-9: Thick composite curing

The resin system is mixed according to table 3-3 after above operations are finished. When 50-layer laminates which size is specified in figure 3-6 are fabricated, at least 2000g Derakane 411-350 resin is needed; 1000g resin is needed for other 50-layer laminates with smaller size (Figure 3-8); 4000g resin is used in fabricating 100-layer laminate (Figure 3-7). It should be noted that when the resin is mixed for manufacturing 100-layer laminate with conventional pre-mixing method, the operation should be divided into two steps because the resin may gel before lay-up operation is finished. At the beginning, 2000g resin is mixed, and then another 2000g resin is mixed just before the first mixed resin is run out. Normally, two operators are better for this job. After all

the layers are finished, a piece of vacuum bag film is covered on the top layer of laminate. A metal template with 15mm thickness is loaded on the top of laminate before the resin starts to gel. The weight can be put on right after the operation has been finished for higher ambient temperature cure (26°C), and extra weight can be added on top of template. The time of loading weight is very important. If the time is too early, the resin could be squeezed out, and the resin content should be lower. If the time is delayed, the laminate can not be well compacted; as a result, a large amount of void could be produced, and the interlaminar shear strength can be weak.

The data acquisition system starts to record the cure temperature every 30 seconds right after the resin is mixed and applied on fiber for pre-mixing method, or when the resin applying operation starts for pre-catalyzing method. The recording was kept for the whole curing procedure, and it was stopped only after the exothermal peak is observed and cooling step starts.

In this study, six thick-section laminates were fabricated for studying pre-catalyzing method using polystyrene as a binder. Among them, laminates Exp-1 and Exp-5 were made by pre-mixing method for the comparison with the results from 50 and 100 layer composites fabricated by pre-catalyzing method. Five of final product pictures are shown in figures 3-10, 3-11, 3-12, 3-13 and 3-14.

Also, another six laminates (see Figure 3-15, 3-16, 3-17, 3-18, 3-19 and 3-20) were manufactured for studying improved pre-catalyzing method using Epon 828 as a binder . Like Exp-1, another 50-layer laminate in Exp-7 was made by pre-mixing method for comparison with this improved pre-catalyzing method.

Experiments 1 and 7 were performed with same process and resin system with two different batch numbers of Derakane 411-350 which were used in two different pre-catalyzing methods. In order to achieve convincible comparison results, Exp-1 was repeated in Exp-7 for studying improved pre-catalyzing method.

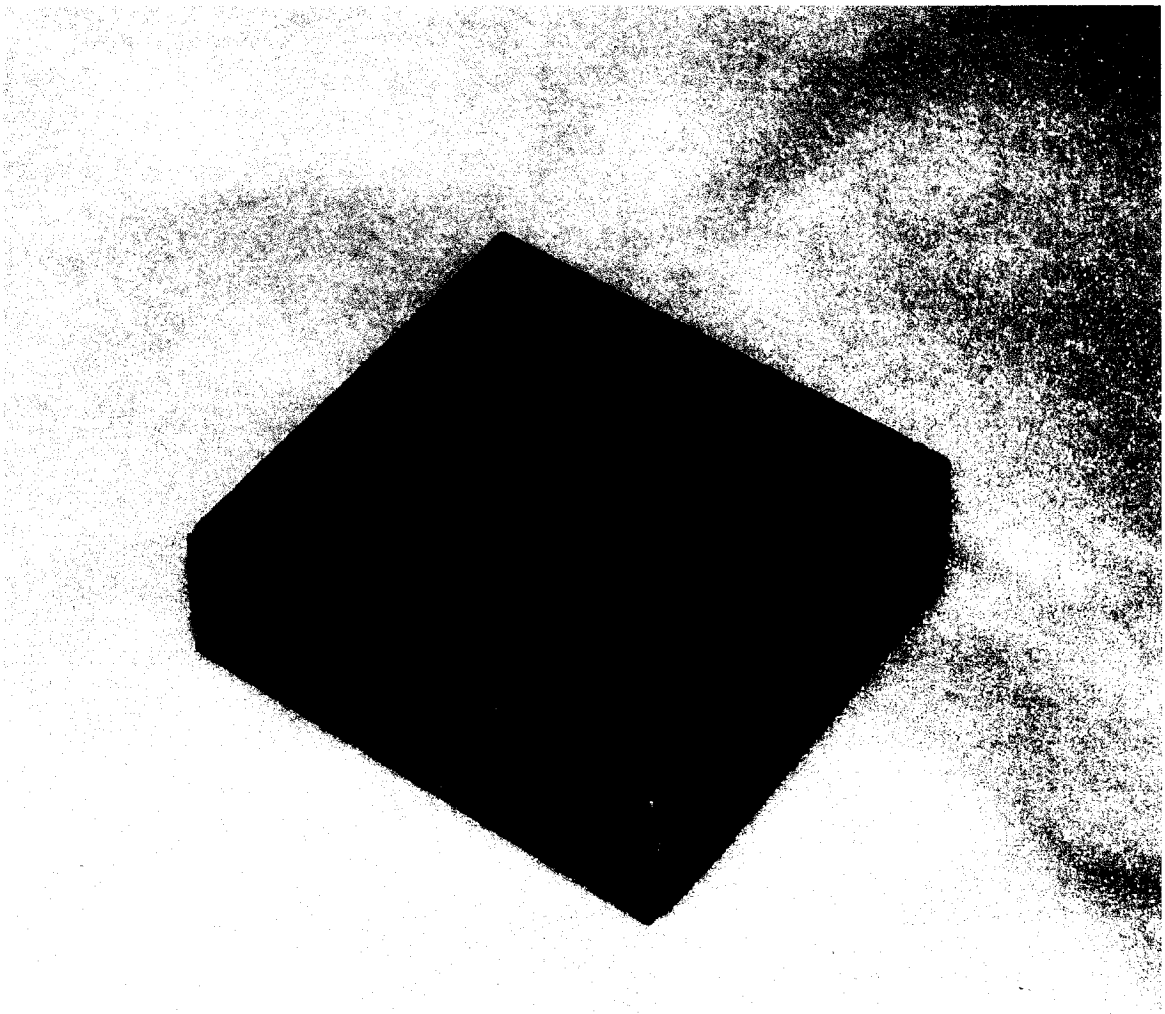


Figure 3-10: Picture of laminate from Exp-1

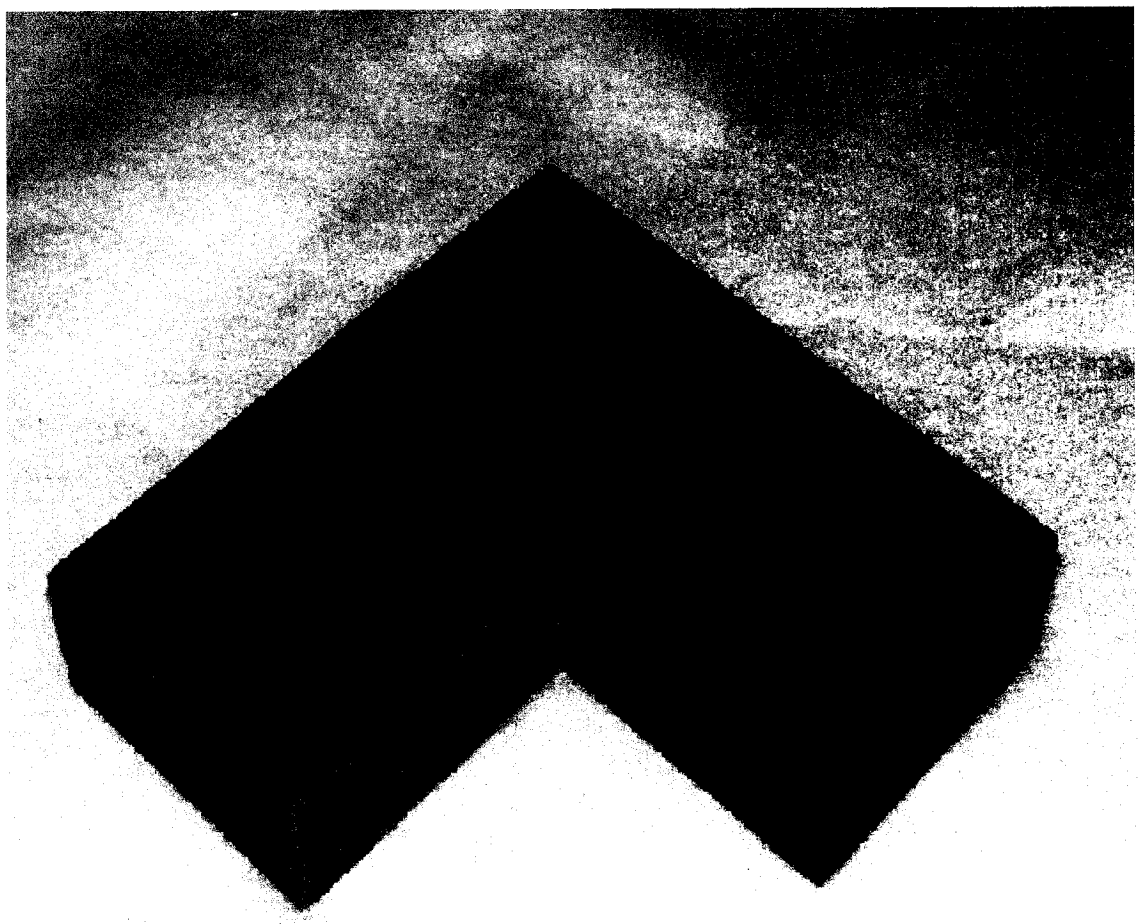


Figure 3-11: Picture of laminate from Exp-2

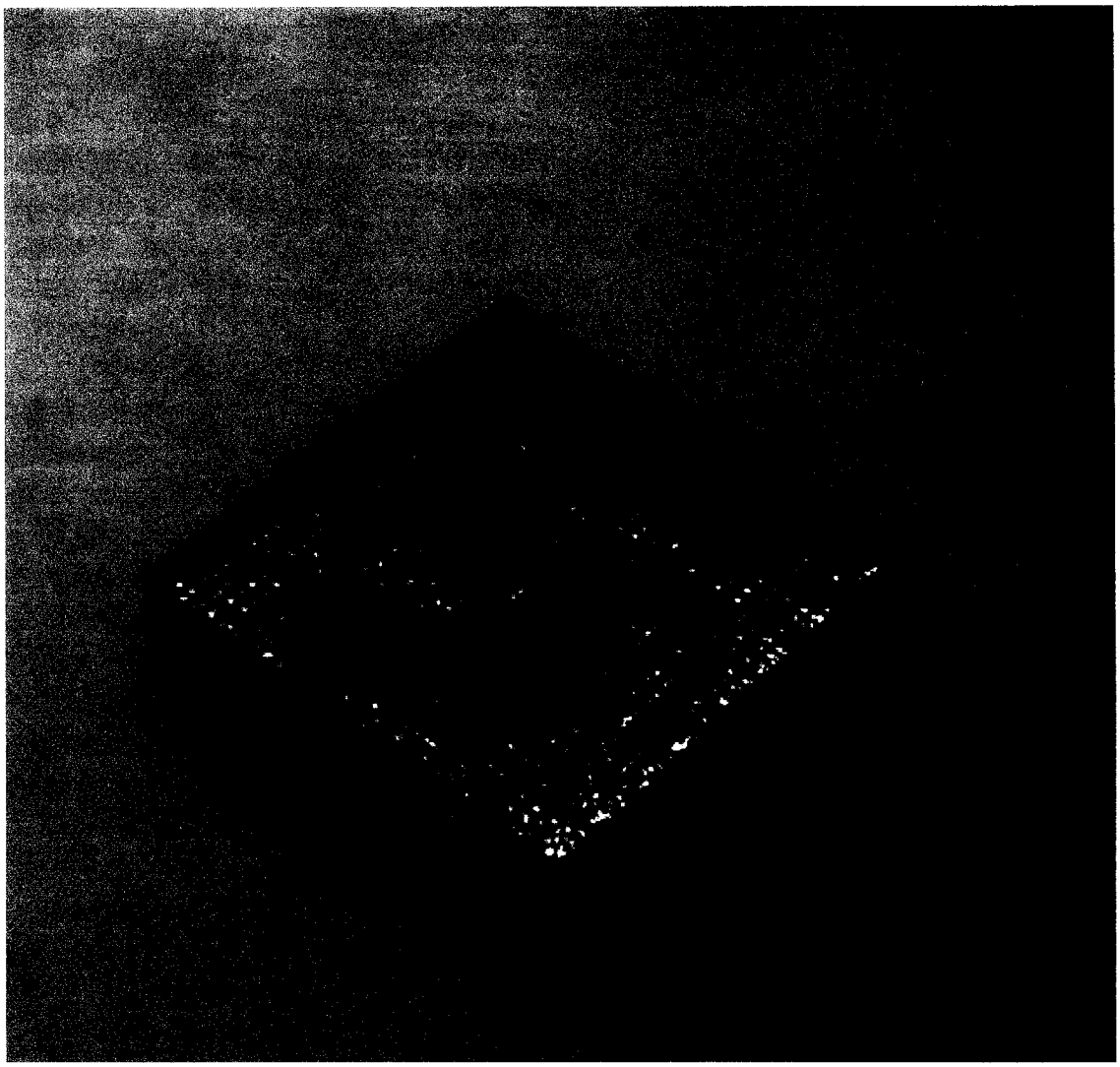


Figure 3-12: Picture of laminate from Exp-4

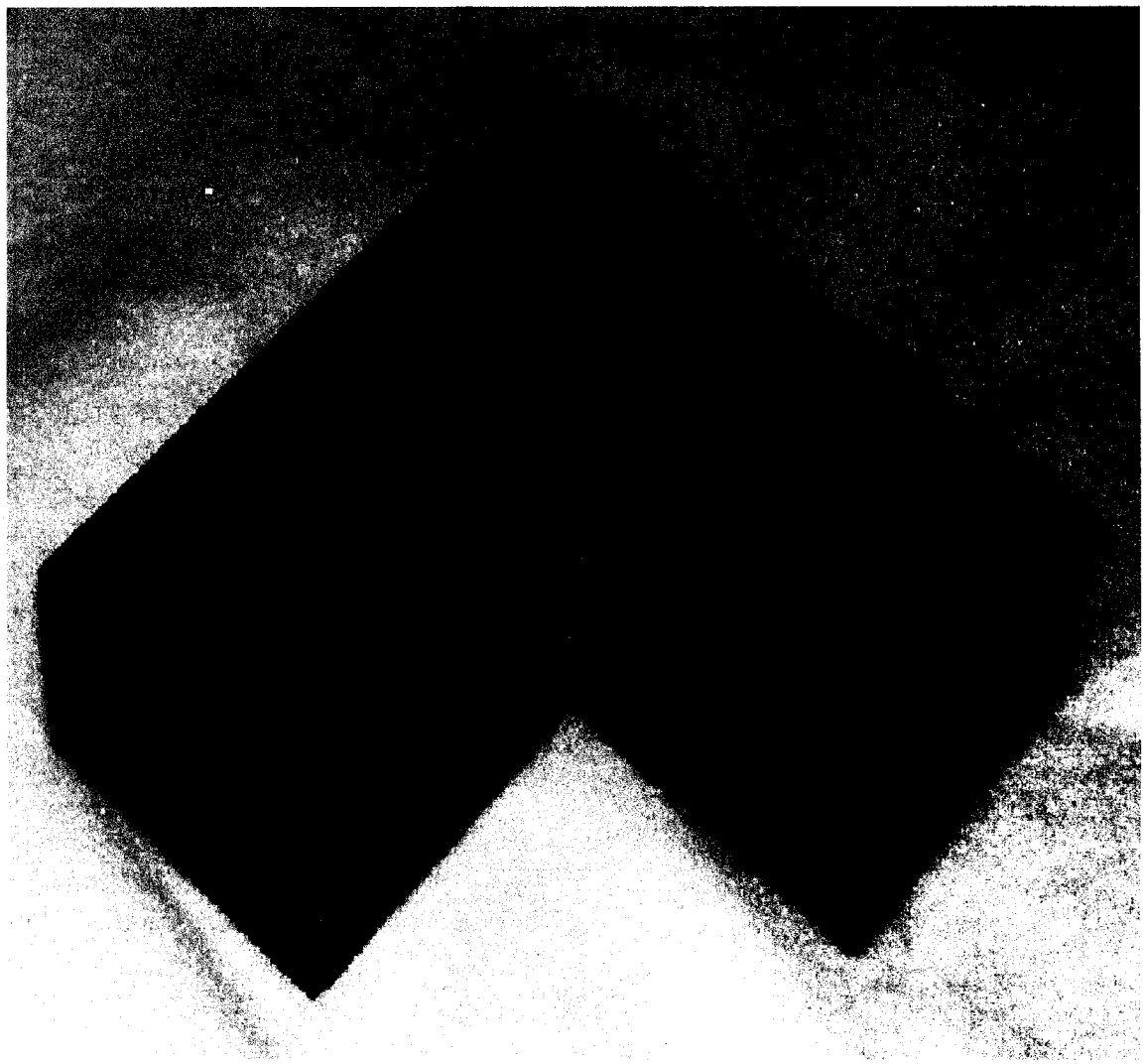


Figure 3-13: Picture of laminate from Exp-5

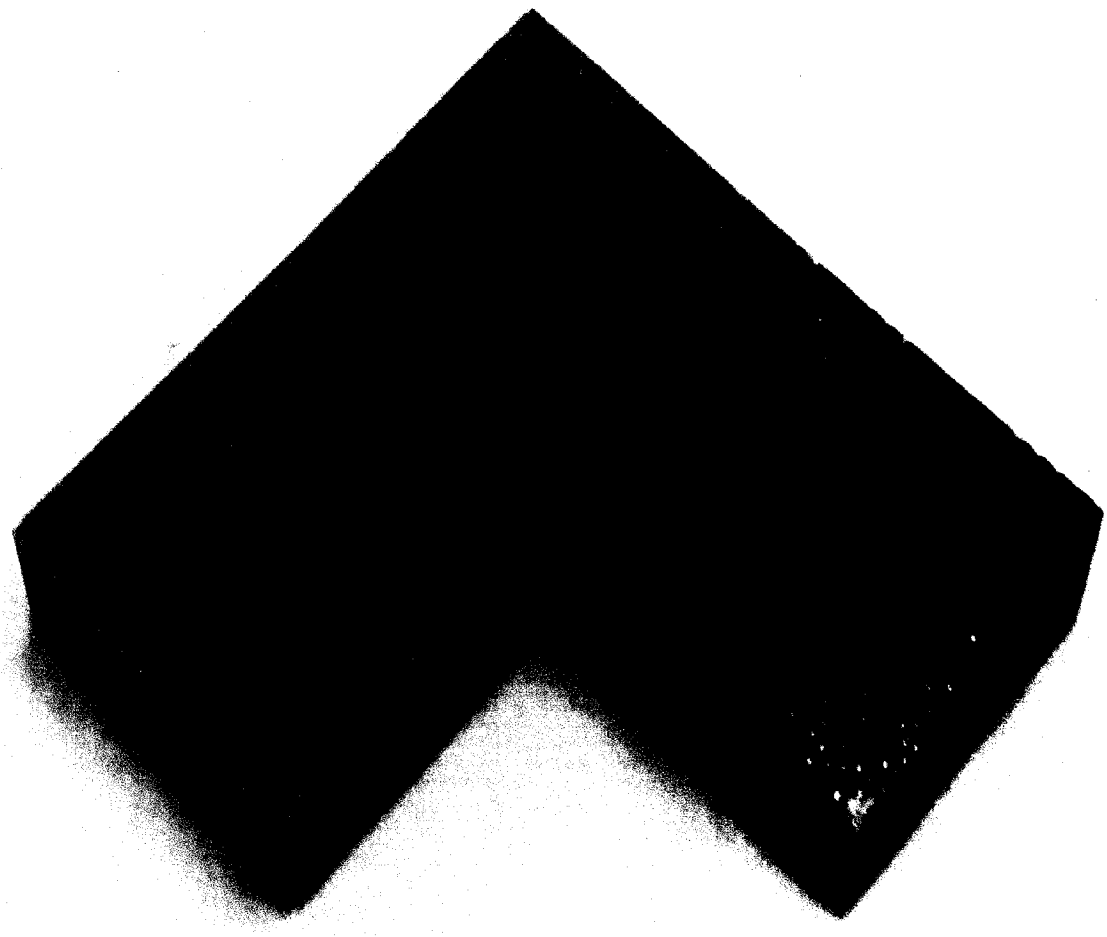


Figure 3-14: Picture of laminate from Exp-6

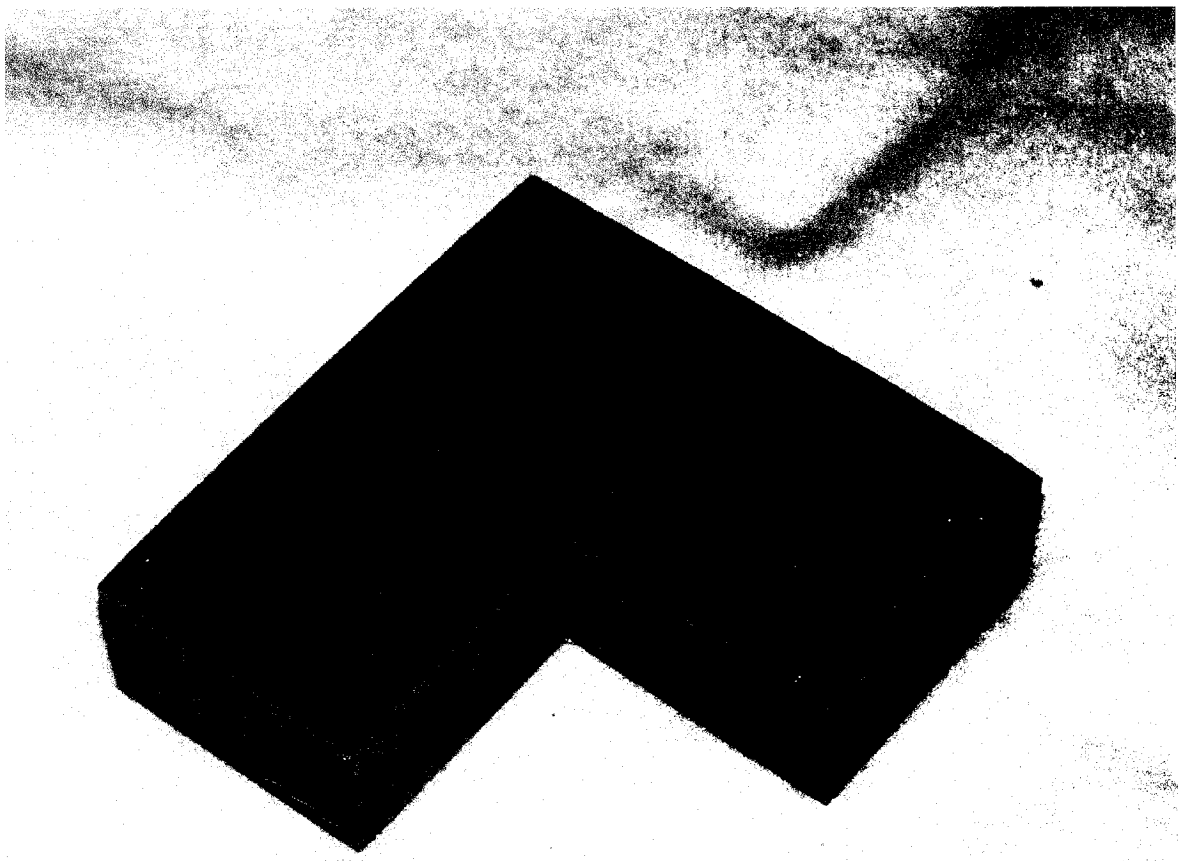


Figure 3-15: Picture of laminate from Exp-7

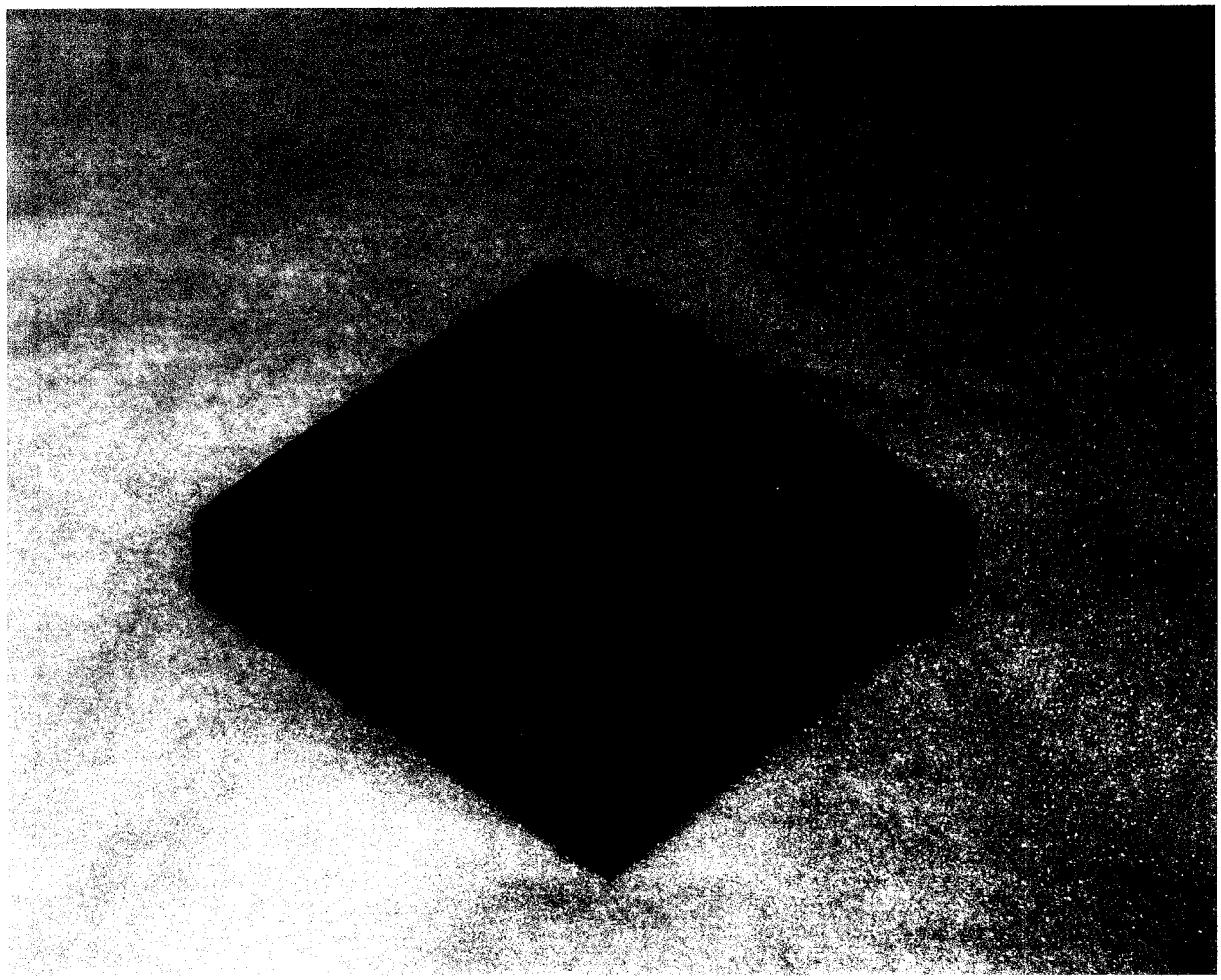


Figure 3-16: Picture of laminate from Exp-8

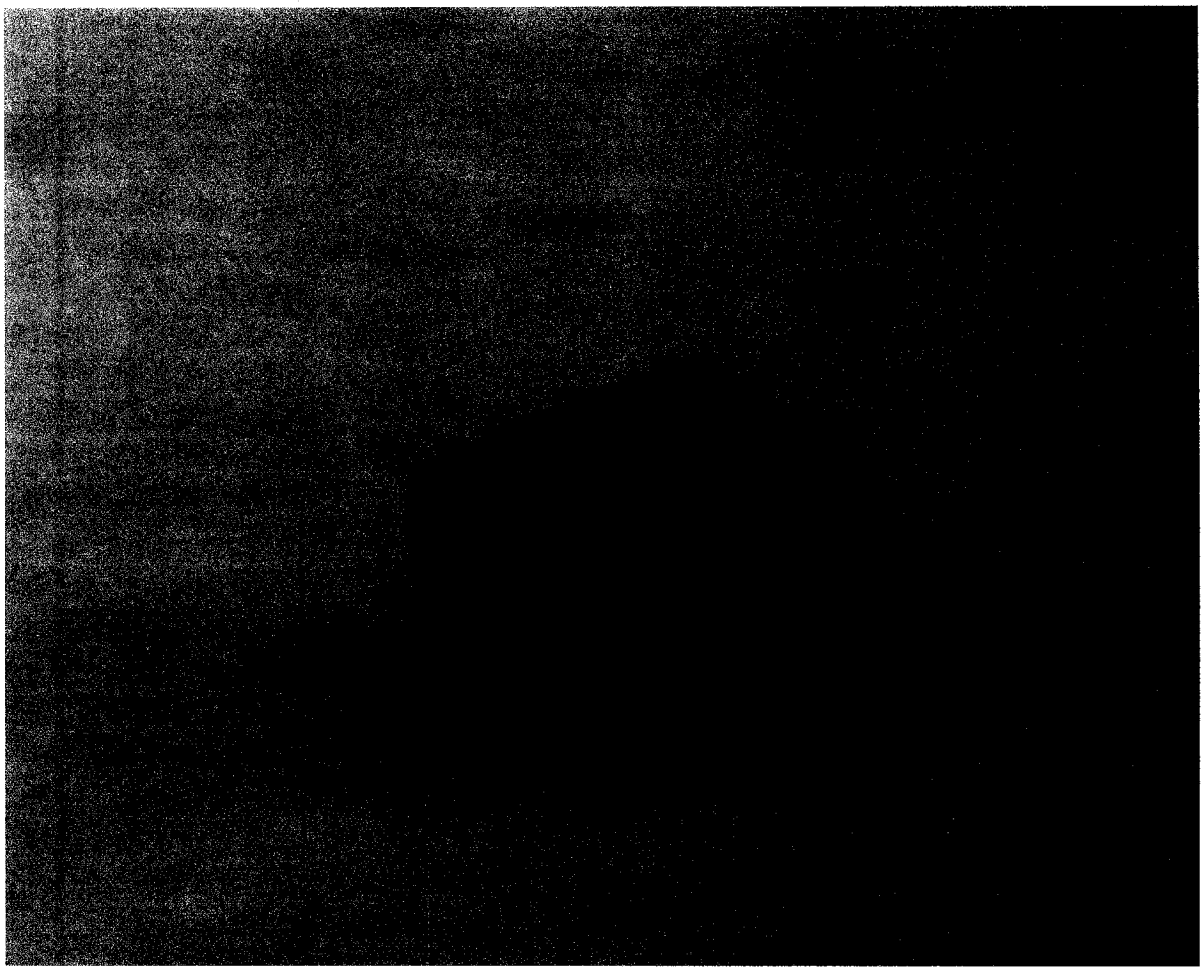


Figure 3-17: Picture of laminate from Exp-9

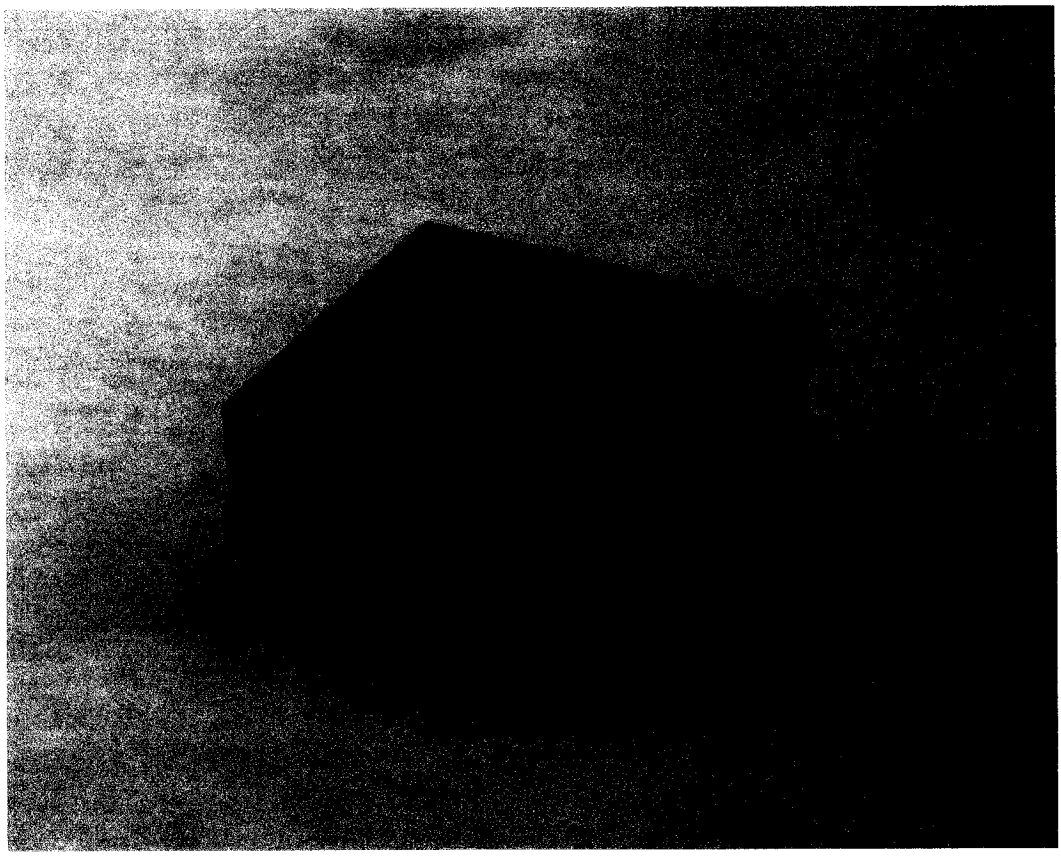


Figure 3-18: Picture of laminate from Exp-10

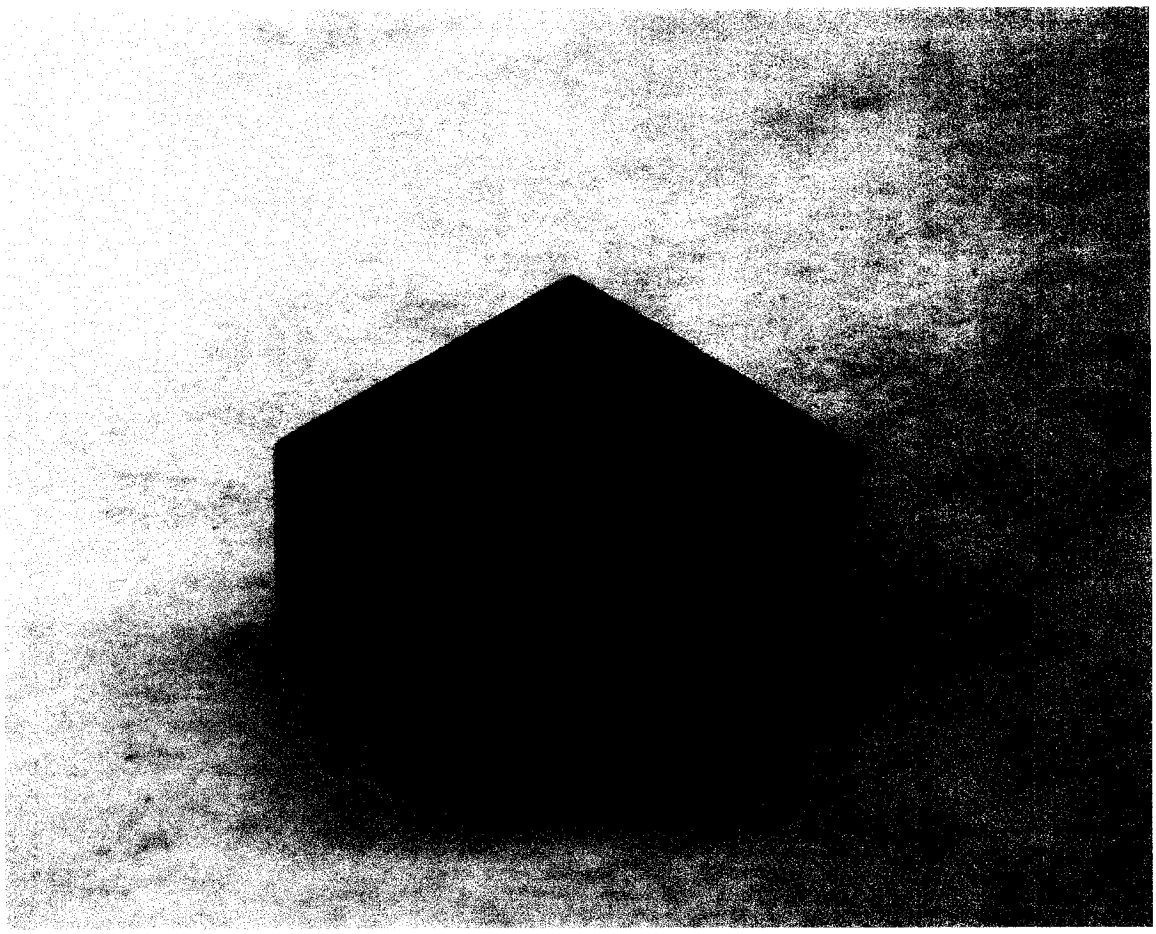


Figure 3-19: Picture of laminate from Exp-11

Figure 3-20: Picture of laminate from Exp-12

The samples were left overnight at ambient temperature before they were taken out. In order to reach high cure degree and reduce residual styrene, post cure was performed according to the suggestion of supplier (93°C for 2 hours). As an alternative, same result with the post cure on cure degree can be achieved by leaving the sample for a long time at ambient temperature. In this project, post cure was performed on those samples for DSC tests (Table 4-2). Also, samples were post-cured before mechanical property tests.

The supplier, Dow Chemical, recommends that post cure can be performed for 2 hours at 93°C, but this is only for thin structure composites. In this experiment, 50-layer samples were post-cured for two and half hour at 93°C, and 100-layer samples were post-cured for 3 hours.

The colors of final products are very different because the different pre-catalyzing materials and manufacture methods (pre-mixing and pre-catalyzing) were used. In pre-mixing method, the color of laminates (Exp-1, Exp-5 and Exp-7) is dark green, and the laminates appear somewhat transparent and clear. In pre-catalyzing technique, the color of laminates is changed with the catalyst binder. When polystyrene was used as the binder, the laminates (Exp-2, Exp-3, Exp-4 and Exp-6) are in yellow-green color which was caused by white polystyrene layer existing between fiber and matrix. When Epon 828 was used as the binder, the laminates (Exp-8, Exp-9 and Exo-10) have the similar color to the laminates fabricated with pre-mixing method, but they look slightly less clear because the epoxy binder, which is half transparent and in light-green color, is coated on

the fiber. The color of the other two laminates (Exp-11 and Exp-12) is yellow-brown which was caused by hardener 3046 added in the bulk vinyl ester resin.

3.6 Resin Content Test

The resin content, as we know, can affect the mechanical properties of composites greatly; also, when DSC results are analyzed (refer to Section 4.2), it is an important factor which must be taken account. In this study, resin content test was performed according to ASTM D2584 [31] which is a standard test method by measuring the ignition loss of cured reinforced resin. The test procedure can be described as follows:

- Cut three specimens for each sample, and each one weighs approximately 5g with a maximum size of 2.5 cm by 2.5 cm by thickness.
- Put the three specimens into three crucibles separately, and then, put the crucibles into an electric muffle furnace.
- Raise the temperature of muffle furnace to 565 ± 28°C until all the resin has disappeared. This period is around 5 hours.
- Calculate the resin content with following equation:

$$W_R = [(W_1 - W_2)/W_1] \times 100 \qquad (3\text{-}1)$$

Where:

W_R : Weight% of resin

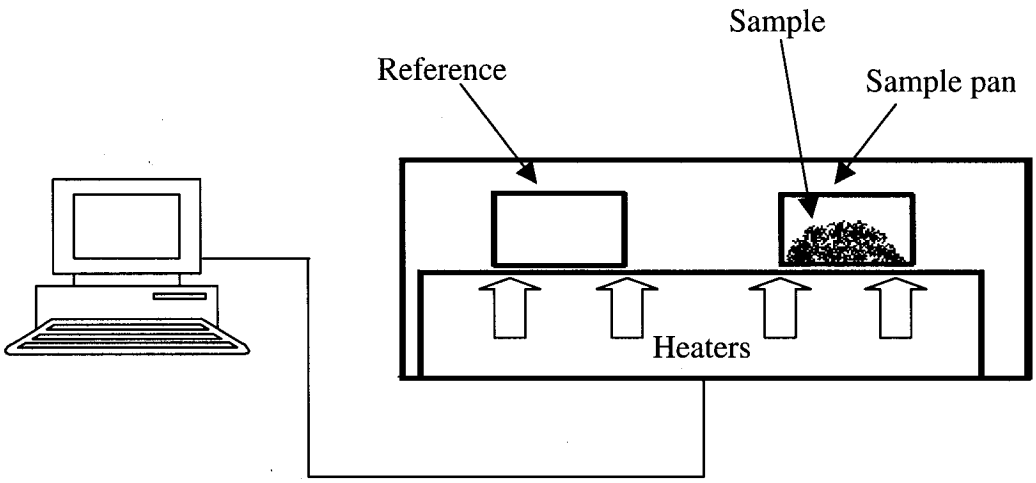
W_1 : Weight of specimen

W_2 : Average weight of residue

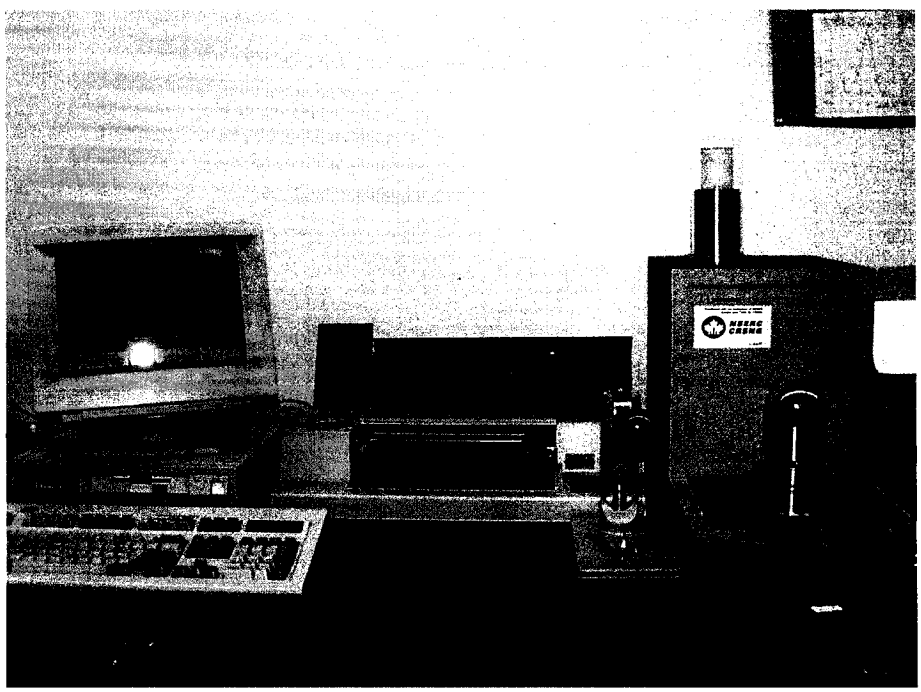
The results of resin weight contents for all the experiments are given in Table 3-7.

3.7 DSC Test

In this study, Differential Scanning Calorimetry (DSC) was used to measure the residual heat of reaction and glass transition temperature of the samples. The samples that are in the form of sawdust by sawing the laminates are obtained from the laminates after cure procedure is finished. The hermetic pans, made of aluminum, were used for the samples and the reference. The sample weights are around 10mg. When the DSC cell is stabilized at room temperature, the residual heat of reaction of the sample is measured under the constant heating rate of 10°C/min, until no further exotherm was observed (about 180°C). Once the heating is completed, the DSC cell is set in the stand-by mode. The sample pan is picked up from the DSC cell, and then is cooled rapidly to room temperature. In this study, DSC 2010 Differential Scanning Calorimeter of TA Instruments Co. is used. DSC test is shown in figure 3-21.



(a) System of DSC test



(b) Picture of DSC instrumentation

Figure 3-21: DSC instrumentation

3.8 Atomic Force Microscopy (AFM) Test

AFM is a form of scanning probe microscopy where a small probe is scanned across the sample to obtain information about the sample's surface. The purpose of using AFM test in this study is to examine the properties of composite interfaces between fiber and matrix.

In order to obtain reliable test results, the test surface of sample should be prepared very carefully. The detail preparation procedure is described below:

- Cut the composite samples to the size 3 × 5 × 3 mm (length×width×height). It should be cautious that the test surface (length×width) must be the cross section of a laminate where the fibers are cut off. This can produce the clear region of the fiber and the surrounding matrix when AFM test being performed.
- Sand the test surface using $240^{\#}$ sanding paper.
- Polish the test surface using $400^{\#}$, $800^{\#}$ and $1200^{\#}$ sanding paper successively.
- Smooth the surface with 1 μ grinding cream. .

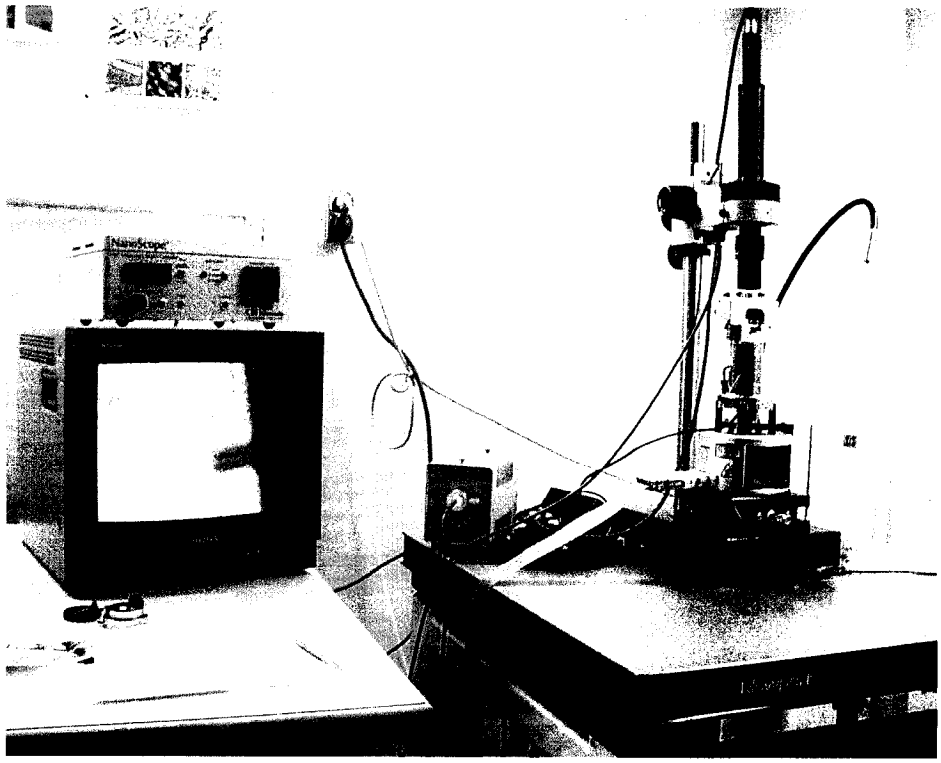


Figure 3-22: Picture of AFM test machine

In this test, NanoScope Ⅲa, Multimode AFM machine, of Digital Instrument Company was used. The picture of the machine is shown in Figure 3-22. TappingMode™ test mode and Tapping Mode Etched Silicon Probe (TESP) were selected in the test.

3.9 Short Beam Shear (SBS) Text

The short beam shear (SBS) strength test is designed to measure the interlaminar shear strength (ILSS) for thick composites, which is dependent on the resin matrix properties and the fiber-matrix interfacial shear strengths. ILSS is affected by processing condition, unlike other tests which are primarily dominated by fiber properties. The

method of short beam shear test is described in ASTM D2344 [32] in which a three point bend test is used, where the span to depth ratio is set low enough to facilitate transverse shear in the sample.

The testing method of ASTM D2344 cannot be used for design criteria for composites, but can be used for comparative testing with other composite shear tests and also for quality control for the composite materials.

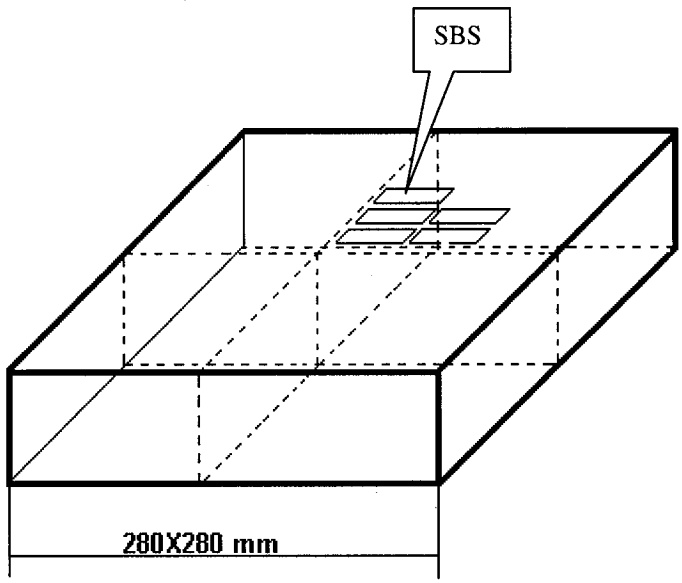


Figure 3-23: Location of SBS specimens in 50-layer thick composites

In order to examine the effect of temperature gradients on the ILSS at different layers along the across section of thick composites, three groups of specimen were cut from top, center and bottom layers. Figure 3-23 shows the specimen positions at the top layer only. The specimens in the center and bottom layers were cut just below them. At least 5 test specimens were cut in each group. The specimens were cut with a cutting machine of which the feeding speed and the size of specimens are controlled manually.

Care was taken to operate in order to avoid large variation of specimen size. The specimen size, specified in ASTM D2234, is shown in figure 3-24. The ratio of specimen length to its thickness is 7.0 to ensure failure is in shear.

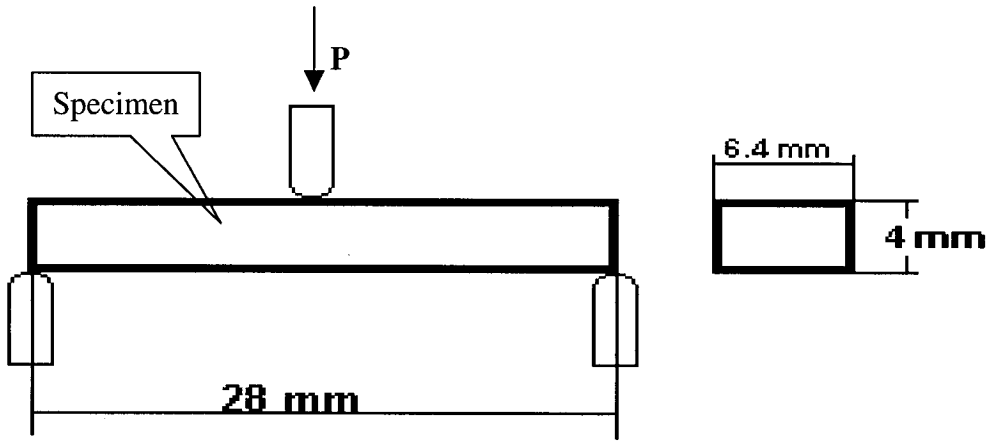


Figure 3-24: Diagram of short beam shear test

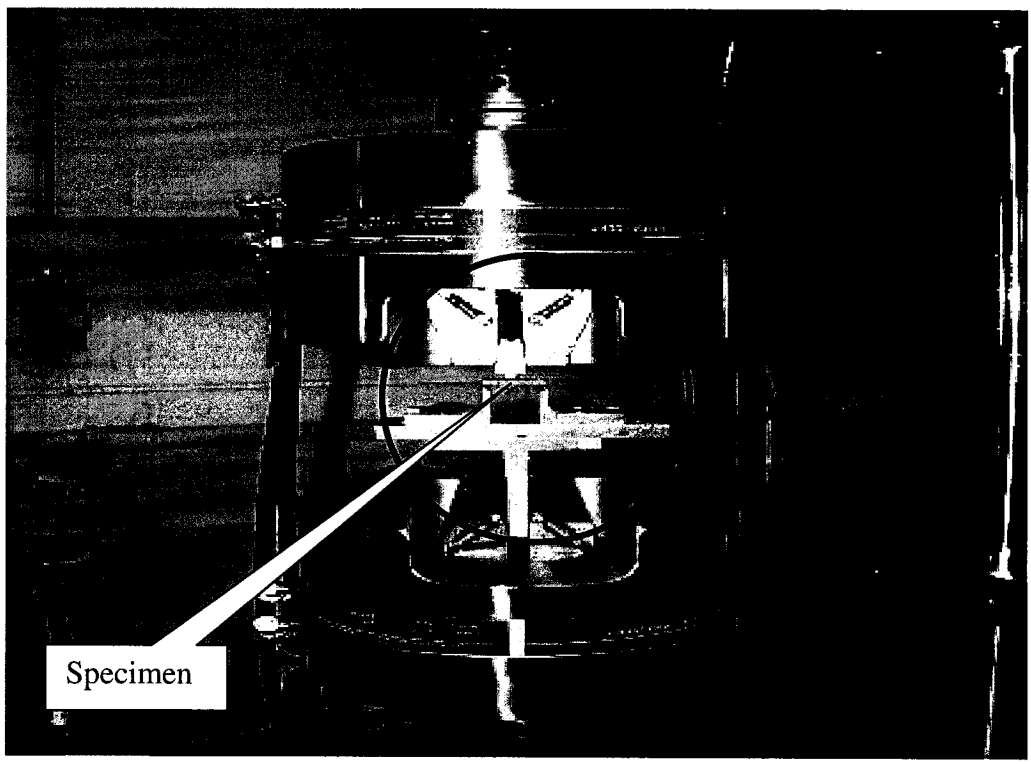


Figure 3-25: Picture of short beam test

MTS testing machine was used for performing the short beam shear tests (Figure 3-25). The specimen is placed on two supports and the load is applied by means of a loading nose placed directly above at the midpoint of the specimen. The specimen is tested at a rate of crosshead movement of 1.3 mm /min.

The interlaminar shear strength of a specimen is determined from following equation:

$$S = 0.75 \times \frac{P_B}{b \times d} \tag{3-2}$$

Where: S = shear strength, N/m^2

P_B = breaking load, N

b = width of specimen, m

d = thickness of specimen, m

3.10 Summary of Experiment Results

All the experiment results are summarized in Table 3-7. This table includes all the experiments regarding two pre-catalyzing methods in which polystyrene and epoxy binders were used respectively. Exp-1 ~ Exp-6 were performed for the purpose of studying pre-catalyzing method in which polystyrene was used, and Exp-7~Exp-12 were for the purpose of investigating the method in which epoxy binder was used.

In all the experiments, it can be found that the thickness of laminates and resin content are varied with the experiments because hand-lay-up is a kind of traditional hand-

operation process. The final product is affected by human factors, such as the operation time and resin amount applied on the fiber. Normally, the thicker is the laminate, the higher is the resin content. The thickness of laminate is influenced by human factor, ambient temperature (the lower the temperature, the higher the viscosity is, and high viscosity produces thicker laminate.), raw materials (new resin has higher content of styrene which produces low viscosity) and amount of weight and time when applying on it.

In the experiments in which polystyrene is used as binder, comparing Exp-2 and Exp-4 (50-layer fabric was used), the thickness of laminate of Exp-2 is 30mm, and the resin content is 47.3%. In Exp-4, the thickness of laminate is 26mm which is less than Exp-2, and its resin content is lower too, only 33%. Also, in the experiments where epoxy is used as binder, it can be observed that the laminate (Exp-10) is thicker than the laminates (Exp-11 and Exp-12) which thickness is 34mm, and its resin content is 33.4%, which is also higher than 28% (Exp-11 and Exp-12).

In this table, the item of "**Initial time of polymerization**" is equivalent to the onset of cure reaction which is demonstrated in Figure 1-1. The item "**Highest peak temperature**" and "**Lowest peak temperature**" present the peak temperatures which happen in different places of the laminate. Normally, highest peak temperature happens at the center of laminate, and lowest peak temperature happens at the edge (refer to Figure 1-1).

The colors of laminates have been discussed in section 3.5, and the results of interlamimar shear strength will be discussed in section 4.1.3 and 4.2.3.

Table 3-7: Summary of experimental results

Experiment	Manufacture method	Layers	Color of laminate	Ambient temperature (°C)	Thickness of final product(mm)	Initial time of polymerization (min)	Highest peak temperature (°C)	Lowest peak temperature (°C)	Temperature difference (°C)	Resin content (%) (by weight)	SBS test (MPa)
Exp-1	Pre-mixing	50	Dark green	19	30	225	104	86	18	40.3	34.28
Exp-2	Pre-catalyzing fabric using **polystyrene** as the binder (formula I in Table 3-4) & drying fabric for 3 days	50	Yellow-green	20	30	95	80	71	9	47.3	/
Exp-3	Pre-catalyzing fabric using **polystyrene** as the binder (formula I in Table 3-4) & drying fabric for 2 weeks	50	Yellow-green	22	29	Can not be observed	27	25	2	35.9	27.72
Exp-4	Pre-catalyzing fabric using **polystyrene** as the binder (formula II in Table 3-4) & drying fabric for 2 weeks	50	Dark green	20	26	Can not be observed	22	20	2	33	29.55

To be continued

Table 3-7 Continued

Experiment	Manufacture method	Layers	Color of laminate	Ambient temperature (°C)	Thickness of final product(mm)	Initial time of polymerization (min)	Highest peak temperature (°C)	Lowest peak temperature (°C)	Temperature difference (°C)	Resin content (%) (by weight)	SBS test (MPa)
Exp-5	Pre-mixing	100	Dark green	21	51	170	88	76	12	32.3	/
Exp-6	Pre-catalyzing fabric using **polystyrene** as the binder (formula I in Table 3-4) & drying fabric for 2 weeks	100	Yellow-green	21	55	Can not be observed	30	24	6	34.8	/
Exp-7	Pre-mixing (using same method as Exp-1 but different resin batch)	50	Dark green	25	37	25	83	65	18	36.6	31.8
Exp-8	Pre-catalyzing fabric using **epoxy** as the binder (formula I in Table 3-5)	50	Dark green	22	30	30	34	30	4	38.8	31.48

To be continued

Table 3-7 continued

Experiment	Manufacture method	Layers	Color of laminate	Ambient temperature (°C)	Thickness of final product(mm)	Initial time of polymerization (min)	Highest peak temperature (°C)	Lowest peak temperature (°C)	Temperature difference (°C)	Resin content (%) (by weight)	SBS test (MPa)
Exp-9	Pre-catalyzing fabric using **epoxy** as the binder (formula II in Table 3-5)	50	Dark green	22	37	30	59	43	16	32	31.42
Exp-10	Pre-catalyzing fabric using **epoxy** as the binder (formula III in Table 3-5)	50	Dark green	21	36	30	39	36	3	33.4	31.33
Exp-11	Pre-catalyzing fabric using **epoxy** as the binder (formula II in Table 3-5) & adding **hardener 3046** in the bulk resin system	50	Yellow brown	22	34	200	31	28	3	28.1	32.34
Exp-12				28			36	34	2	28.7	32.43

CHAPTER 4

RESULT, DISCUSSION AND ANALYSIS

This study has focused on investigating the effects of pre-catalyzing technique on the exothermic reaction, cure degree and interlaminar strength of thick glass/vinyl ester composites particularly those produced by hand lay-up process. In this chapter, two pre-catalyzed fabric methods are discussed. First, the method using polystyrene as the binder for pre-catalyzing the fabric is discussed. Then, the improved pre-catalyzing method, which uses the epoxy resin as the binder is investigated. For both pre-catalyzing methods, the cure temperature profiles are analyzed in order to examine the influence of both pre-catalyzing methods on exothermic reactions. The DSC results, obtained from the samples of the composites fabricated by pre-mixing and two pre-catalyzing methods, are compared to examine the influence of pre-catalyzing method on the cure degree. Finally, the results of short beam shear tests are analyzed to examine the influence of two pre-catalyzing methods on the interlaminar shear strength of thick-section composites.

4.1 Discussion of Pre-catalyzing Method Using Polystyrene as the Binder

In chapter 2, it has been introduced that Reuss [9] has successfully made high quality thick composite with pre-catalyzing method using polystyrene as the binder. In their study, they selected polyester as the matrix material and Benzoyl Peroxide (BPO) as the catalyst. Hand lay-up process was applied, and the composites were cured at 80°C using hand lay-up procedure. Their research shows that this pre-catalyzing technique can reduce the exothermal peak temperature form 165°C to 119°C. As we know, hand lay-up

process is the commonly used technique in composite manufacture industry, and many products produced with this technique are cured at room temperature, especially for those parts with large size. This chapter presents the feasibility of applying this pre-catalyzing technique on large and thick parts which are cured at room temperature with hand lay-up process.

4.1.1 Discussion of Cure Temperature Profiles and Analysis of Reaction Mechanism

4.1.1.1 Discussion of Cure Temperature Profiles

Experiment with pre-mixing method (Exp-1)

In order to examine the effectiveness of pre-catalyzing method on alleviating the exothermal reaction, the sample was produced by traditional pre-mixing method for comparison with the pre-catalyzing method. Figure 4-1 shows the cure temperature profile of 50-layer composite manufactured by pre-mixing method (Exp-1). In this figure, six different curves which present six temperature points distributed in the laminate (refer to figure 3-6) can be seen. It can be seen that the polymerization was initiated approximately at 167 minutes after the resin system was mixed using the composition in Table 3-3. Then, the reaction temperature rose at very fast speed, which can be seen in Figure 4-1. At 230 minutes, the exothermal peak temperature appeared. The highest peak temperature (104^0C) happened at points T1 and T3. Point T3 is at the center of the laminate, and T1 is the nearest point to the center compared with other points. The lowest peak temperature happened at T5 and T6. Point T5 and T6 are near the top layer of the

laminate where the metal weight was loaded. The temperature at T5 was 86 ^{0}C which was 18^{0}C lower than the peak temperature at point T3. So, when curing 50-layer composites with the pre-mixing method, the exothermal reaction was very strong, and the reaction temperature is higher at the center than at the edge. This large temperature gradient was caused by the poor heat transfer of composites. The heat generated at the center finds it is difficult to escape. This phenomenon may degrade the properties of composites.

Experiment with pre-catalyzing method I (Exp-2)

Figure 4-2 shows the cure temperature profile of 50-layer composite manufactured by pre-catalyzing method (Exp-2). During the pre-catalyzing process, the fabric had been pre-catalyzed with Formula I (Table 3-4) and dried for 3 days after pre-catalyzing process was finished. From this figure, it can be seen that the polymerization was initiated around 95 minutes after the resin was applied on the fabric, and at 160 minutes, the peak of exothermic temperature appeared. The highest peak temperature of 80 ^{0}C happened at point T3 which was located at the center of the laminate. The lowest peak temperature of 71 ^{0}C happened at T2 which was near the bottom and the side-edge of the laminate. The difference of temperature between T3 and T2 is 9 ^{0}C. Comparing Exp-2 with Exp-1, the exothermic peak temperature of Exp-2 is 24 ^{0}C lower than Exp-1, and its temperature gradient is reduced significantly because of lower temperature difference between the center and the edge. Also, it needs much longer time to reach the exothermic peak from the initiating point, so the reaction is milder. It is obvious to see that that pre-catalyzing technique can reduce the exothermic temperature and the temperature gradient. It should be noted that the initial time of polymerization in this experiment is about 83 minutes as

compared to about 167 minutes in Exp-1. Normally, the lower the exothermic temperature, the longer the initial time of polymerization is. This is not true for Exp-1 and Exp-2. Exp-1 has higher exothermic temperature, but has longer initial time. This phenomenon may be caused by non-precise mixture of resin system. Since the content of promoter (CONAP) is very small (only 0.17%), it is difficult to measure accurately. CONAP can significant influence the cure process (Figure 4-9).Less decrease of CONAP can cause large delay of the exothermic reaction. Only a little error when measuring can cause big change in cure process. So, here the initial time of polymerization in Exp-1 (pre-mixing method) and Exp-2 (pre-catalyzing method) can not be compared and discussed.

Effect of drying time of fabric after being pre-catalyzed (Exp-3)

Even though Exp-2 showed that the exothermic temperature was reduced to 80^0C as compared to 104^0C for pre-mixing method after the fabric was dried 3 days, this temperature was still very high. Exp-3 (Figure 4-3) shows that, when the fabric was dried 2 weeks after being pre-catalyzed, the exothermic temperature of a 50-layer laminate can been reduced significantly. From the curve it can be seen that from the beginning of hand lay-up operation until 335 minutes later, the peak exotherm cannot be observed. Even though the cure temperature had a slight tendency to go up at 335-minutes, the resin had already gelled, and the sample became rigid. So, no peak exotherm could be expected. During the curing process, the difference of highest (27°C) and lowest temperature (25°C) shown in Figure 4-3 was less than 2°C, and it appeared in the whole curing process. So, it cannot be considered that this temperature difference was caused by the polymerization

reaction. From this experiment, it was found that the content of volatile could significantly affect the exothermic polymerization. The higher the volatile (toluene) content, the stronger the reaction is. In this pre-catalyzing method, toluene was used as the solvent and diluent. Its content in the fabric depends on the drying time after pre-catalyzing operation has been performed. This experiment can prove that eliminating the content of volatile by increasing the drying time of fabric can get rid of the peak exotherm and temperature gradient.

Even though this experiment (Exp-3) can eliminate the peak exotherm, the Interlaminar Shear Strength (ILSS) of samples is 16.7% lower than traditional pre-mixing method (Exp-1).

Effect of polystyrene layer (Exp-4)

Because the fabric is pre-catalyzed with polystyrene as the binder, and the vinyl ester resin cannot dissolve the polystyrene when hand lay-up procedure is being performed, there should be a layer of polystyrene existing between fiber and matrix. This can be proved by a simple experiment. The detail of this experiment is described in Section 4.1.1.3. As a result, this layer of polystyrene may make interface weaker than traditional pre-mixing method. The results of short beam shear test (Section 4.1.3) can prove this.

In order to improve the interlaminar properties, Exp-4 was performed. Figure 4-4 gives the result of 50-layer laminate made by pre-catalyzing method in which the amount of polystyrene in the catalyst solution was reduced (refer to formula II in Table 3-4).

Meanwhile, the molecular weight of the polystyrene was taken into account. In this experiment, the polystyrene with molecular weight of 250,000 g/mol was used instead of unknown polystyrene used in previous experiments, and the fabric was dried for 2 weeks after being pre-catalyzed. From this curve, it can be noticed that, like Exp-3 and Exp-4, no peak exotherm happened in the curing process, and no obvious temperature gradient was caused by polymerization reaction. In this experiment, the highest temperature was 22 ^{O}C which was occurred at T1, and the lowest temperature was 20^{O}C which occurred at T3. They are very near the ambient temperature with which the composite was cured. So, this experiment with formula II in Table 3-4 is still feasible to eliminate the peak exotherm and the temperature gradient. This experiment (Exp-4) can improve ILSS as compared to Exp-3, but it is still 12.8% lower than pre-mixing method (Exp-1) (refer to section 4.1.3).

Effect of thickness of composites (Exp-5 and Exp-6)

As we know, the exothermal reaction strongly depends on the thickness of the composite for traditional pre-mixing method. Previous experiments demonstrate that the pre-catalyzing technique definitely can restrain the exothermal reaction for 50-layer composites. In order to see if this pre-catalyzing method is still suitable for extra thick composites, 100-layer laminates were fabricated for further investigation.

Figure 4-5 gives the cure temperature profile of the 100-layer composite manufactured by pre-mixing method (Exp-5) for comparison with the other 100-layer composite made by pre-catalyzed fabric technique. In this figure, it can be observed that the polymerization was initiated at 170 minutes after the resin system was mixed (refer to

Table 3-3). Then, the reaction temperature went up very rapidly, and 20 minutes later, it reached the highest point. After that, the temperature decreased gently. The highest peak temperature (88 ^{O}C) happened at point T3 and T4 which were at the middle layer (refer to figure 3-6), and the lowest temperature (76 ^{O}C) happened at point T6 which was near the top layer and the side edge. The temperature difference between the highest and the lowest is 12 ^{O}C. So, the high exothermal temperature and large temperature gradient were caused by pre-mixing method.

Comparing this experiment with Exp-1 (pre-mixing method for 50-layer laminate), it can be found that its peak temperature (88°C) is les than Exp-1 (104°C). Normally, the thicker the laminate, the higher the exothermic temperature is. However, due to the low resin content (32.3%) compared with Exp-1 (40.3%), the exothermic reaction of Exp-5 was not as violent as Exp-1. So, its peak temperature is lower.

Figure 4-6 shows the cure temperature profile or 100-layer composite manufactured by pre-catalyzing method (Exp-6). Before resin was applied, the fabric had been pre-catalyzed with Formula I in Table 3-4, and dried for 2 weeks. From this curve it can be seen that no obvious initial polymerization point can be found and a small peak of temperature (30°C) can be observed around 175 minutes after resin was applied. The difference between the highest and lowest peak temperature (24°C) is 6°C. But at 50 minutes, this temperature difference has already appeared, and no gel happened at this time. So, like experiment No. 3, no peak exotherm happened and no temperature gradient was caused by exothermal reaction was caused. So, it can be concluded that,

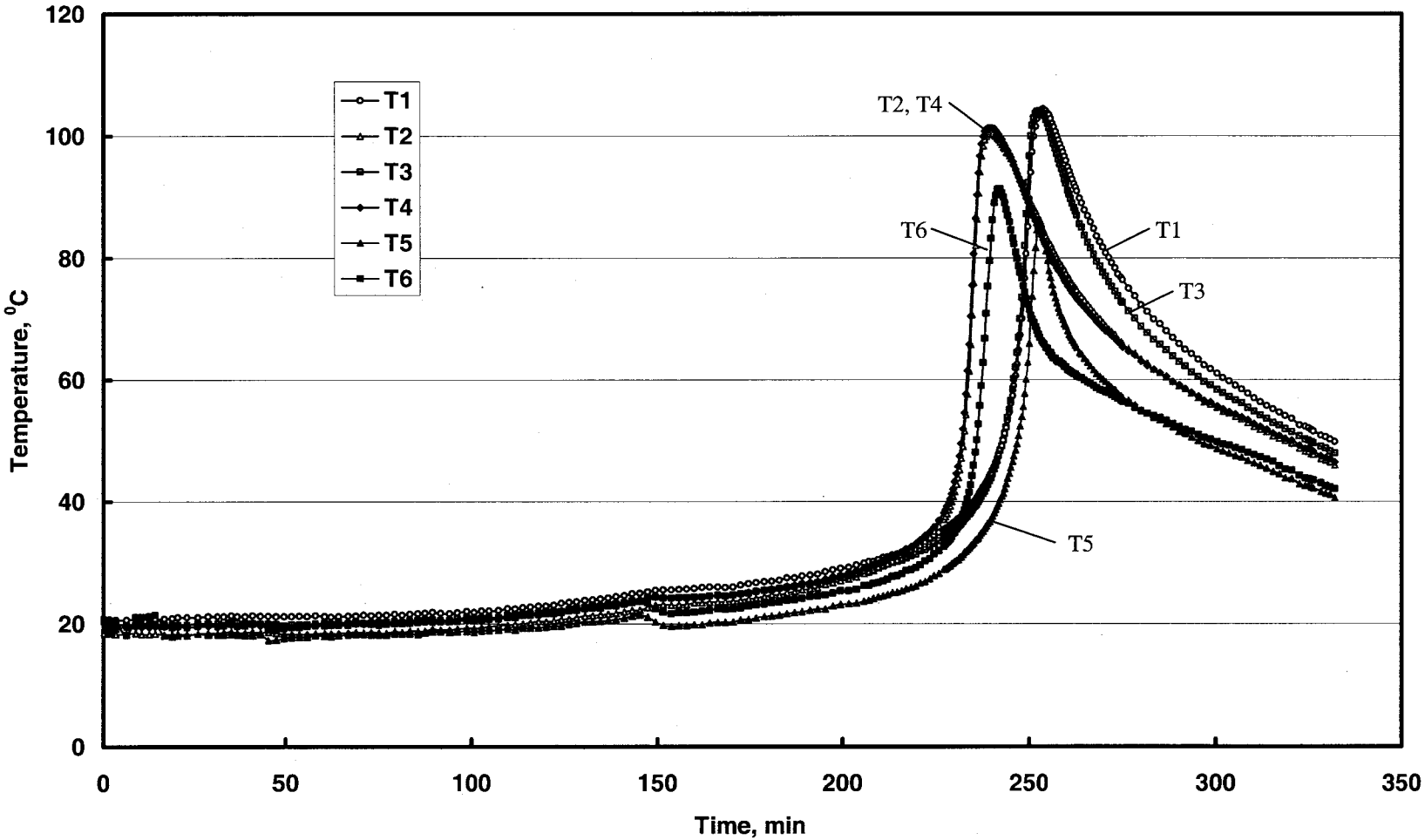


Figure 4-1: Exp-1: Temperature profile of 50-layer composites manufactured by pre-mixing method

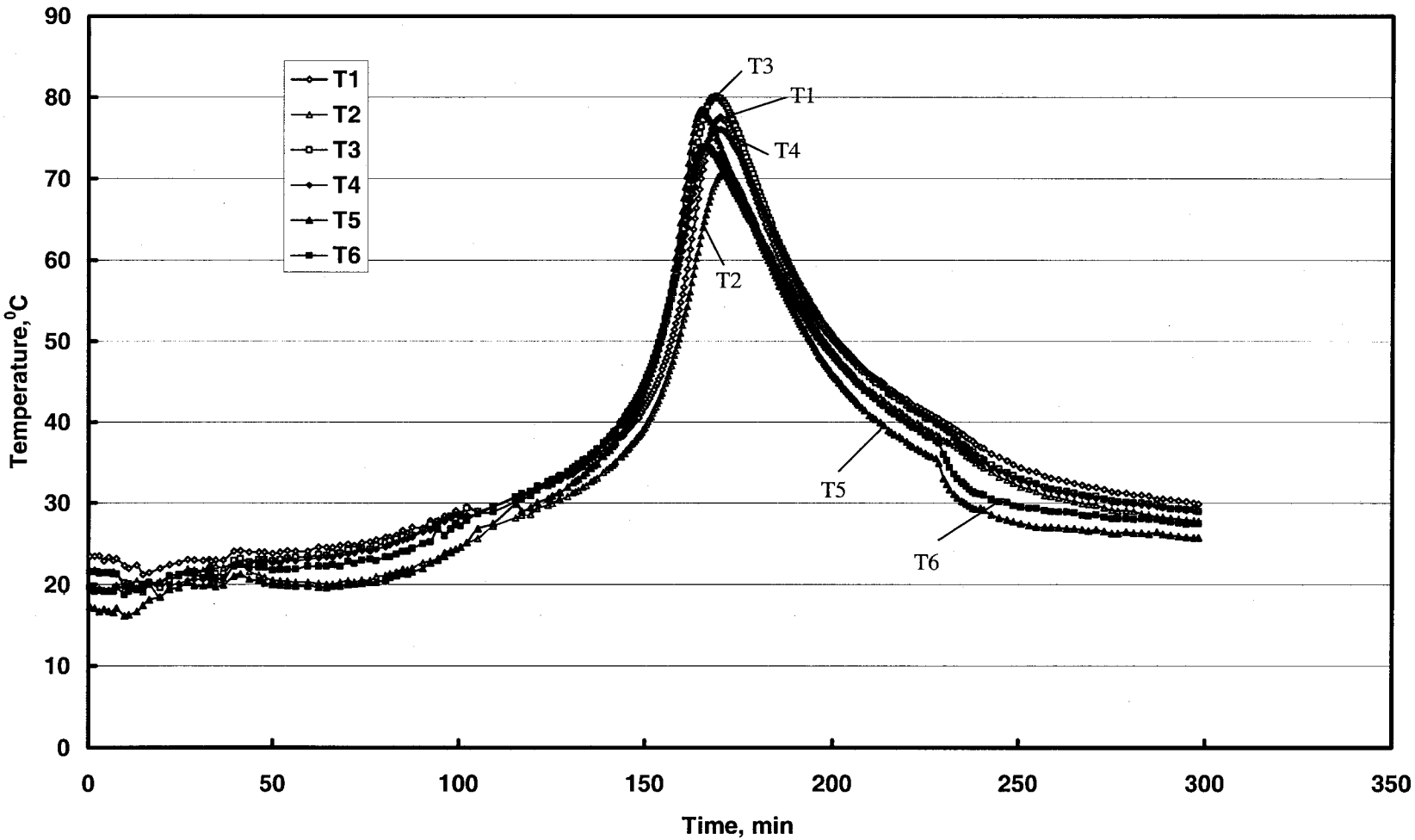


Figure 4-2: Exp-2: Temperature profile of 50-layer composite manufactured by pre-catalyzing method (The fabric was pre-catalyzed according to table 3-4 Formula I and dried for 3 days)

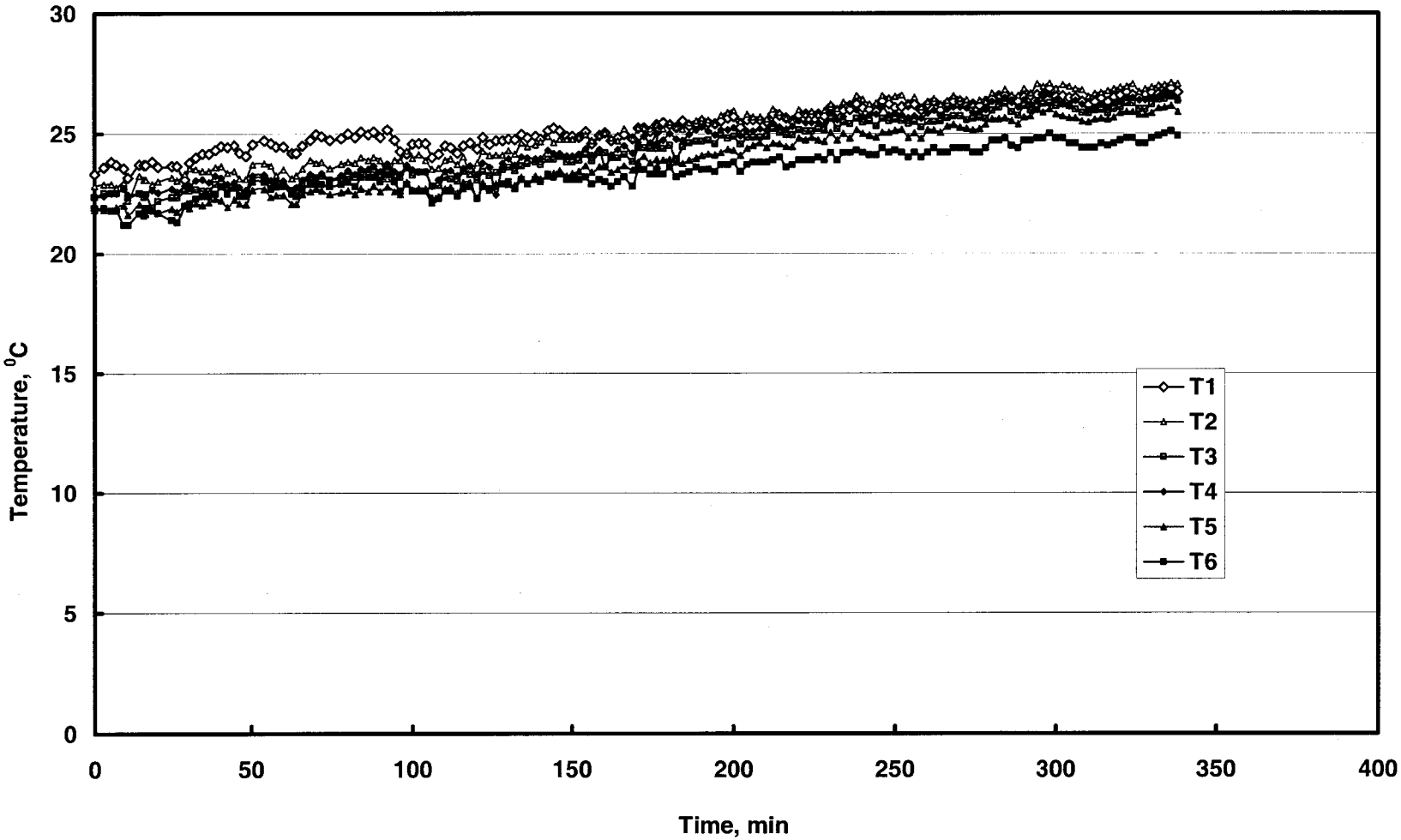


Figure 4-3: Exp-3: Temperature profile of 50-layer composite manufactured by pre-catalyzing method (The fabric was pre-catalyzed according to table 3-4 Formula I and dried for two weeks)

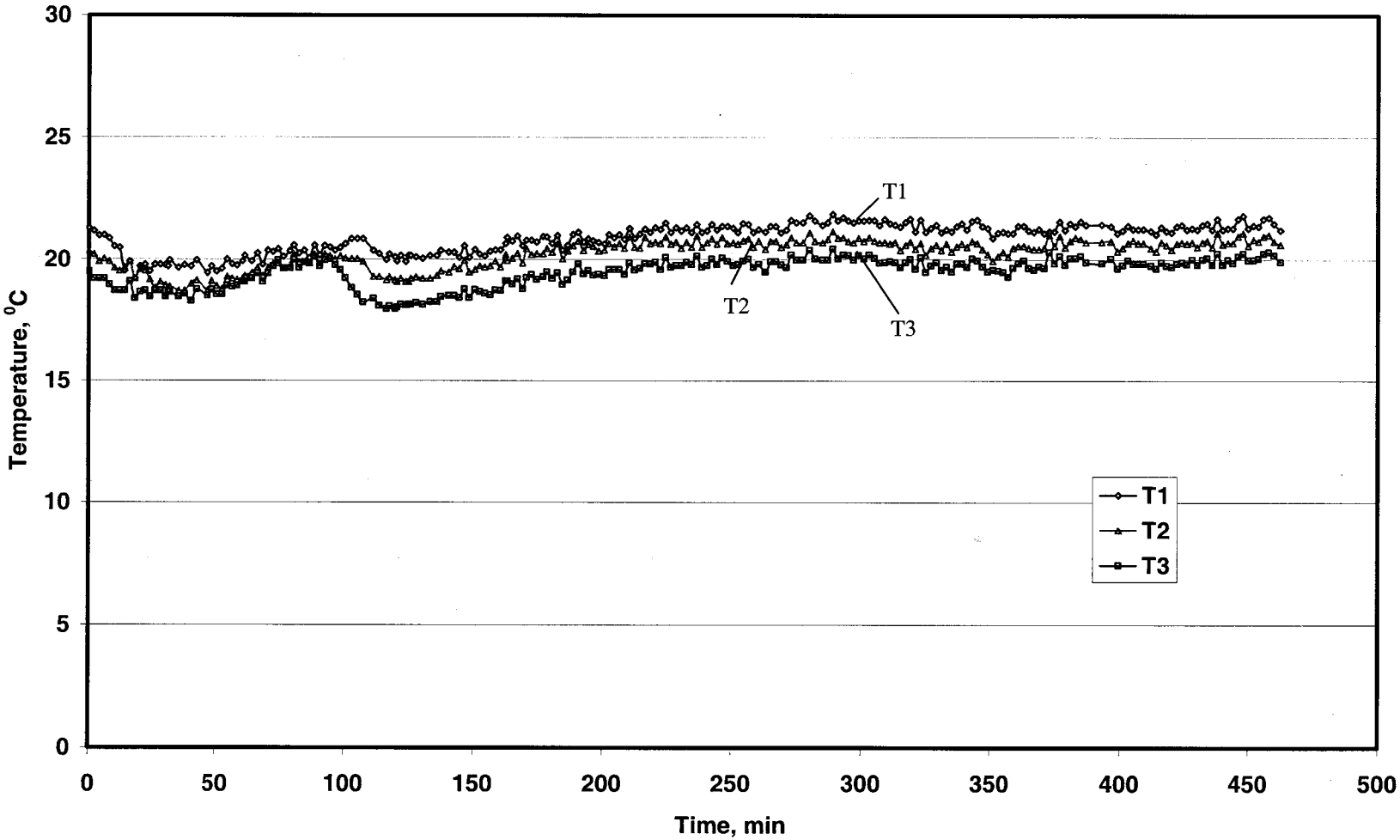


Figure 4-4: Exp-4: Temperature profile of 50-layer composite manufactured by pre-catalyzing method (The fabric was pre-catalyzed according to table 3-4 Formula II and dried for two weeks)

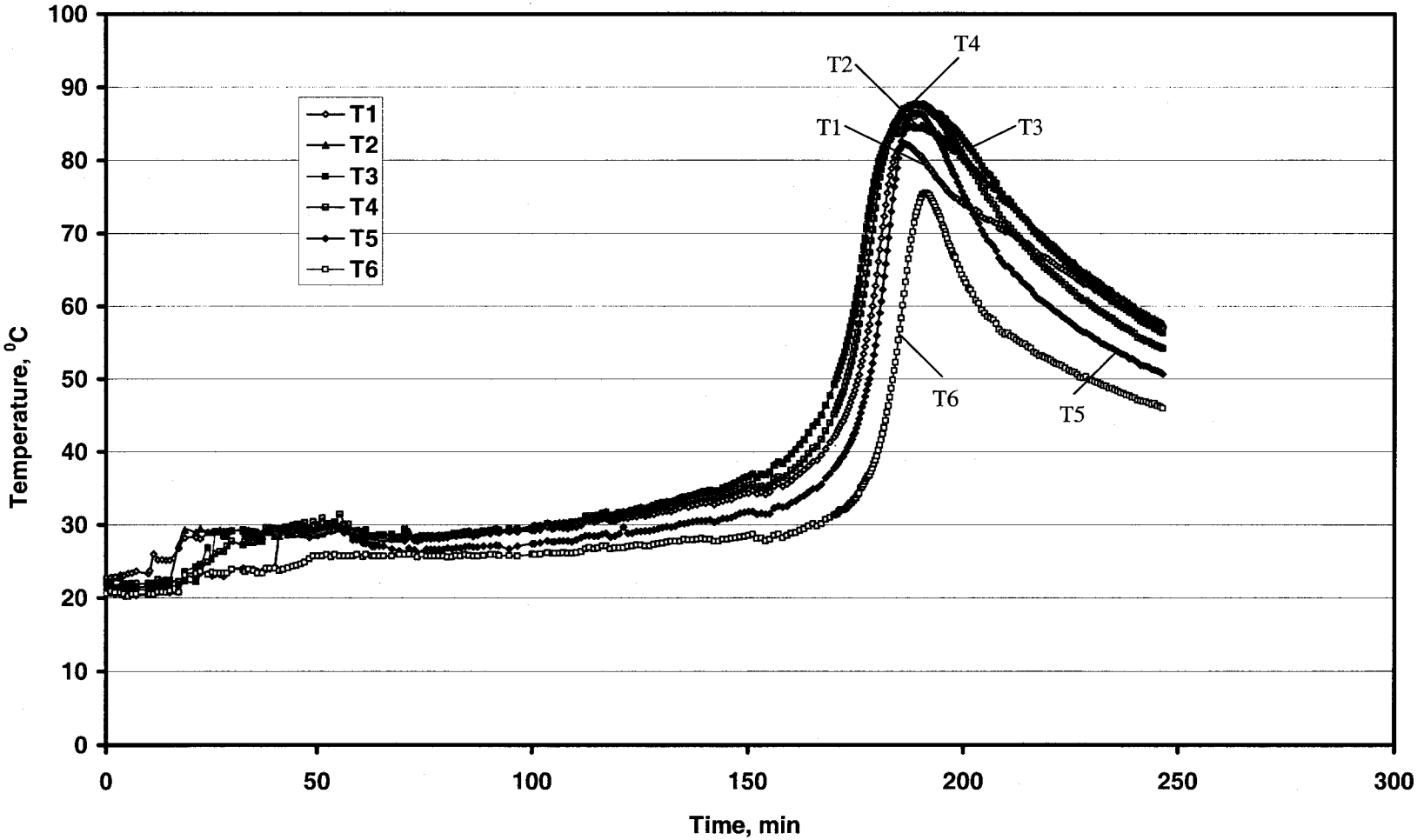


Figure 4-5: Exp-5: Temperature profile of 100-layer composites manufactured by pre-mixing method

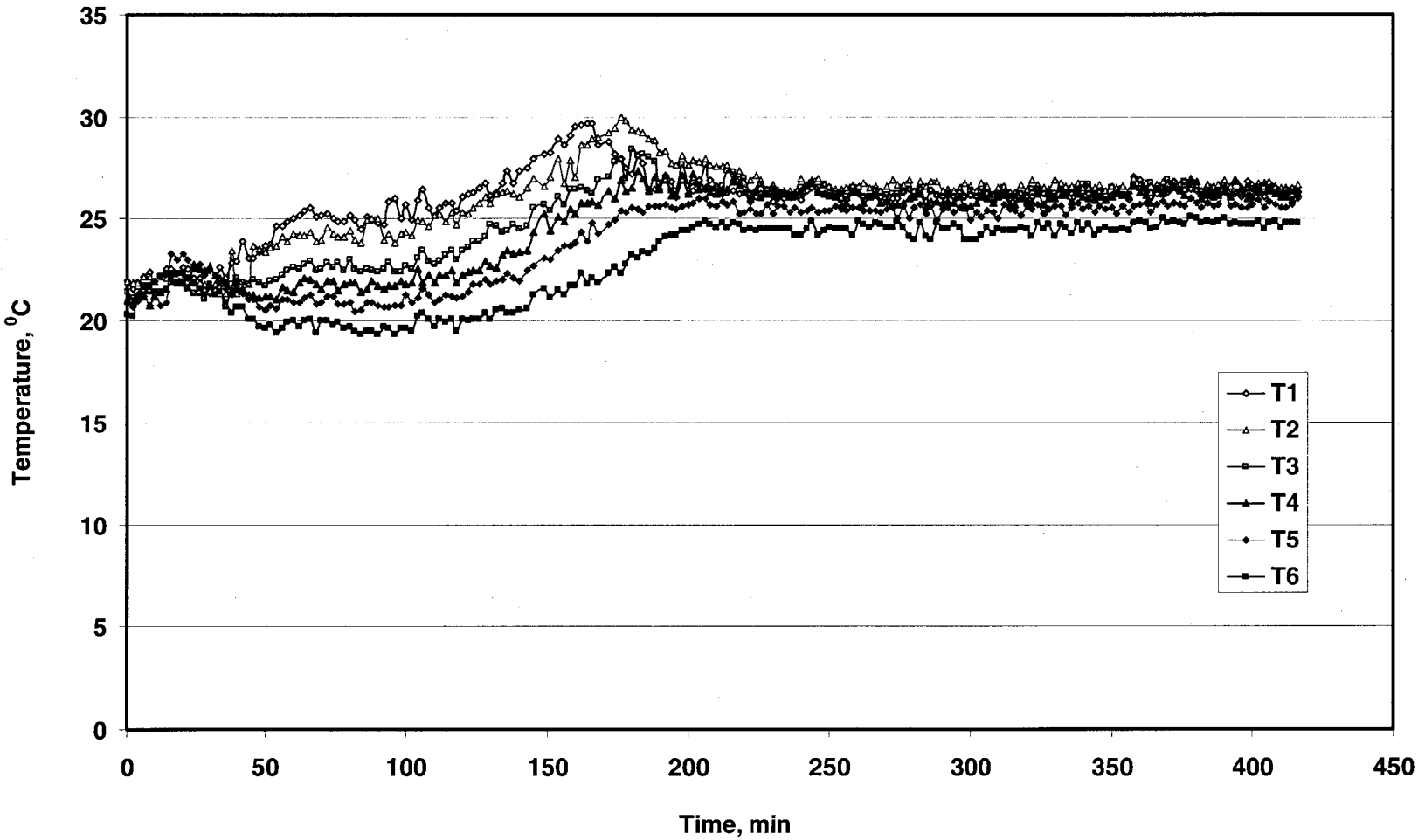


Figure 4-6: Exp-6: Temperature profile of 100-layer composite manufactured by pre-catalyzing method (The fabric was pre-catalyzed according to table 3-4 Formula I and dried for two weeks)

with pre-catalyzing technique, the polymerization reaction is independent of the thickness of the laminate even though its cross section is extra large

4.1.1.2 Discussion and Analysis of Exothermic Reaction for Pre-mixing Method

In traditional manufacture process of glass/vinyl ester composites, resin and catalyst are well pre-mixed together before being used, and the catalyst is equally distributed in the bulk resin system. The polymerization is initiated after a certain time when the catalyst is added. The chemical structure of a typical vinyl ester has been shown in figure 3-2. It can be noted that the location of the reactive sites are positioned only at the ends of the molecular chains. Figure 4-7, compared with Figure 3-2, can clearly represent the molecular chains of vinyl ester of which the reactive sites can been seen obviously, where "B" indicates the reactive sites in the molecule.

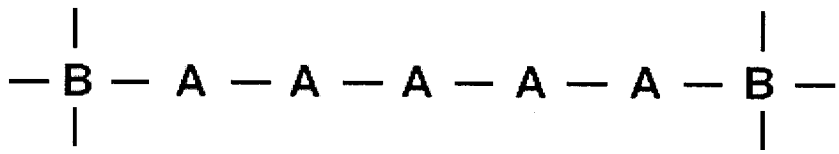


Figure 4-7: Schematic representation of vinyl ester resin (uncured)

With the addition of styrene "S", and in the presence of a catalyst, the styrene cross links the vinyl ester chain at each of reactive sites to form a highly complex three-

dimension network as represented in figure 4-8. In this process, peroxide catalyst does not take part in the chemical reaction but simply activates the process.

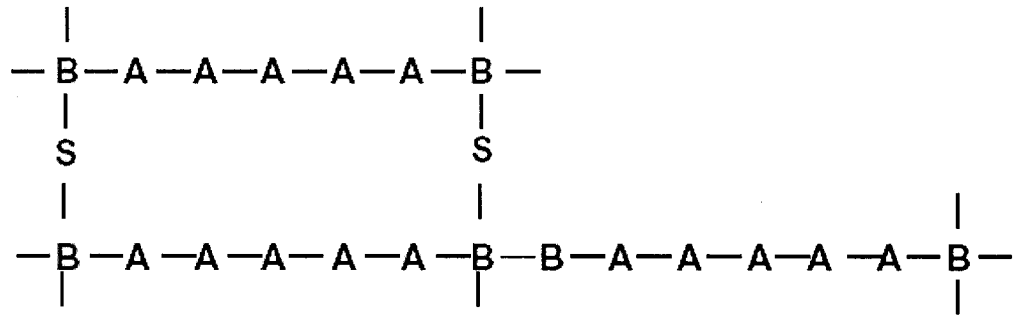


Figure 4-8: Schematic representation of vinyl ester resin (cured)

The free radical crosslinking reaction of styrene-based thermoset is a highly exothermic process. Due to the uniform distribution of the catalyst in bulk resin system, this reaction simultaneously happens everywhere. As a result, a large amount of heat is generated, and this heat usually accelerates the addition polymerization, and more heat is produced again. This exothermal characteristic of styrene-based resin may lead to large temperature gradient and thermal spiking at the center of thick cross-section composites due to their insulating nature. That is why the peak temperatures at the center are higher than at the edge (figure 4-1 and 4-5).

In this study, several pre-mixing experiments using pure resin system (without reinforcement) were performed to examine the exothermic reaction by adjusting the ingredients of resin system.

The 250g vinyl ester resin is used in each experiment. The resin system contains Derakane 411-350 vinyl ester resin, promoter CONAP, accelerator MEKP, retarder 2,4-P and catalyst MEKP. Table 4-1 gives ingredients of resin system for each experiment.

Table 4-1: Ingredients of resin system for pre-mixing experiments

Experiment \ Ingredients		Derakane 411-350	DMA	CONAP	2,4-P	MEKP
#A	Ratio (phr*)	**100**	**0.03**	**0.17**	**0.07**	**1.18**
	Amount (g)	250	0.077	0.425	0.178	2.98
#B	Ratio (phr)	**100**	**0.01**	**0.17**	**0.07**	**1.18**
	Amount (g)	250	0.026	0.425	0.18	2.99
#C	Ratio (phr)	**100**	/	**0.17**	**0.07**	**1.18**
	Amount (g)	250	/	0.424	0.178	3.016
#D	Ratio (phr)	**100**	/	**0.07**	**0.07**	**1.18**
	Amount (g)	250	/	0.206	0.176	2.957
#E	Ratio (phr)	**100**	/	/	**0.07**	**1.18**
	Amount (g)	250	/	/	0.18	2.98

*: phr: per hundred part of resin

The formula of resin system for Experiment #A is exactly same as traditional pre-mixing hand lay-up experiment (Exp-1), in which the ratio of accelerator DMA is 0.03%, and ratio of promoter CONAP is 0.17% (Table 3-3). Experiment #B was performed by reducing DMA from 0.03% to 0.01%. In experiment #C, the content of DMA was eliminated. Experiment #D eliminated DMA, and content of CONAP was decreased from

0.17% to 0.07%. In experiment #5, both DMA and CONAP were not added in the resin system.

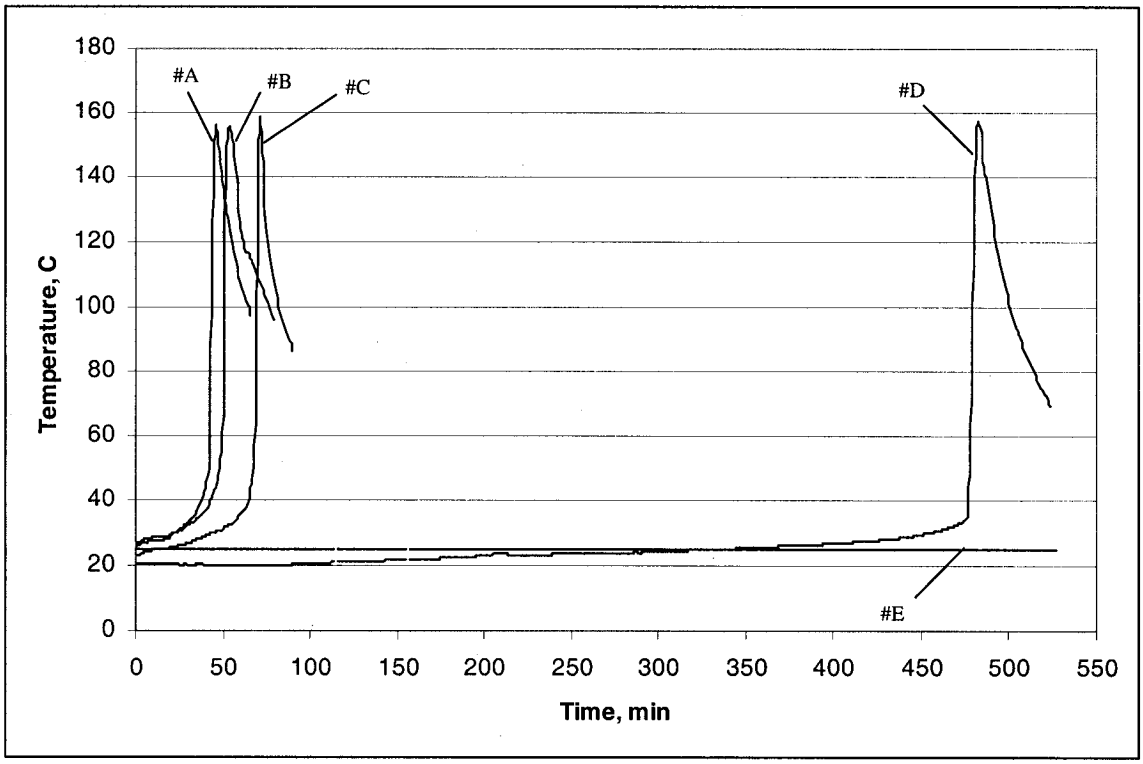


Figure 4-9: Reaction temperatures of pre-mixing experiments

Figure 4-9 presents the results of polymerization reactions for these experiments. It can be observed that experiment #A, #B and #C have the same exothermic peak temperature (near 160°C), but peak temperature of experiment #C (no DMA in resin system) occurred 28 minutes later than experiment #A (the ratio of DMA is 0.03%). So, less or no DMA in resin system can delay the exothermic reaction, but it can not decrease the peak temperature. The exothermic peak temperature of #D occurred more than 400 minutes later than #A, #B and #C. That is because the content of CONAP was decreased from 0.17% to 0.07%. However, the long curing process of experiment #D did not affect the peak temperature which was high up to 157°C. It is obvious that decrease of CONAP

has significant influence in delay of the exothermic reaction, but it has no influence in reducing the peak temperature. The temperature profile of experiment #E shows that no polymerization occurred within 500 minutes when DMA and CONAP were eliminated.

So, with pre-mixing method, it can be concluded that it is difficult to reduce the exothermic temperature by adjusting the content of ingredients in the resin system.

4.1.1.3 Discussion and Analysis of Reaction Mechanism for Pre-catalyzing Method

It is obvious that pre-catalyzed fabric technique can restrain the exothermal reaction effectively. There are three implications. First, the peak temperature, compared with traditional pre-mixing method, can be almost eliminated (Figure 4-3, 4-4 and 4-6). Second, between the center and the edge, no large temperature gradient, which usually happens at thick-section composite curing, can be found. This can be shown in Figure 4-3, 4-4 and 4-6. Third, the total cure time of pre-catalyzing method is longer than pre-mixing method. In order to understand why the pre-catalyzing method can achieve such a significant result of eliminating exothermal reaction, the mechanism of reaction is investigated in this section

Pre-catalyzing technique can significantly restrain the exothermal reaction. With this technique, the cross linking reaction happens gradually from the surface of fabric to the resin layer. This phenomenon can be observed from a simple experiment described as follows.

First, the catalyst solution with 1g MEKP, 1g polystyrene and 20g toluene was mixed according to Formula I in Table 3-4 (See figure 4-10 (a)). Next, after the toluene dissolved the polystyrene totally, the beaker with catalyst solution was put under the fume hood for more than two weeks in order to make the toluene evaporate completely, and a layer of polystyrene film with entrapped MEKP was left (Refer to figure 4-10 (b)). Last, 50g resin system mixed according to the proportions in Table 3-3 (no MEKP added) was put into the beaker (Refer to figure 4-10 (c)).

From this experiment it could be observed that, after resin was put into the beaker for a while, the polystyrene film became soft because the styrene monomer could dissolve the polystyrene (refer to Figure 4-10 (d)). However, after a period of time, it could be found that this polystyrene film became hard because the vinyl ester resin came into contact with the catalyst MEKP diffused from softened polystyrene, and the polymerization occurred on the surface of polystyrene film. After the cure process was finished, the final thickness of cured resin was about 2mm. This cure thickness can definitely be suitable for the application of this technique in laminating process because the thickness of each layer of laminate (for 18 oz/yd^2 glass roving fabric) is only 0.7 mm which includes the thickness of fabric. Figure 4-11 shows the cure temperature profile for this experiment. It can be shown that the cure temperature increased to 26°C from ambient temperature 23°C at 160 minutes, and a little exothermic peak can be observed. Due to the very low peak temperature (26°C), it can be considered that no peak exotherm occurred in this experiment.

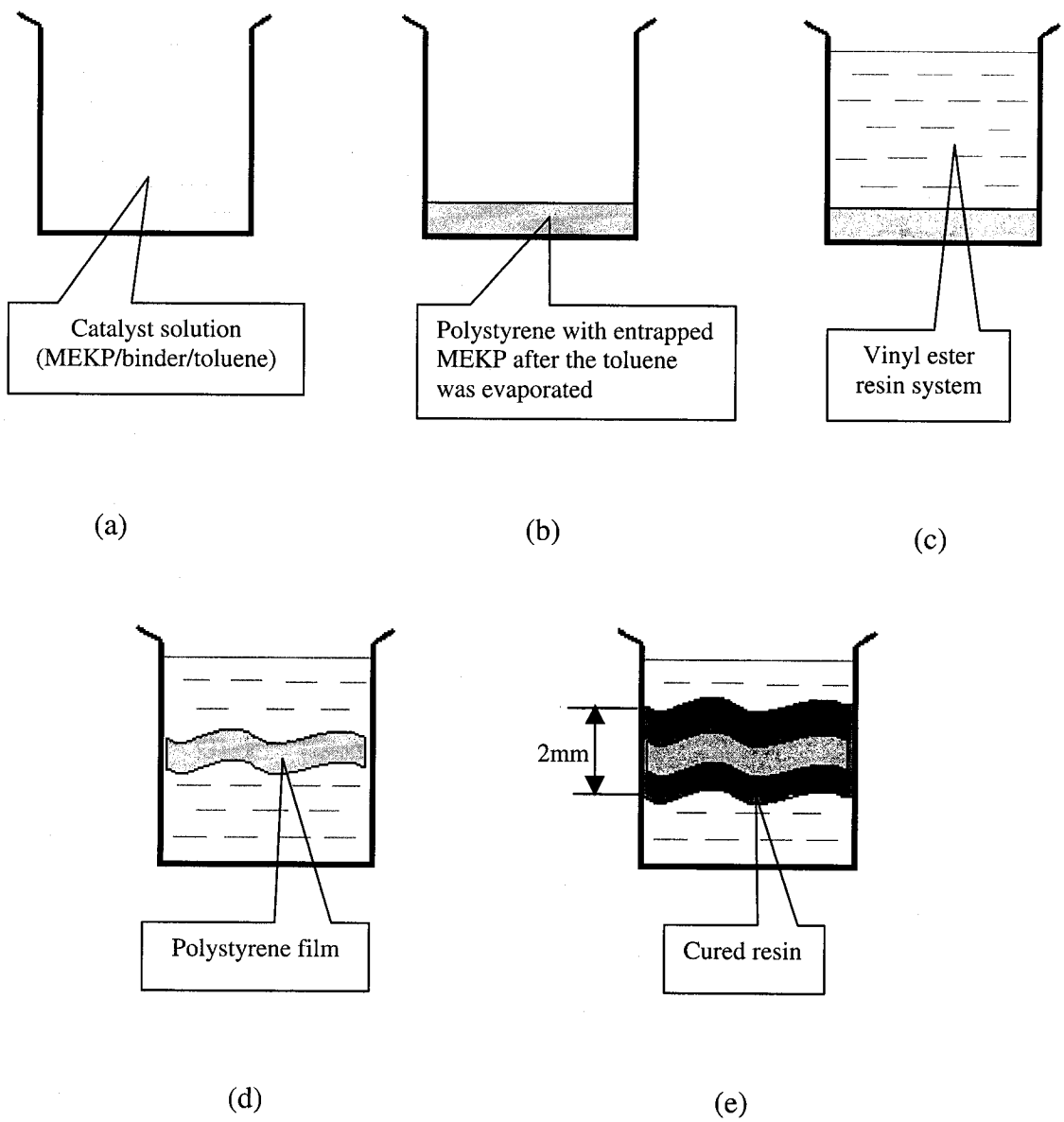


Figure 4-10: Pre-catalyzing experiment for 50g vinyl ester resin using polystyrene binder

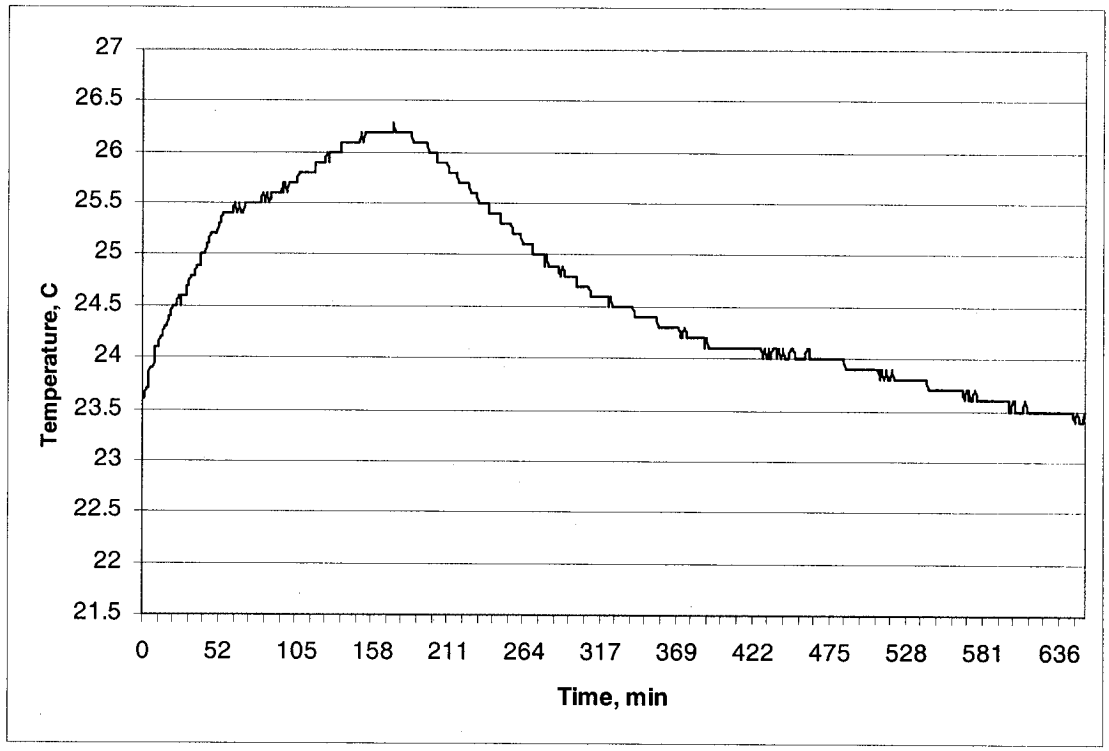


Figure 4-11: Cure temperature of 50g vinyl ester resin with pre-catalyzing method

Compared with another experiment of which the 50g resin system was mixed according to the proportion in Table 3-3, and 1.18% MEKP was added, it could be observed that the exothermic peak temperature was above 130°C when the resin system was cured at ambient temperature. Figure 4-12 shows the cure temperature profile of this experiment with which the pre-mixing method was used.

From two experiments it can be clearly seen that the pre-catalyzing technique can achieve significant result of reducing the exothermic temperature. Further explanation can be described as follows.

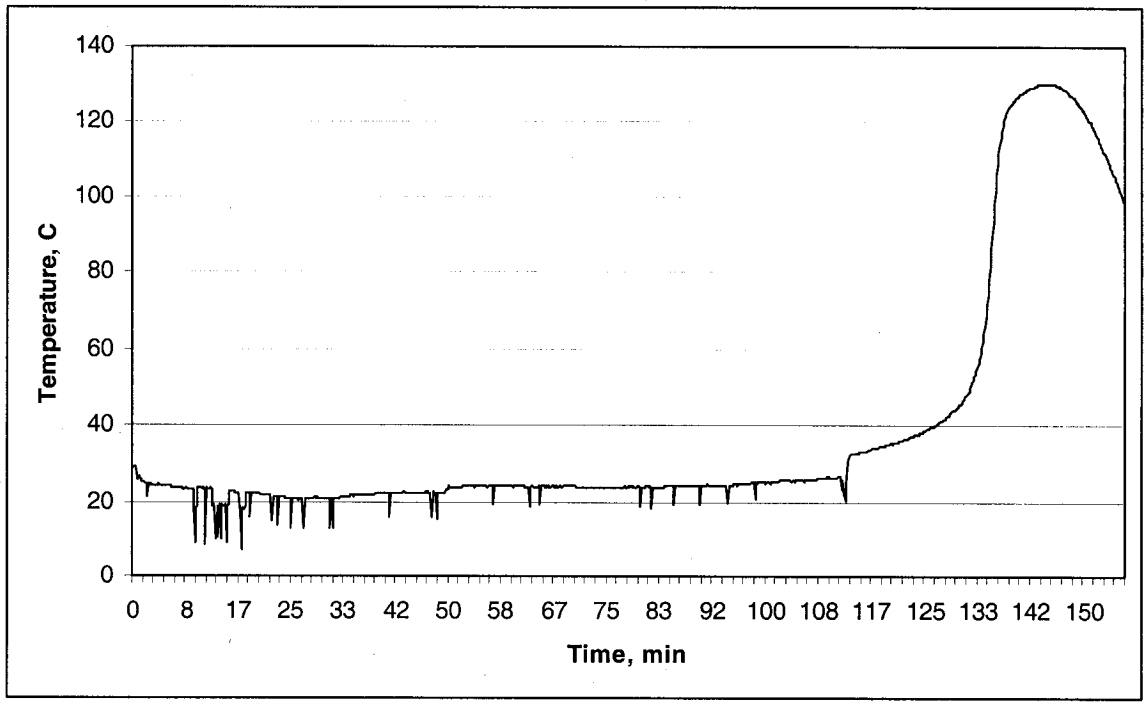


Figure 4-12: Cure temperature of 50g vinyl ester resin with pre-mixing method

When vinyl ester resin system is applied on the surface of polystyrene (figure 4-13 (a)), the styrene monomer (RO-) starts to dissolve the polystyrene, and the polystyrene layer becomes soft. Then, the catalyst escapes from the polystyrene layer, and diffuses to the resin layer under external pressure which can help diffusion fast by increasing the movement of polystyrene molecule (figure 4-13 (b)). Diffusion occurs because of the random movement of molecules of the substance which allows them to separate from one another. The greater the space between these molecules, the greater the ability for the molecular particles to spread out from one another. The more packed the molecules are in the substance, the less space to maneuver, and therefore, the more difficult for diffusion

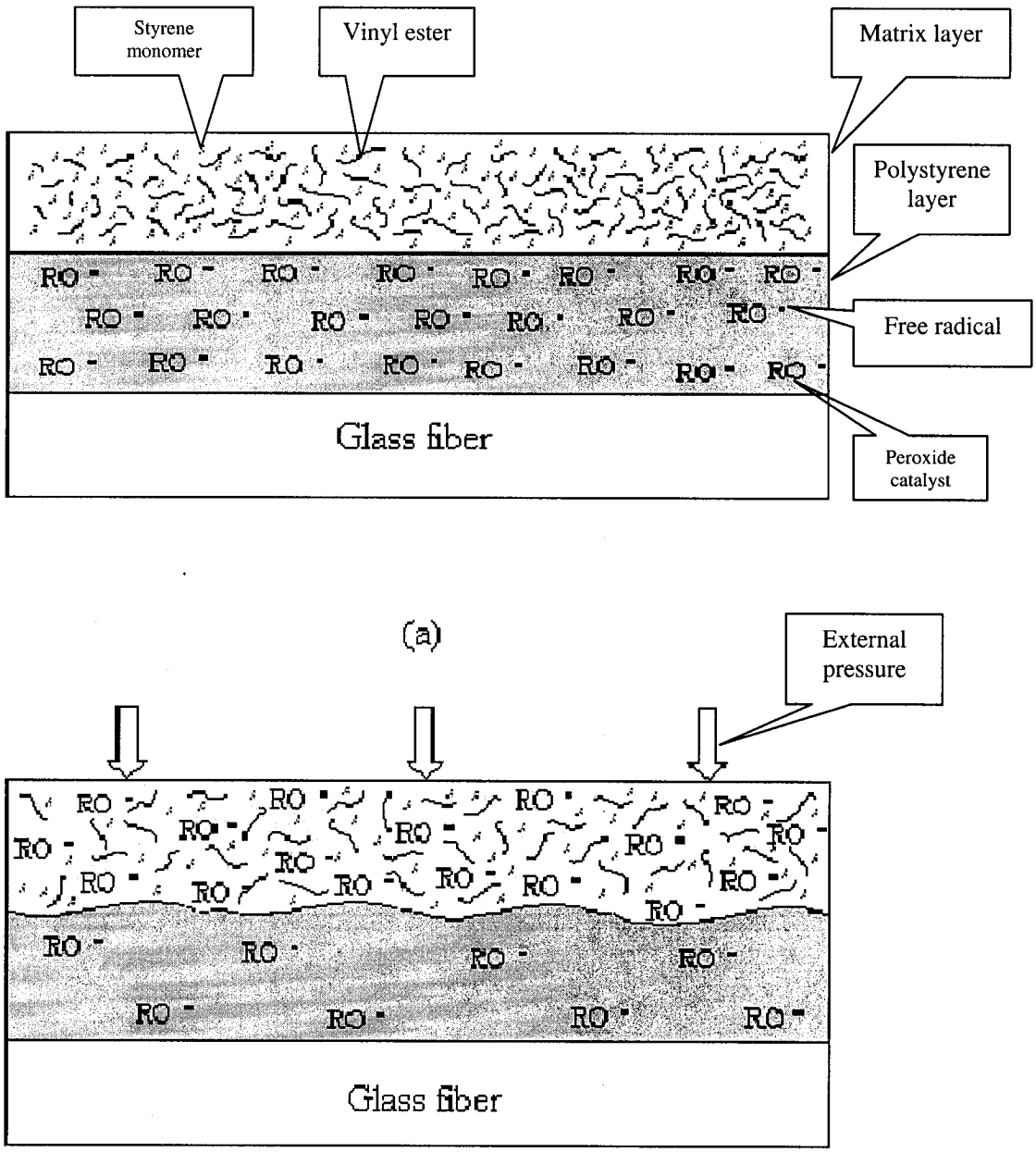


Figure 4-13: Sketch of the initiation process of the pre-catalyzing method with the polystyrene as the binder

to occur. In this study, polystyrene has long molecular chain, and packed tightly, so the particles of catalyst MEKP entrapped in polystyrene are not capable of diffusing very rapidly. Due to the low diffusion rate, the polymerization is initiated in a gradual manner, so no obvious initiation point can be found in Exp-3, Exp-4 and Exp-6 (Figures 4-3, 4-4 and 4-6), and the exothermic phenomenon cannot be observed. Furthermore, the operation of resin application for the 50-layer laminate needs about 45 minutes, so the polymerization reaction should happen 45 minute earlier for the first layers than the last layer. In this process, due to the different time of reaction for different layers, it is difficult for the initiation point of reaction to be observed from the curves of the temperature profiles (figures 4-3, 4-4 and 4-6). In general, whether from the point of view of microstructure (individual layer) or macrostructure (the whole laminate), the polymerization reaction happened in a gentle manner rather than the fierce reaction that happened simultaneously in laminates fabricated with traditional pre-mixing method. Therefore, no obvious initiation points can be found and no peak exotherm happened with the pre-catalyzing technique.

Figure 4-2 shows that exothermic reaction that occurred in Exp-2 even though the pre-catalyzing technique was used. The peak temperature was 18°C lower than pre-mixing method, but still much higher than Exp-3, Exp-4 and Exp-6 in which the pre-catalyzing technique was used also. Comparing the manufacture process of Exp-2 with Exp-3, Exp-4 and Exp-6, it can be found that the key factor which influences the exothermic reaction is the drying time after the fabric was pre-catalyzed. In Exp-2, the fabric was dried for 3 days after being pre-catalyzed, but in Exp-3, Exp-4 and Exp-6, the drying tine was 2 weeks. In Section 3.3.1, it has been described that toluene in the

catalyst solution, compared with other solvent, is an excellent solvent which is used to dissolve the polystyrene pellets, and it is also used to dilute the catalyst solution in order to make MEKP and polystyrene distribute among the fabric equally. As we know, solvent strongly influences the mechanical properties of composites because it can produce voids inside composites during the curing process. So, it is better to limit the content of volatile to as low as possible. On the other hand, the existence of toluene in the pre-catalyzed fabric softens polystyrene, and part of polystyrene is still in dissolved state. In this case, the MEKP could not be entrapped in the polystyrene tightly or bound on the fabric surface tightly. As a result, when the resin is applied, it was very easy for MEKP to escape from the polystyrene layer, and initiate the free radical of the vinyl ester in a fast pace. This reaction should be stronger in Exp-2 than Exp-3, Exp-4 and Exp-6. The initiation point of reaction and the peak of exothermic temperature can be clearly observed from Figure 4-2.

From above discussion, it can be concluded that pre-catalyzing technique can significantly reduce the exothermic temperature. Several factors in this technique play important roles. First, polystyrene can allow MEKP to gradually escape from it to the vinyl ester resin layer because it takes time for styrene to dissolve the polystyrene. Next, the existence of toluene in the pre-catalyzed fabric cannot decrease the exothermic temperature effectively because it makes polystyrene layer soft, so the MEKP can escape from this layer easily. Furthermore, unlike the traditional bulk mixed catalyst and resin method, in pre-catalyzing technique, the polymerization reaction happens earlier for the first layers than the later ones because no catalyst is mixed in the bulk resin system, and

polymerization reaction can occur only when the resin is applied on the surface of pre-catalyzed fabric. This process can also reduce the exothermic temperature.

4.1.2 Comparison and Discussion of Cure Degree with DSC Results

The cure reaction of Derakane 411-350 vinyl ester resin is initiated by adding small quantities of catalyst MEKP, and the decomposition rate of MEKP can be increased by adding small amount of accelerator CONAP when the resin is cured at room temperature. Normally, post cure at 93^0C is recommended by the supplier to achieve complete cure. However, some large parts, such as big tanks and reservoirs, cannot experience the post cure because of the size limit of facilities.

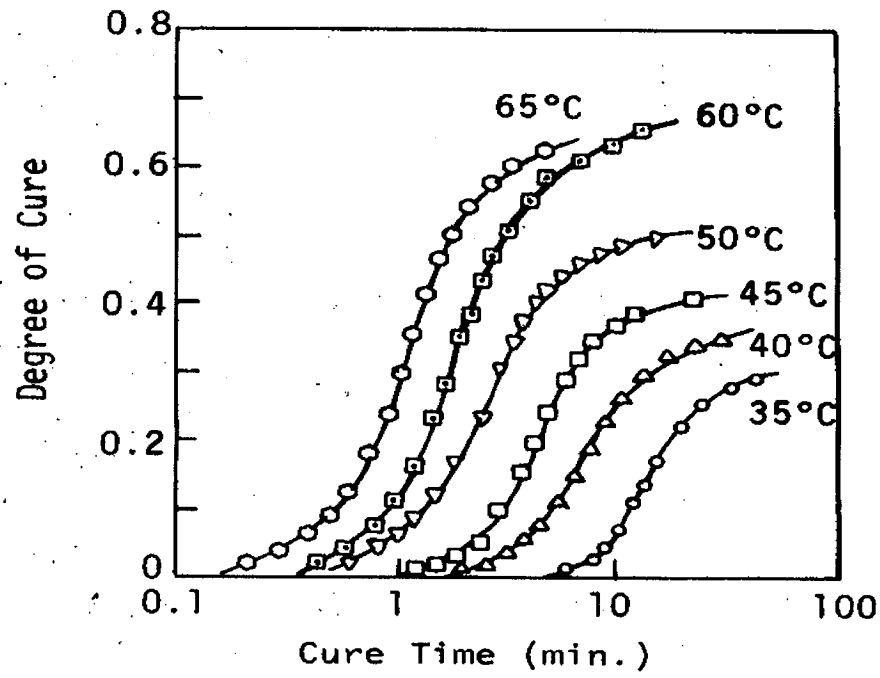


Figure 4-14: Degree of cure for a vinyl ester resin at various cure temperatures [33]

As we know, the degree of cure increases with both time and temperature. Figure 4-14 shows a number of curves relating the degree of cure to cure time for a vinyl ester resin at various cure temperature [33]. Due to the decrease of reaction temperature when pre-catalyzing method is used, the degree of cure should be investigated to examine how much it is influenced by the process method, or how long it can reach the same degree of cure achieved by pre-mixing method.

The degree of cure α_{DOC} can be expressed as [34]:

$$\alpha_{DOC} = \frac{\Delta H_{\text{total}} - \Delta H_{residual}}{\Delta H_{total}} \qquad \text{(Equation 4-1)}$$

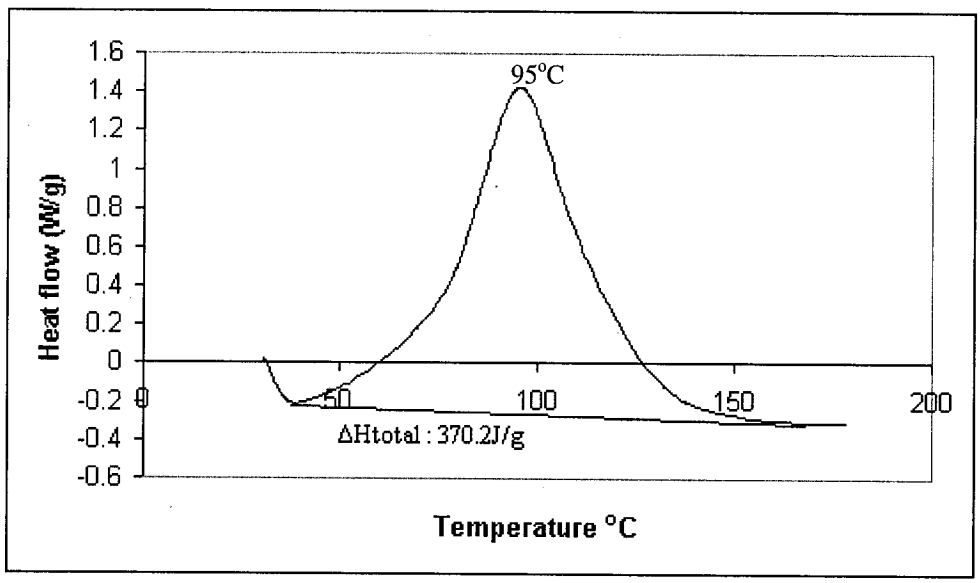


Figure 4-15: Thermal behavior of Derakane 411-350 vinyl ester resin system

ΔH_{total} represents the ultimate heat of reaction liberated per gram of uncured sample prepared according to Table 3-3 (the ingredient of pre-mixing method). ΔH_{total} is obtained from dynamic DSC measurement in which the temperature is increased uniformly. Figure 4-15 gives the thermal behavior of Derakane 411-350 vinyl ester resin system. In this figure, ΔH_{total} is equal to the area under the curve obtained in the dynamic heating experiment.

$\Delta H_{residual}$ represents the residual heat obtained from a composite sample. It should be noted that when DSC analysis is performed, the weight of samples cannot be used for analyzing because the weight of reinforcement is included. The real weight needed for DSC should be the resin weight in the composite sample. It can be simply calculated with the weight of composite sample multiplied by the resin content (Table 3-7).

In order to avoid large deviation of the degree of cure with time, it should be better to perform the DSC tests within 24 hours after the curing process was finished. Five samples of each laminate were uniformly taken from the panel's center along the cross section.

Figure 4-16 gives the DSC dynamic test results of 50-layer laminates (Exp-1, Exp-2, Exp-3 and Exp-4). The curve of Exp-1 shows that the samples fabricated by traditional pre-mixing method have the lowest residual heat flow $\Delta H_{residual}$ as compared to pre-catalyzing experiment Exp-2, Exp-3 and Exp-4. According to Equation 4-1, the lower the $\Delta H_{residual}$ is, the higher the degree of cure is. The average degree of cure of Exp-1 is 98.6% (Table 4-2), which is the highest compared with others. Also, it can be

observed that the center has higher degree of cure than the edges. This phenomenon was caused by the nature of high exothermal temperature and low heat conduction of thick composite. This non-uniform cure is harmful to composites because it can produce internal stress and cracks.

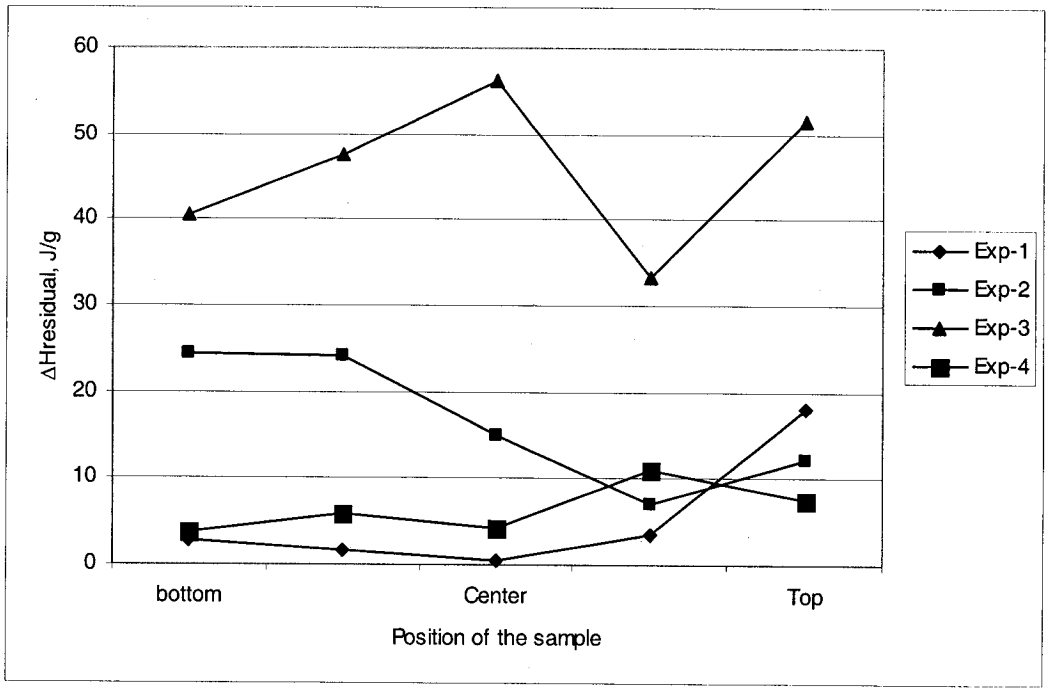


Figure 4-16: DSC results of 50 layer composites fabricated with pre-catalyzing method using polystyrene as the binder

Table 4-2: Average degree of cure

Experiment	Degree of cure (%)		
	Within 24 hours	**Post cure**	**Other condition**
Exp-1	98.6	99.8	/
Exp-2	95.6	99.8	99.97 (4 months)
Exp-3	87.6	99.98	98.4 (10 weeks)
Exp-4	98.3 (in 48 hours)	/	/
Exp-5	96	99.8	/
Exp-6	90	/	97.3 (5 weeks)

The curves of Exp-2, Exp-3 and Exp-4 have higher $\Delta H_{residual}$ than that of Exp-1. Compared with Exp-3, Exp-2 has lower $\Delta H_{residual}$ because it had higher exothermal temperature which was caused by the high content of volatile. Exp-3 had the highest $\Delta H_{residual}$ (or the lowest degree of cure) because no exothermal heat to accelerate the polymerization during the cure process. Even so, this degree of cure (87.6%) still can make the laminate rigid enough to handle and machine. Due to one more day delay to perform the DSC test, Exp-4 shows better cure property than Exp-2 and Exp-3 because the degree of cure increased with time. In the DSC tests for Exp-2, Exp-3 and Exp-4, no gradient of cure degree, which is higher in the center than at the edges, can be observed,

and their degrees of cure can be improved through post cure or extending the aging time of the laminates.

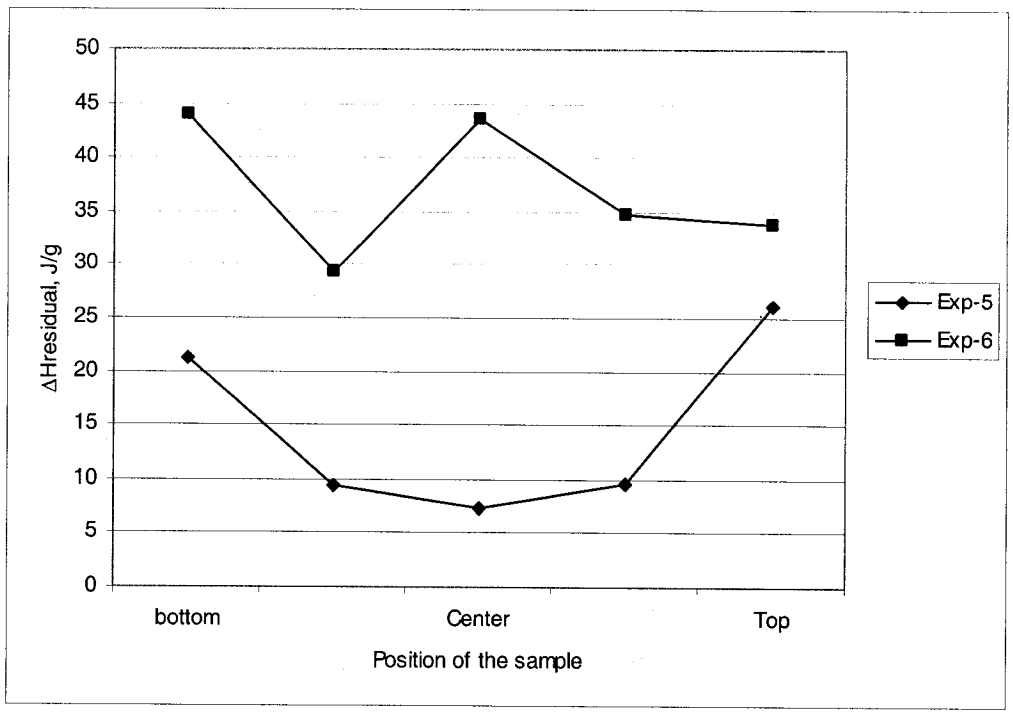


Figure 4-17: DSC results of 100 layer laminates

Figure 4-17 shows the DSC results of 100 layer laminates fabricated with both pre-mixing (Exp-5) and pre-catalyzing (Exp-6) methods. Obviously, due to the high exothermal temperature produced during the curing process, Exp-5 has lower $\Delta H_{residual}$ than Exp-6, and the cure degree at its center is higher than the edges. The gradient of cure degree existed in Exp-5 after the curing process.

The results of DSC measurement for post cured laminates of Exp-1, Exp-2 Exp-3 and Exp-5 are given in table 4-2. All the degrees of cure, whether for pre-mixing

experiment Exp-1 and Exp-5 or for pre-catalyzing experiment Exp-2 and Exp-3, reached more than 99.8%.

Figure 4-18 shows the DSC tests results for the samples from Exp-2, Exp-3 and Exp-6 which cure time was increased by leaving the laminates at room temperature for 4 months, 10 weeks and 5 weeks respectively after the hand lay-up processes had finished. Compared with pre-mixing experiment Exp-1, the sample from Exp-2 achieved higher degree of cure (99.97%) than Exp-1 (98.6%) after it was left for 4 months. The sample from Exp-3 was left for 10 weeks, but it still achieved almost same degree of cure with Exp-1. The degree of cure of Exp-6 is the lowest in this figure because it had only 5 weeks for waiting the DSC test, but it is satisfactory that its degree of cure is more than 97%.

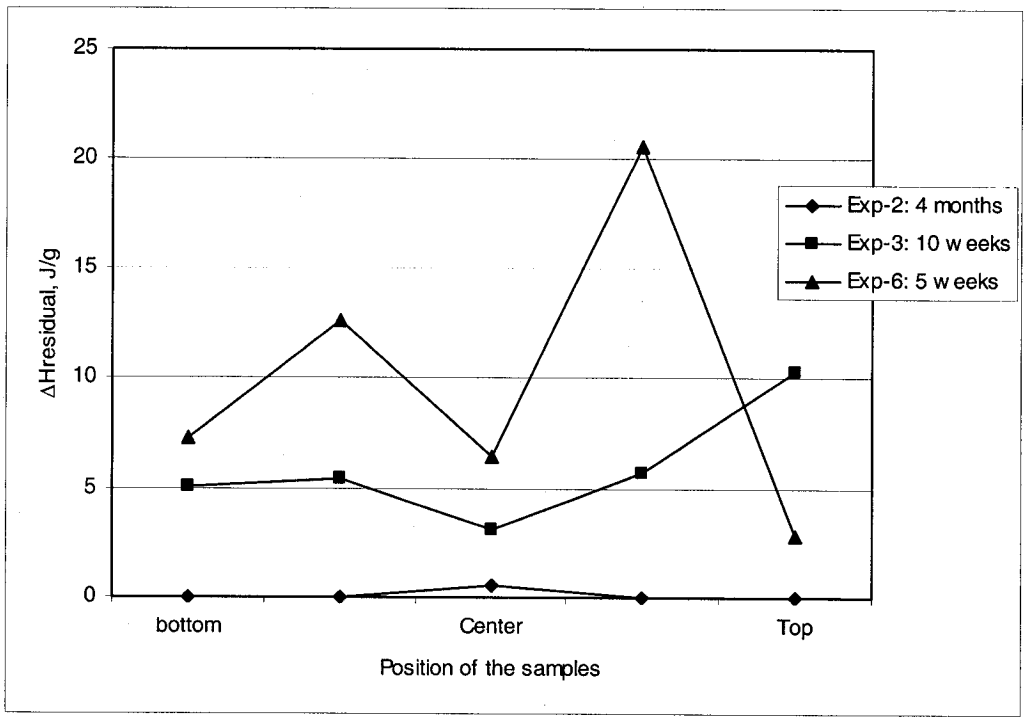


Figure 4-18: DSC results with increasing the cure time in room temperature

From the discussion of DSC results, it can be concluded that the thick-section composites fabricated with pre-catalyzing method have lower degree of cure than pre-mixing method, but it can be increased though the post cure or increasing the cure time at room temperature. The test result (Table 4-2) shows that the satisfactory degree of cure can be achieved by leaving the samples for five weeks.

4.1.3 Comparison And Discussion of The Interlaminar Shear Strength (ILSS)

It has been mentioned (Section 4.1.1) that the existence of polystyrene between the fiber and vinyl ester resin may degrade the interlaminar shear strength of composites. In this study, short beam shear (SBS) tests were used to evaluate the ILSS. It should be noted that all the samples prepared for SBS tests had endured the post cure before the tests were performed.

Figure 4-19 gives the SBS test results of Exp-1, Exp-3 and Exp-4. In each experiment, 50 layer fabrics were used, and three groups of sample were obtained from different positions of a laminate (top, center and bottom, refer to Figure 3-23). From Figure 4-19, it can be seen that even though a little differences exist among the ILSS values of top, center and bottom for each laminate, it is still difficult to figure our whether these differences depend on the thickness of the laminates. So, in this section, only average ILSS values are discussed. From this figure, it can be found that the ILSS of Exp-1 (pre-mixing experiment) is the highest as compared to Exp-3 and Exp-4 in which the pre-catalyzing method is used. The average ILSS of Exp-1 is 34.5MPa, and the average ILSS of Exp-3 is 28.5MPa, 17.4% lower than Exp-1. In order to improve the

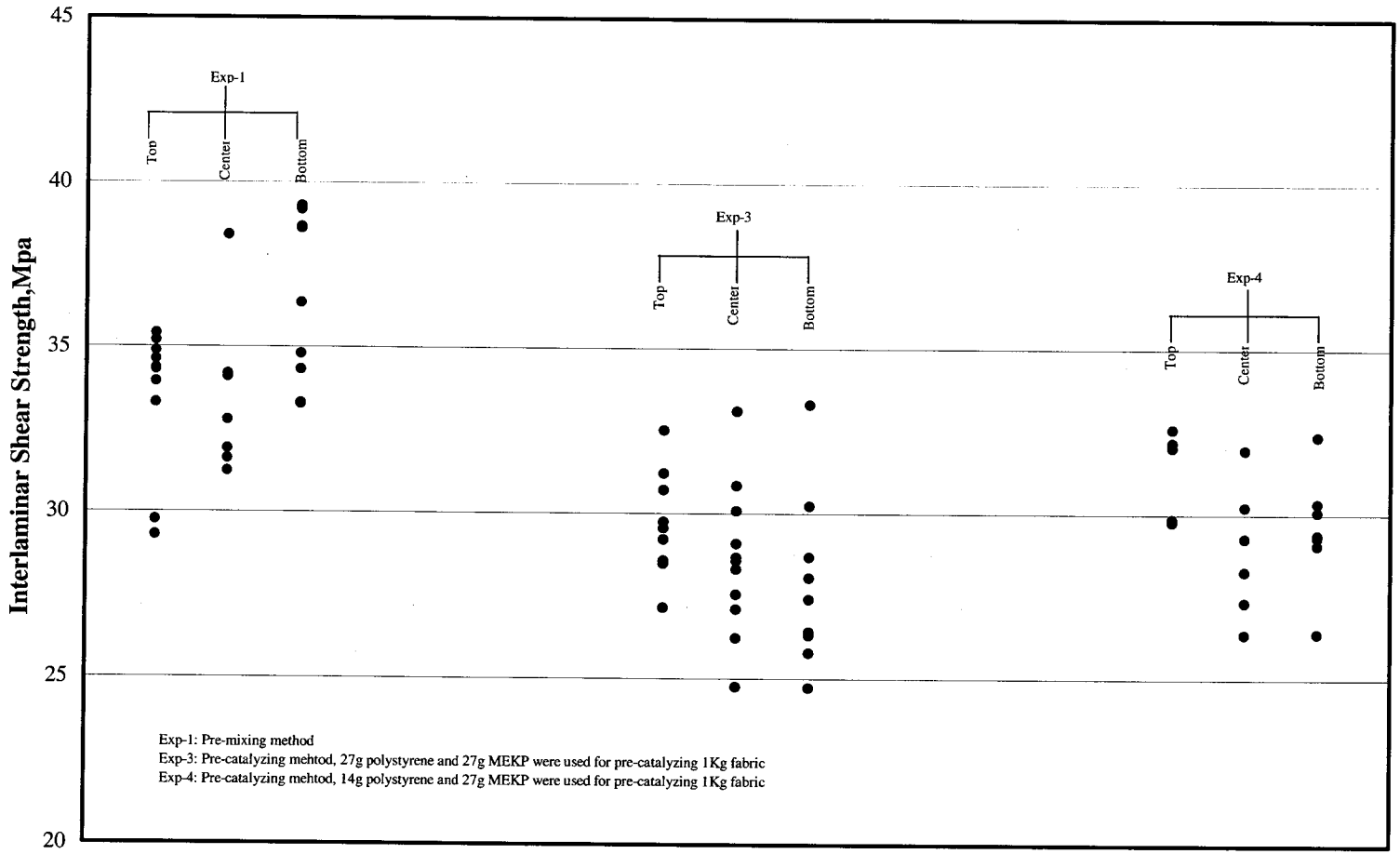


Figure4-19: Interlaminar Shear Strength of 50-layer laminates fabricated with pre-mixing method (Exp-1) and pre-catalyzing method (Exp-3 and Exp-4) in which polystyrene binder was used

ILSS, in Exp-4, the amount of polystyrene was reduced from 27g per 1kg fiber to 14g, so the average ILSS of Exp-4 is 29.8 MPa which is higher than Exp-3, but still 13.6% lower than pre-mixing method (Exp-1).

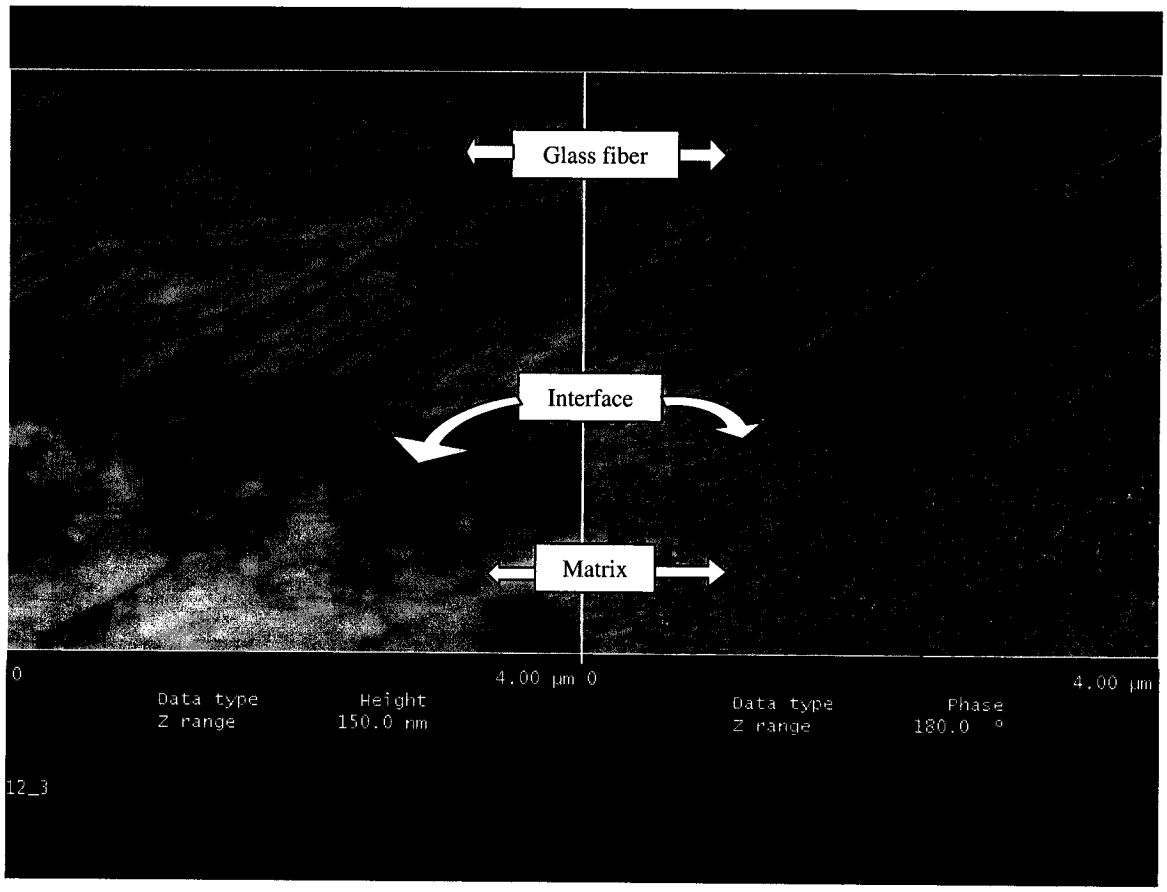
As we know, the poor bond between fiber and matrix could cause the decline of interlaminar shear strength. Contrast to the pre-mixing method, in pre-catalyzing technique, the fabric has been "sized" with polystyrene before hand lay-up process is applied. After the toluene, the diluent and solution in catalyst solution, had evaporated completely, the pre-catalyzed fabric became stiffer than before because the polystyrene almost restored its original rigid state on the fiber surface. According to the interphase theory [35], the load transfer from the matrix to the fibers is influenced by the interphase which exists between the matrix and reinforcement. This interphase is a polymer network formed by the coupling compound or the size and into which resin or matrix can penetrate. The network may have occasional chemical attachments (bonds) to the fibers surface. In our experiments, the glass fiber was sized by a kind of "Volan", a bonding agent which is a formulated solution containing unique surface-complexing monomers. It is able to attach tenaciously to a glass surface which composes a polar hydrogen bonding chemical environment. During application, the active molecules attach to the surface of the thermosetting resins to permit good-bonding. In pre-catalyzing experiments, the fiber was "sized" with the polystyrene, a kind of inert plastic, so the interface between the vinyl ester resin and polystyrene, as well as polystyrene and glass fiber, could not be very strong. Even though the quantity of the polystyrene of Exp-4 was reduced to half, it was still difficult for the resin to penetrate into the fiber through the rigid polystyrene layer.

The results of Atomic Force Microscopy tests clearly demonstrate the interface status of composites fabricated with pre-mixing and pre-catalyzing methods (Figure 4-20). In this figure, two modes of image, topological image and phase image, are used for each sample. In the topological image, the surface with brighter color is higher than the surface with darker color. In phase image, different phase is presented by different picture pattern.

Figure 4-20 (a) gives AFM results of samples fabricated with pre-mixing method. In topological image, it can be seen that the area of glass fiber is as bright as the matrix area, and the interface area looks dark. That means the surface of dark area is lower than fiber and matrix area, so it can be taken as the voids produced in fabrication. In phase image, only two main phases, fiber and matrix, can be observed. Some spot with dark color can be considered as voids.

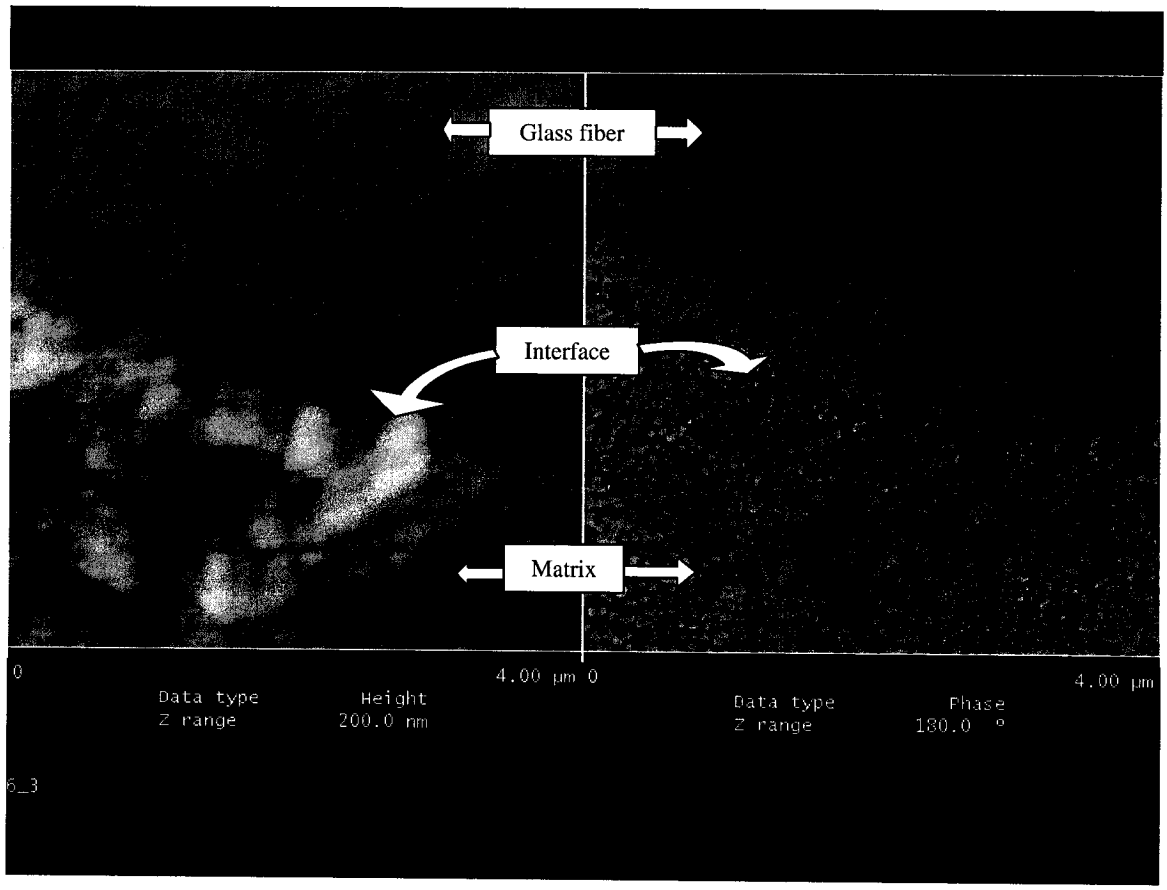
Figure 4-20 (b) gives AFM result of sample fabricated with pre-catalyzing method. In topological image, the interface between fiber and matrix area has the brightest color, so its surface is the highest compared with fiber and matrix surface. This high surface is caused by the catalyst binder-polystyrene. Polystyrene is a kind of material with high toughness and modulus of elasticity, and this material almost could not be able to remove by sanding when the sample being prepared. In phase image, it can be observed that, except the phases of fiber and matrix, there is a strip area between the fiber and the matrix. The image pattern of this area is obviously different from other two, so it can be taken as the third phase. Combining the topological image and phase image, it can be deducted that the material in this phase should be the polystyrene.

Polystyrene is a kind of inert material with long molecular chain. It could not be able to be attached on the glass fiber firmly. Also, even though the high toughness and elasticity of polystyrene, its tensile strength (several thousands psi) is very low compared with fiber (500,000 psi) and matrix (12000 psi). This low strength makes the interface very weak, and results in low interlaminar shear strength.



Left: Topological image Right: Phase image

(a)



Left: Topological image Right: Phase image

b)

Figure 4-20: AFM test results for samples fabricated with

(a) pre-mixing method and

(b) Pre-catalyzing method using the polystyrene as the binder

4.2 Discussion on the Improved Pre-Catalyzing Method Using Epoxy Resin as Binder

Previous study presents that the novel pre-catalyzing technique using polystyrene as the binder can significantly reduce the exothermal reaction when the thick-section composites are fabricated. However, this technique can also cause side effects. First, due to the application of polystyrene, the interface between the fiber and matrix becomes weaker than pre-mixing method. For example, the interlaminar shear strength of the laminate fabricated with pre-catalyzed method (Exp-4) decreased 12.8% as acquired from the short beam shear tests. Second, the large amount of toluene in the catalyst solution could pollute the air and is harmful to people's health when evaporating to the air. These disadvantages make this technique difficult to be extended to the manufacturing industry. Last, the fabric could not be used until 2 weeks after being pre-catalyzed. This long period is unsatisfactory because it will increase the production time. Therefore, in order to overcome these shortcomings, an improved pre-catalyzing technique was developed.

In the improved pre-catalyzing method, epoxy resin Epon 828 was selected as the binder in the catalyst solution (refer to Table 3-5) because of the following reasons: Firstly, Epon 828 is a medium viscosity resin which is able to make catalyst MEKP adhere on the surface of the fiber. Secondly, Epon 828 can be completely dissolved by acetone, which is much less toxic than toluene, within minutes, and only hand stirring is required. Thirdly, acetone can evaporate faster than toluene, and only two-days drying is needed after the pre-catalyzing process has been finished. Fourthly, after the acetone evaporates completely, unlike polystyrene layer, no rigid pre-catalyzing layer is formed,

and the binder Epon 828 does not cause fabric to be sticky or wet because only a small amount of epoxy was used in pre-catalyzing process. It is easy for operators to handle.

In the following sections, the cure temperature histories of laminates made with the improved pre-catalyzing method are analyzed, and the degrees of cure and the interlaminar shear strength are discussed as well.

4.2.1 Discussion of Cure Temperature Profiles and Analysis of Reaction Mechanism

4.2.1.1 Discussion of Cure Temperature Profiles

Pre-mixing experiment (Exp-7)

Figure 4-21 shows the temperature profile of Exp-7, a 50-layer laminate fabricated with pre-mixing method. This experiment is a repeat of Exp-1 due to the different batch resin used in this study for comparison. From the curve it can be noticed that the initiation point of polymerization happened around 25 minutes after the resin system was mixed according to Table 3-3, and the peak of exothermal temperature appeared when cure time was about 80 minutes. The highest peak temperature (83°C) occurred at point T2, the center of the laminate. The lowest peak temperature (65°C) occurred at point T3, only 6 layers to the top surface covered by metal weight. This large temperature difference (18°C) between point T2 and T3 was caused by low heat transfer coefficient of the composite.

Compared with Exp-1which peak temperature was 104°C, Exp-7 had a lower exothermic temperature (83°C). This phenomenon was caused by the lower resin content of Exp-7 (36.6%) than the content of Exp-1 (40.3%).

Pre-catalyzing method II (Exp-8)

Figure 4-22 gives the temperature profile of Exp-8, a 50-layer laminate fabricated with improved pre-catalyzing method (Table 3-5 Formula I). In this experiment, like Exp-2, 3 and 6, the data acquisition system started to record the temperature when the hand lay-up operation was performed. It can be seen that initiation onset of polymerization appeared approximately at 30 minutes, and peak exothermal temperature happened at 126 minutes. The maximum peak temperature was 34°C which happened at the center of the laminate (T2). The lowest peak temperature was 30°C which happened at point T3, only six layers to the top layer. The peak temperature difference between T2 and T3 is only 6°C. From this figure it also can be observed that T3 had a sudden drop at 63 minutes because the metal weight was loaded on the top surface of the laminate at that time, and some heat near top area was dispersed through the metal material. Curve T1 is similar with curve T2 because it was near center layer.

Effect of epoxy binder and MEKP content (Exp-9 and Exp-10)

Exp-8 shows that the improved pre-catalyzing method using epoxy resin as the binder instead of the polystyrene can still restrain the exothermal polymerization. However, even though a small amount of Epon 828 was added, it could affect the interlaminar shear strength of the composites because it cannot cure without hardener

(refer to section 4.2.3). In experiment Exp-9, the amount of Epon 828 (Table 3-5, Formula II) was reduced to one-quarter of amount used in Exp-8 (Table 3-5, Formula I) when the fabric was pre-catalyzed. Its temperature profile is presented in Figure 4-23. The figure shows that, compared with Exp-8, Exp-9 has a higher exothermal peak temperature (59°C). This phenomenon was caused by the reduction of Epon 828. Due to the decrease of Epon 828, some amount of MEKP could not be trapped between fibers; instead, it drifted at the outside of resin. So, when hand lay-up procedure was performed, the extra catalyst MEKP can catch vinyl ester resin more quickly than the catalyst entrapped in the epoxy resin. As a result, the polymerization reaction was faster, and exothermal temperature was higher than Exp-8 even though they had similar onset of initiation and time when the peak temperature appeared. However, compared with Exp-7, this experiment still successfully decreased the exothermal peak temperature.

Exp-9 shows the increase of exothermal temperature due to the extra MEKP which came out from the epoxy layer. In order to decrease this temperature, in experiment Exp-10, in which the amount of MEKP and Epon 828 (Formula III in Table 3-5) was reduced to half of amount used in Exp-8 (Table 3-5, Formula I). Figure 4-24 shows the temperature profile of Exp-10. From the cure temperature history it can be found that this experiment had similar time when the peak temperature appeared and initiation onset with Exp-8 and Exp-9, but the exothermal peak temperature was reduced to 39°C compared with 59°C of Exp-9. So, this experiment with Formula III can significantly reduce the exothermal temperature and save pre-catalyzing materials.

Effect of curing agent for epoxy (Exp-11 and Exp-12)

Exp-10, in which the amount of MEKP and Epon 828 (Formula III in Table 3-5) was reduced to half of amount used in Exp-8 (Table 3-5, Formula I), successfully reduced the exothermal temperature, but the epoxy resin served as the binder for pre-catalyzing the fabric was still in uncured status. In order to solve this problem, curing agent 3046 was added in the bulk vinyl ester resin system. Figure 4-25 shows the cure temperature history of the laminates made with improved pre-catalyzed method. In this experiment, the fabric, like Exp-9, was pre-catalyzed with Formula II in Table 3-5. The difference between Exp-11 and Exp-8, Ecp-9, Exp-10 is that hardener 3046 was added in the bulk resin system (Table 3-3) for curing the epoxy resin to adhere on the fiber surface. Exp-12 is a repeat experiment of Exp-11 for examining reliability of the experimental results (including cure temperature, DSC and SBS) of this method. The temperature profile of Exp-12 is shown in Figure 4-26. Figures 4-25 and Figure-26 show that the two experiments have very similar temperature profiles. This method has a rather long cure time. The onset of initiation was located at around 200 minutes after cure procedure started. The peak temperatures appeared after 330 minutes. The exothermal reaction was very gentle, and the highest temperature was about 31°C for Exp-11 and 36°C for Exp-12. So, this method can also restrain the exothermal reaction successfully.

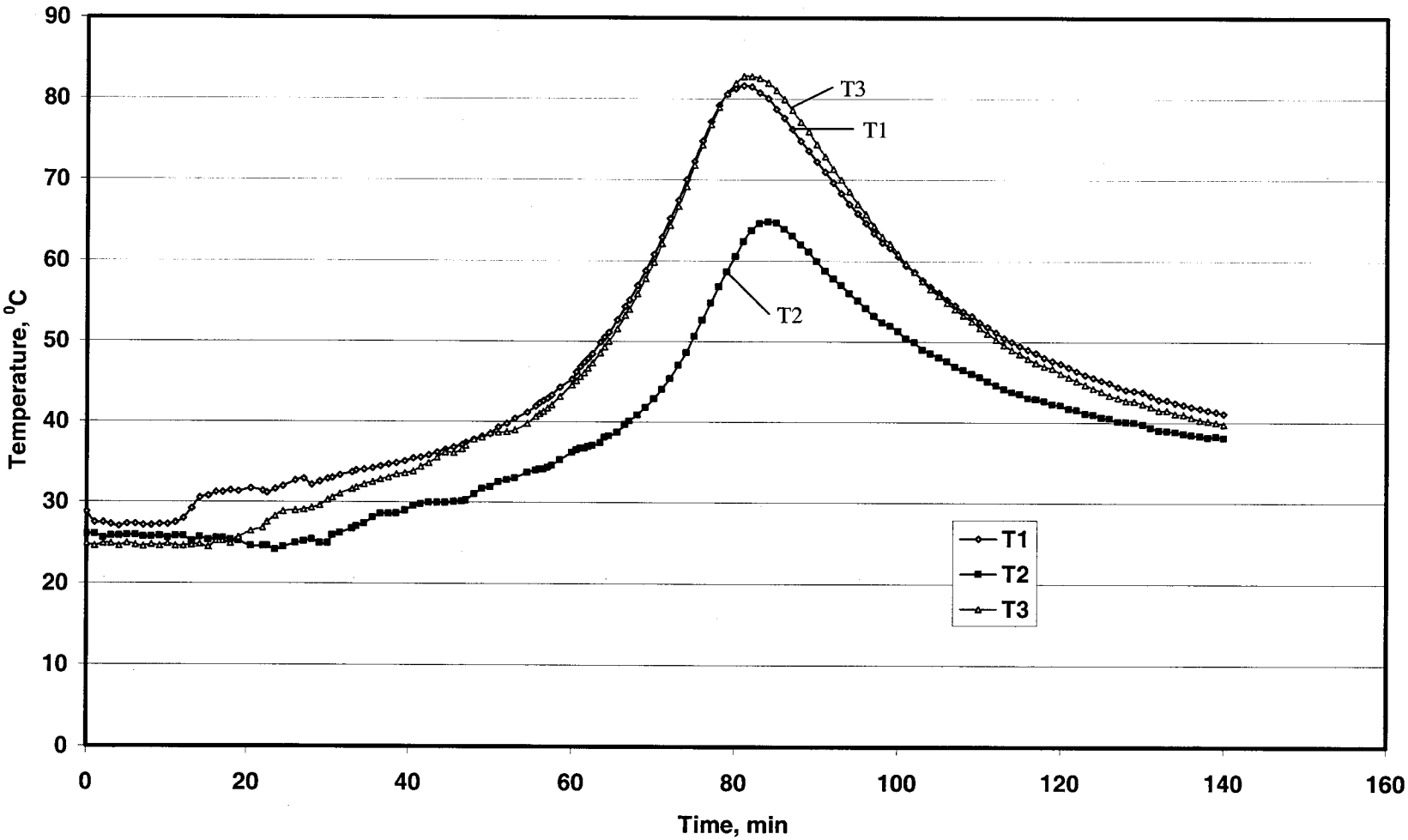


Figure 4-21: Exp-7: Repeated experiment of Exp-1 with different batch of resin

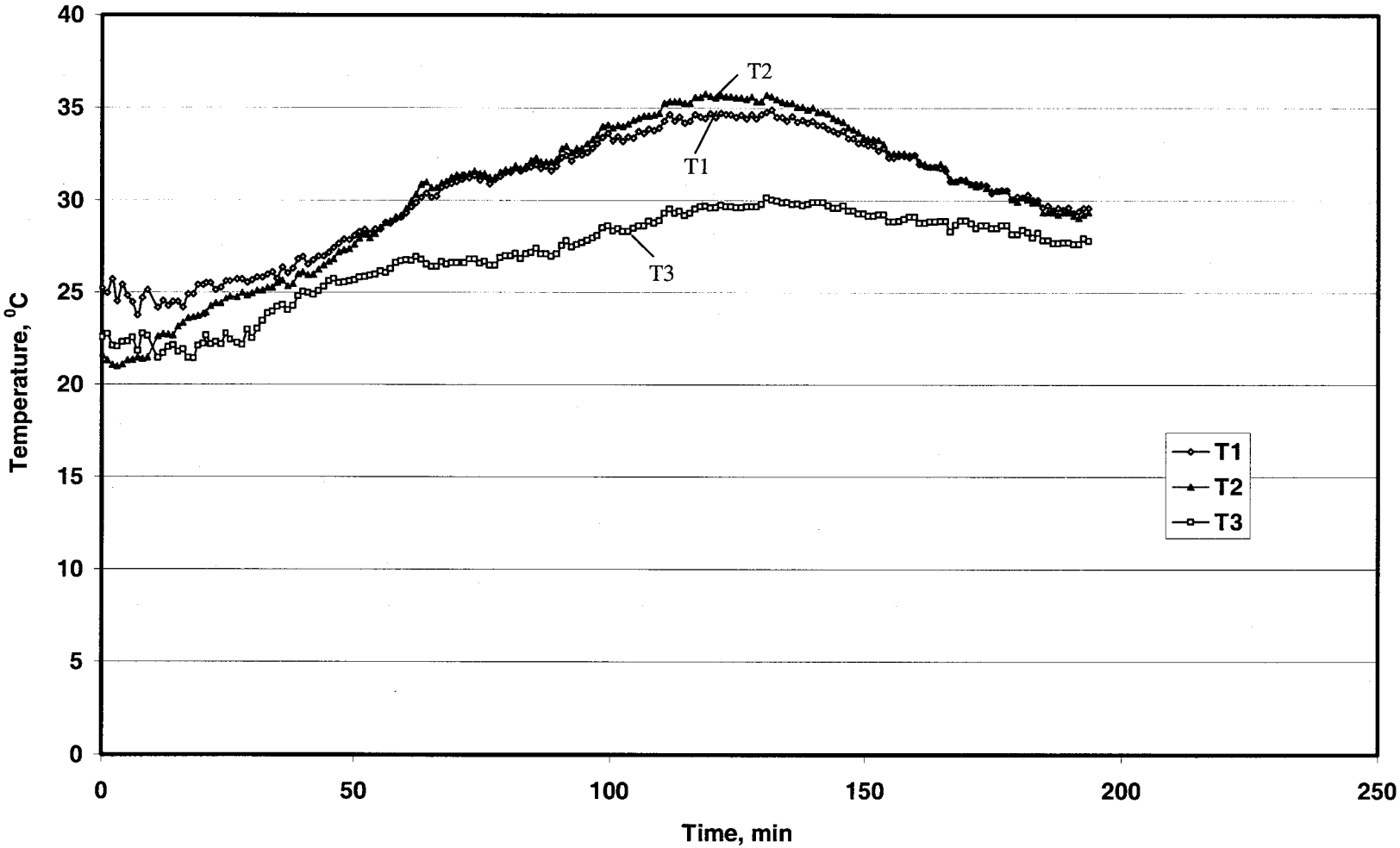


Figure 4-22: Exp-8: Temperature profile of 50-layer composites manufactured by the improved pre-catalyzed method (The fabric was pre-catalyzed according to table 3-5 Formula I)

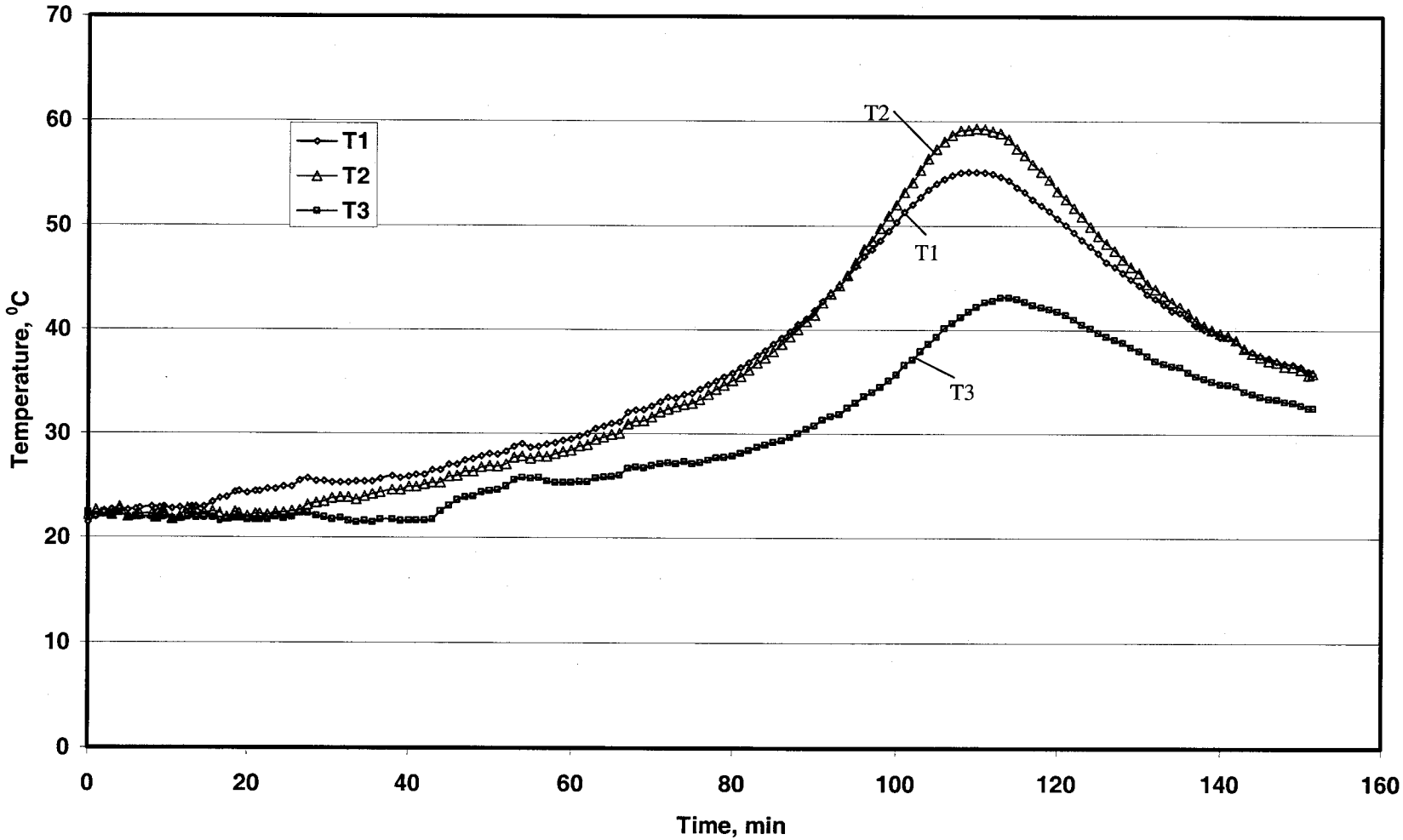


Figure 4-23: Exp-9: Temperature profile of 50-layer composites manufactured by the improved pre-catalyzed method (The fabric was pre-catalyzed according to table 3-5 Formula II)

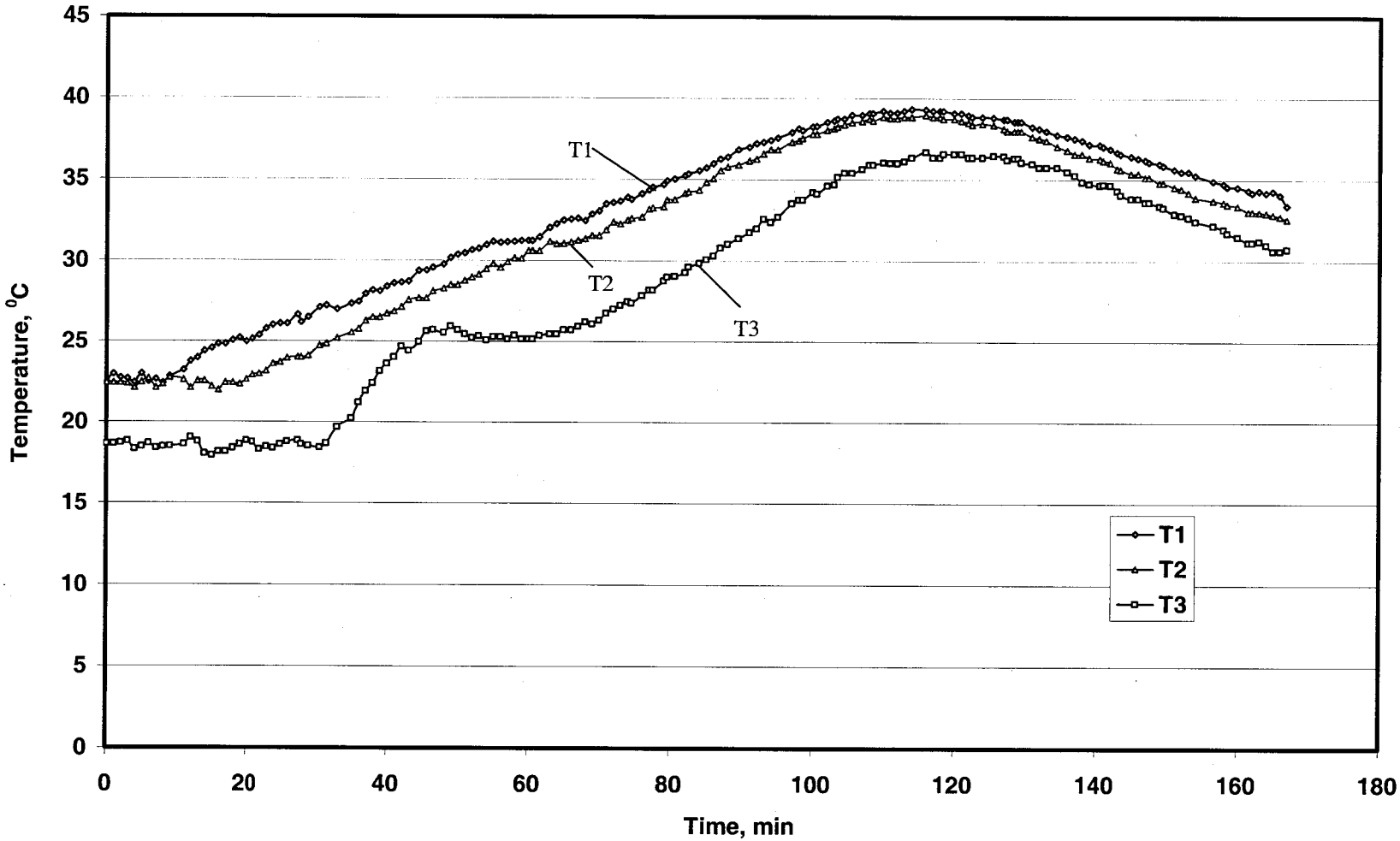


Figure 4-24: Exp-10: Temperature profile of 50-layer composites manufactured by the improved pre-catalyzed method (The fabric was pre-catalyzed according to table 3-5 Formula Ⅲ)

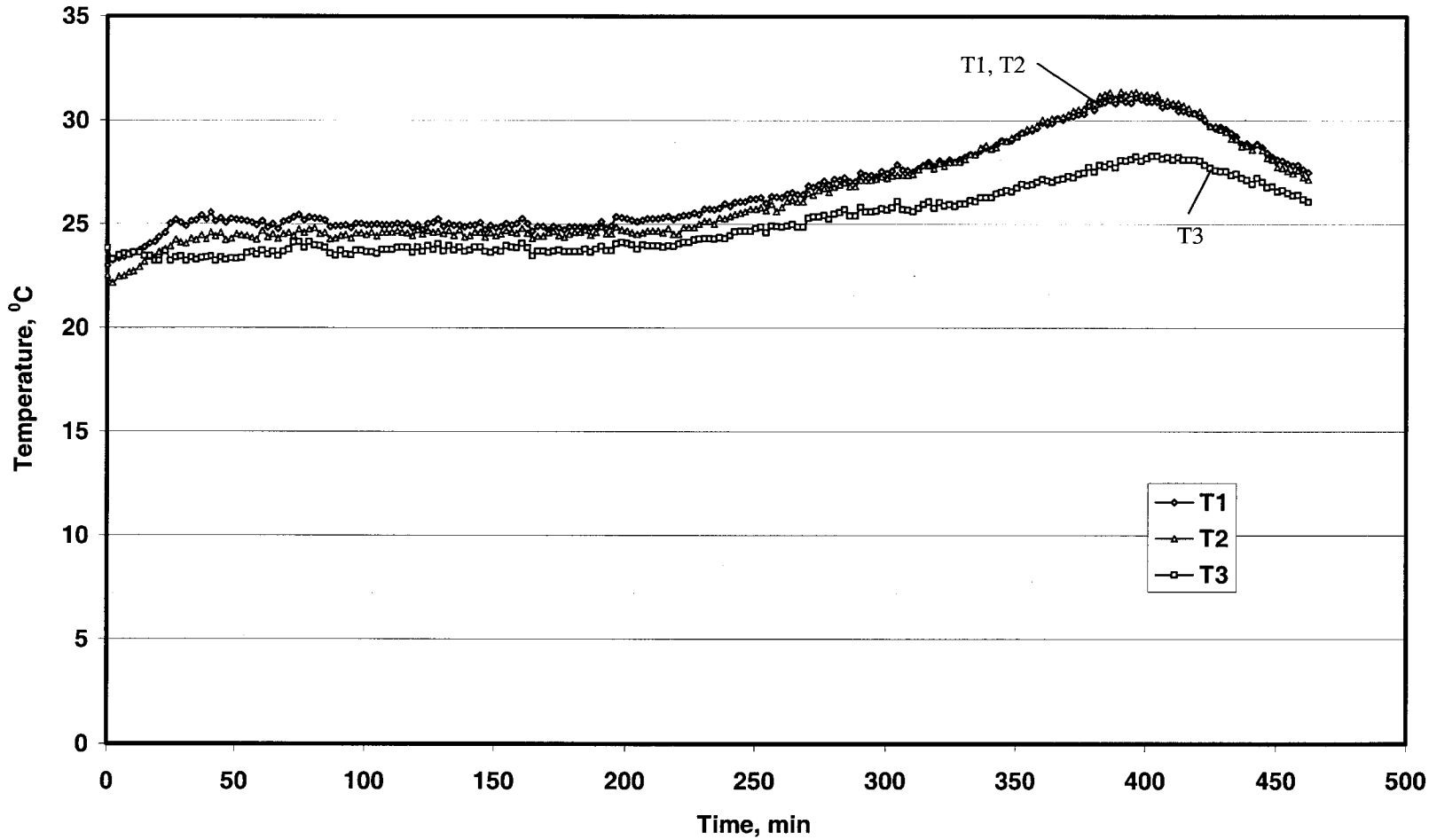


Figure 4-25: Exp-11: Temperature profile of 50-layer composites manufactured by the improved pre-catalyzed method (The fabric was pre-catalyzed according to table 3-5 Formula II and hardener 3046 was added in the bulk resin system (table 3-3))

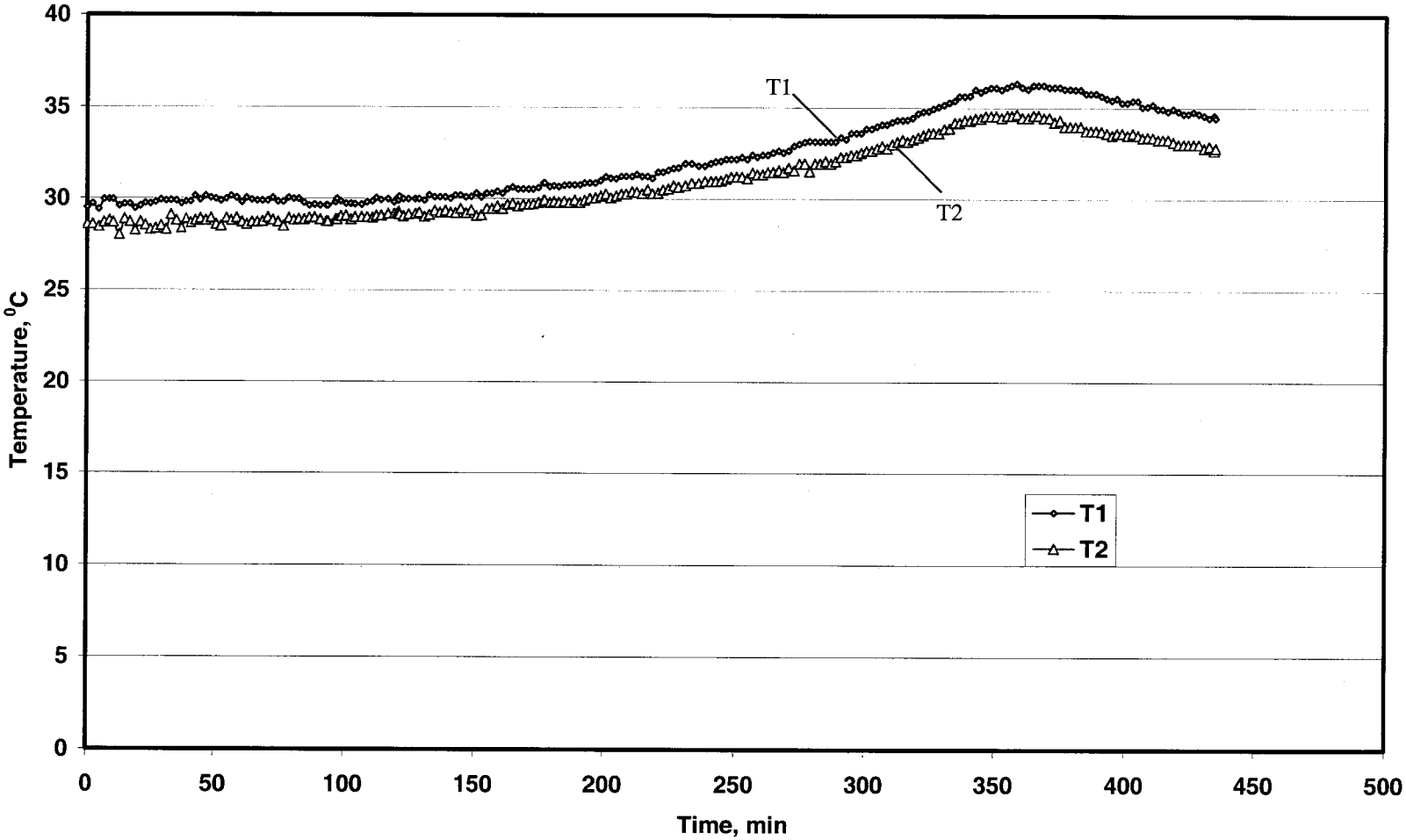
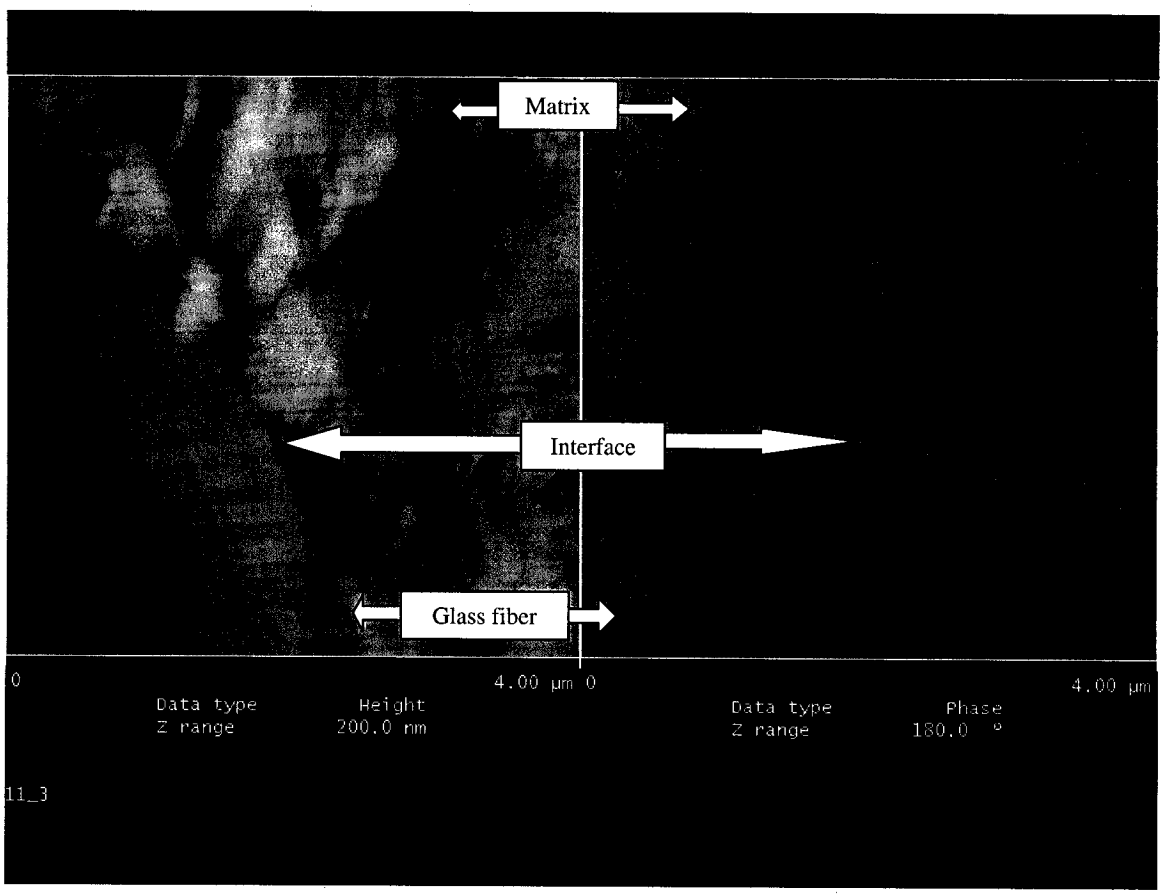


Figure 4-26: Exp-12: Verification of Exp-11

4.2.1.2 Analysis of Reaction Mechanism

The experiments show that the improved pre-catalyzing method can almost restrain the exothermal reaction. Comparing with the pre-catalyzing method using the polystyrene as the binder, firstly, even though the small exothermal peak temperatures appeared in Exp-8, Exp-10 (different formula of pre-catalyzing solution was used.), Exp-11 Exp-12, compared with pre-mixing method (Exp-7), the exothermic temperatures of them were dramatically decreased by more than 40°C, and the temperature differences between the center and the edge are less than 4°C. Secondly, the onset of initiation reaction is earlier in Exp-8, Exp-9 and Exp-10 than the previous pre-catalyzing method, so the total cure time is shorter.

Previous discussion (Section 4.1.1.2) revealed that the pre-catalyzing technique using polystyrene as the binder can make the cross linking reaction happen from the surface of fabric to the resin layer in a gradual manner. During the curing process, the catalyst MEKP escaped from the polystyrene layer and initiated the free radical. At the same time some vinyl ester resin penetrates to the polystyrene layer and get in contact with the MEKP. In this process, the polystyrene layer could not be completely dissolved.



Left: Topological image Right: Phase image

Figure 4-27: AFM test results for the samples fabricated with pre-catalyzing method using epoxy resin as the binder

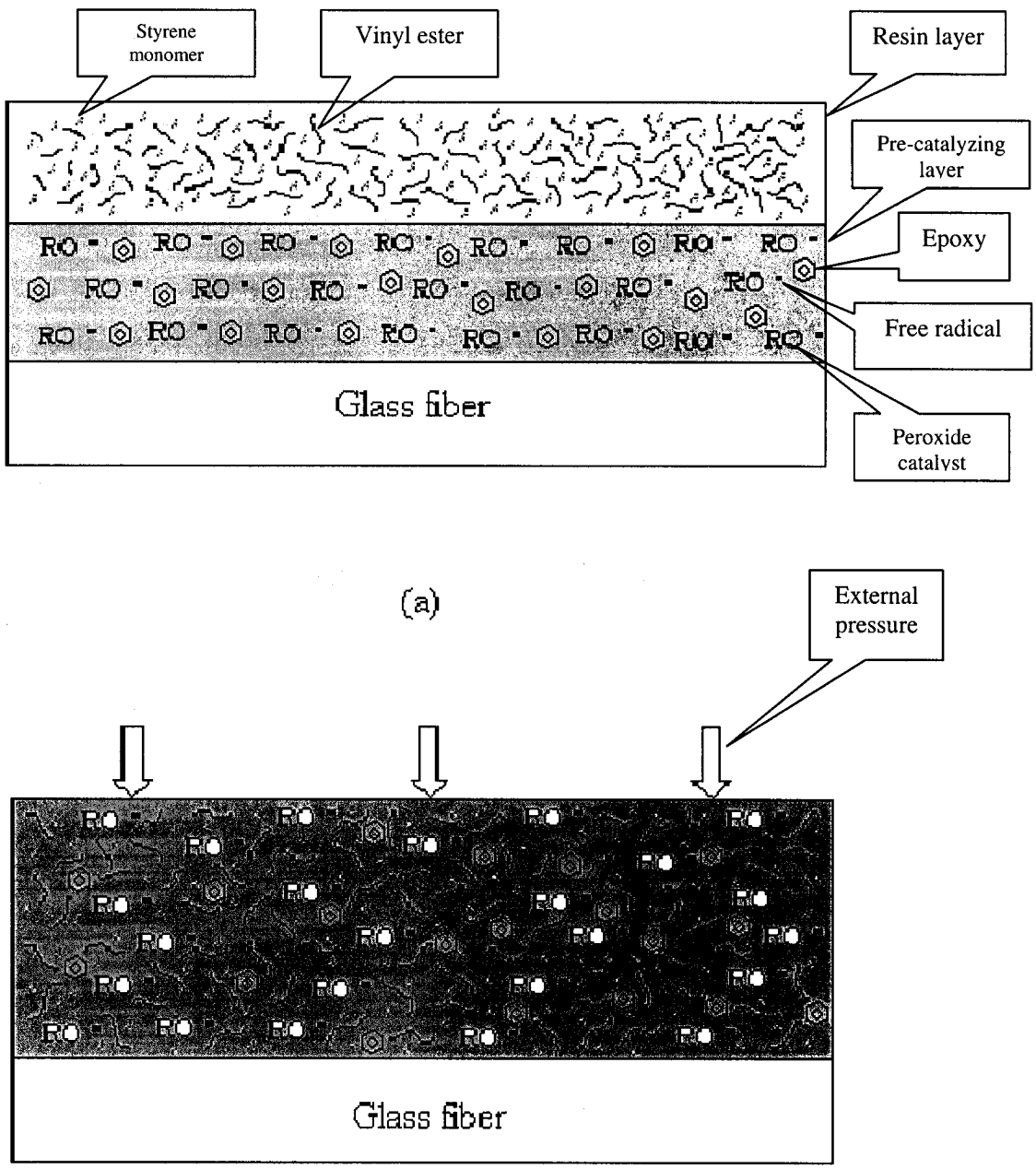


Figure 4-28: Sketch of initiation process with the epoxy as the binder

In the improved pre-catalyzing method, the epoxy resin was used as the binder to pre-catalyze the fabric. This pre-catalyzed layer consists of epoxy and MEKP, and both of them are liquid materials which are less packed and indeed can move more freely. Also, they have more space between the liquid particles, so that makes diffusion more likely to occur at a faster rate than polystyrene. In this diffusion process, not only MEKP can diffuse into liquid resin layer, but also the liquid epoxy binder can diffuse into bulk resin system. Meanwhile, the liquid vinyl ester resin can diffuse into epoxy binder layer. As the result, the pre-catalyzing layer does not exist any more. This can be shown in Figure 4-27, a picture of AFM test result for pre-catalyzing method using epoxy resin as the binder. Unlike Figure 4-20 (b), no brighter area can be observed in topological image in this figure, and no third phase between phases of fiber and matrix can be found in phase image. A sketch in Figure 4-28 can clearly demonstrate this for further understanding. Figure 4-28 (a) presents the status before diffusion occurs, and Figure 4-28 (b) presents the status after diffusion is finished. Because this diffusion process still needs a curtain time, the exothermal peak temperature can be controlled to be very small.

It can be found that Exp-11 and Exp-12 had a very long initiation time. That is because the hardener 3046 was added in the bulk resin system to cure the epoxy resin to increase the degree of cure and improve the mechanical properties. The hardener 3046 is an aliphatic amidoamine, and it has the character to terminate the polymerization. An experiment shows that when the content of hardener 3046 was increased to more than 1% of bulk vinyl ester resin system from 0.28% (Table 3-3), the 50 layer laminate could not be cured within 24 hours. Normally, 47 part hardener 3046 is needed to cure 100 part

Epon 828. According to this ratio, 1.3% hardener is required in the bulk vinyl ester resin system if the fabric is pre-catalyzed with Formula I or II in Table 3-5. So, the epoxy resin in Exp-11 and Exp-12 could not be cured completely with 0.28% content of the hardener, but the cure-time was really prolonged. The results of short beam shear tests (refer to section 4.2.3) show that the ILSS has no obvious improvement compared with Exp-8, Exp-9, and Exp-10. So, Exp-11 and Exp-12 did not show the advantages over them.

4.2.2 Comparison and Discussion of Cure Degree with DSC Results

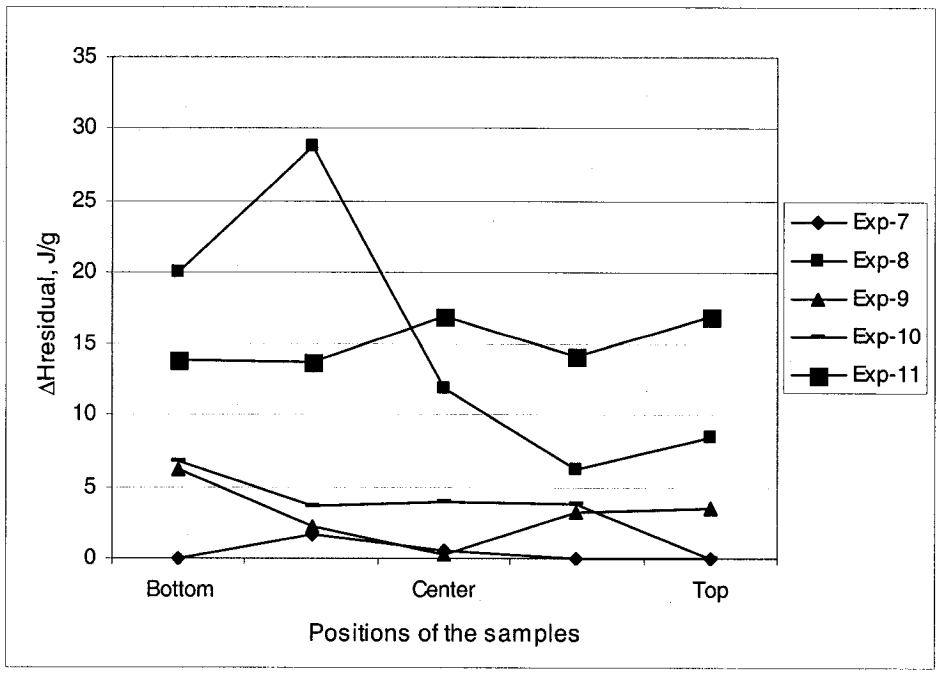


Figure 4-29: DSC results of 50 layer composites fabricated with pre-catalyzing method using epoxy resin as the binder

Figure 4-29 gives the DSC results for Exp-7, Exp-8, Exp-9, Exp-10 and Exp-11. These tests were performed within 48 hours after the cure process was finished. The figure shows that the sample of Exp-7 has a lowest residual heat $\Delta H_{residual}$ because of the high exothermal reaction, and according to Equation 4-2, its average degree of cure reached 99.9%. Exp-8 and Exp-9 have the highest $\Delta H_{residual}$, and the average degree of cure for both of them are 96%. This level of cure degree is high enough for the laminates to be handled or processed. To achieve higher degree of cure, the post cure can be performed, or the cure time can be increased by leaving the laminates at the room temperature environment for more than 5 weeks.

4.2.3 Comparison and Discussion of the Interlaminar Shear Strength (ILSS)

Due to the existence of the polystyrene between the matrix and fiber in previous pre-catalyzing experiments, the interlaminar shear strength decreased by 13.6% as compared to pre-mixing method. The improved pre-catalyzing method was developed for the purpose of improving the ILSS. In this method, the epoxy was used as the binder instead of the polystyrene. The Short Beam Shear test results are given in Figure 4-30. It should be noted that all the samples prepared for SBS tests had endured the post cure before the tests were performed.

In Figure 4-30, each laminate has three groups of values which stand for the ILSS at top, center and bottom of laminate. The test results demonstrate that, compared with pre-mixing method (Exp-7), it is difficult to find the obvious decrease of Interlaminar Shear Strengths for pre-catalyzing method (Exp-8, Exp-9,Exp-10, Exp-11 and Exp-12).

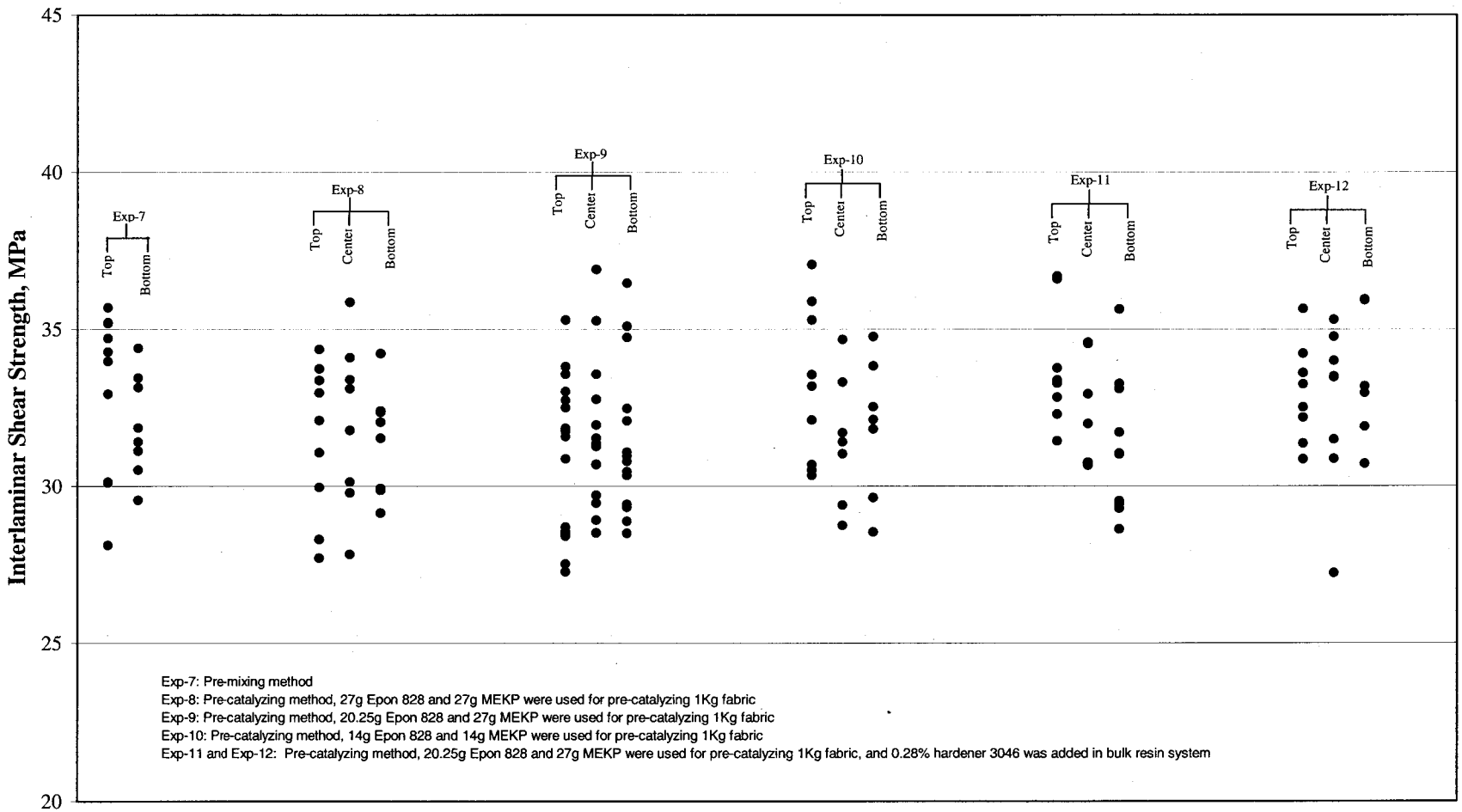


Figure 4-30: Interlaminar Shear Strength of 50-layer laminates fabricated with pre-mixing method (Exp-7) and pre-catalyzing method (Exp-8, Exp-9, Exp-10, Exp-11 and Exp-12) in which epoxy binder was used

Compared with pre-catalyzing method I in which polystyrene binder was used, the improved pre-catalyzing method II does not influence the ILSS of the laminates a lot when epoxy binder was used. In Exp-8, Exp-9 and Exp-10, the average ILSS is decreased by 3.1%, 4% and 1.2% respectively because of uncured epoxy resin existing in the samples. Due to the less epoxy content of Exp-10 (only half amount of Exp-8), its interlaminar shear strength has less decrease when compared with Exp-8 and Exp-9. In Exp-12 (hardener 3046 was added in this experiment to cure epoxy resin), the ILSS is 32.95MPa, 1.07% higher than 32.6 MPa, the value of Exp-7 (pre-mixing method). This results shows that with adding some hardener in bulk resin system, the ILSS is higher that Exp-8, Exp-9 and Ex-10 in which no hardener used. Considering the standard deviation of Exp-10 (2.2MPa), it can be recognized that no ILSS degradation occurred in Exp-10. Even though the experiment (Exp-12) in which hardener 3046 was mixed achieved the best Interlaminar Shear Strength, but the long curing process makes it difficult to apply (Figure 4-26).

Unlike polystyrene, no rigid pre-catalyzing layer was formed after the fiber was pre-catalyzed with the epoxy as the binder. When the hand lay-up was performed, it is easy for epoxy resin and vinyl ester resin to diffuse into each other and distribute within each layer uniformly. Since the epoxy pre-catalyzing layer disappeared after the bulk resin was applied, the fiber would come in direct contact with bulk resin system in which a small amount of epoxy resin was mixed (Figure 4-28 (b)). The result of Atomic Force Microscopy test (Figure 4-27) shows that there is no strip-liked phase between the vinyl ester resin and fiber. As we have known, the glass fiber used in the experiments was sized by a kind of volan, which is able to securely attach to inorganic and polar substrate of

glass fiber and thermosetting resins, such as epoxy and vinyl ester. So, the property of interface between the matrix and fiber for the improved pre-catalyzing method should be similar with the pre-mixing method when a small amount of epoxy resin is used.

4.3 Summary

In this chapter, the experiment results for two pre-catalyzing techniques (one uses polystyrene as the catalyst binder, another uses epoxy) are presented and analyzed. It can be summarized as follows:

- The pre-catalyzing technique using polystyrene binder can eliminate the peak exotherm, and degree of cure can achieve above 87%, but the interlaminar shear strength is reduced by 13.6% compared with pre-mixing method due to the existence of polystyrene layer between fiber and matrix.

- The pre-catalyzing technique using epoxy binder can significantly reduce the exothermic peak temperature by more than 40°C compared with the temperature of pre-mixing method (83°C), and cure degree can achieve above 96%. The interlaminar shear strength is improved, and no ILSS degradation was found when this technique is used. The fabric is not sticky at all after being pre-catalyzed by epoxy resin. It is easy to handle.

Generally, pre-catalyzing technique using epoxy binder has privilege over using polystyrene binder. In all the experiments in which the epoxy binder was used, the experiment with the lowest content of MEKP and Epon 828 (14g MEKP and 14g Epon

828 for pre-catalyzing 1kg fabric) can be considered optimum. Its exothermal temperature is 39°C, and it has no ILSS degradation, and the amount of pre-catalyzing materials (MEKP and Epon 828) consumed is minimum.

CHAPTER 5

CONCLUSION, CONTRIBUTION AND FUTURE WORK

Conclusion

Pre-catalyzing method is a novel technique for fabricating large composite parts with thick cross-section and complex geometries. It is different from conventional techniques that catalysts are mixed with bulk resin system before application. It introduces a new methodology that a catalyst can "pre-coat" the surface of the fiber, like the sizing process of glass fiber. When the bulk resin is applied, the catalyst diffuses into matrix layer and activates the free radicals in a gradual manner. Thus, the peak exotherm can be controlled or eliminated. In this process, the catalyst binder plays an important role. It can control the diffusion speed of the catalyst towards the matrix, and may influence the interlaminar shear strength. In this study, glass fiber was chosen as the reinforcement; vinyl ester resin was used as the matrix material, and MEKP was selected as the catalyst. Also, the hand lay-up process was applied in the study because of its vast applications. Two pre-catalyzing methods have been investigated: one method used the polystyrene as the catalyst binder and toluene as the solvent; another used epoxy as binder and acetone as solvent.

Polystyrene/toluene/MEKP catalyst solution

In the study of the pre-catalyzing method using polystyrene/toluene/MEKP pre-catalyzing solution, it can be concluded that:

- Eliminating the content of toluene volatile by increasing the drying time of fabric can eliminate the peak exotherm and temperature gradient. In this study, the toluene was used as the solvent and diluent in the catalyst solution. The experiment results show that the drying time of the fabric after being pre-catalyzed can significantly affect the exothermic reaction. With 3 day drying, the exothermal peak temperature was reduced to 80°C from 104°C as produced in the pre-mixing experiment. When the fabric was dried for 2 weeks, the peak temperature decreased to 27°C which is much lower than 3 days drying. Meanwhile, the temperature gradient can be eliminated. However, this significant effect of eliminating the peak exotherm is at the cost of the large delay of cure time.

- The polymerization reaction is independent of the thickness of the laminate even though its cross section is larger. Compared with 50-layer laminates, a 100-layer laminate was fabricated with pre-catalyzing method using polystyrene/toluene/catalyst solution, and its fabric was dried for 2 weeks. Its temperature profile shows that no peak exotherm and temperature gradient can be observed.

- The degree of cure of the samples fabricated with pre-catalyzing method (polystyrene/toluene/catalyst) was lower than pre-mixing method when DSC tests were performed right after the cure process. The values of degree of cure are between 87% ~ 95% which is high enough for the laminates to be handled and processed. The degree of cure can be improved by post cure or increasing

aging time. Leaving the samples for 5 weeks after laminating can achieved 97.3% degree of cure.

- The interlaminar shear strength is decreased for the laminates manufactured with pre-catalyzing method (polystyrene/toluene/catalyst) than pre-mixing method due to the existence of polystyrene layer between the matrix and fiber. Polystyrene is only softened by styrene but not dissolved by the styrene, a monomer in the vinyl ester resin. This layer of polystyrene is not able to attach to glass fiber surface and vinyl ester resin strongly. Even though the amount of polystyrene was reduced to as low as possible, the ILSS is still 12.8% lower than that obtained from pre-mixing method.

- Toluene can dissolve the polystyrene very well for the catalyst solution, but this process takes long time. First, the stirring time is long. It takes about more 40 minutes to totally dissolve polystyrene by using of stirring machine. Then, toluene needs long time to evaporate completely after the pre-catalyzing process. The most concerned problem is that toluene is harmful to people's health, and it pollutes the air severely.

Epoxy/acetone/MEKP catalyst solution

In order to improve the interlaminar shear strength, the epoxy/acetone/MEKP catalyst solution was used. From the study, it can be concluded that:

- The pre-catalyzing method using epoxy resin as the binder and acetone as solvent can still reduce the exothermic temperature and the temperature

gradient greatly. Even though the reaction temperature is a little higher than the method using polystyrene as the binder, it could still satisfy the expectation. This reaction temperature was lowered when the hardener 3046 was mixed in the bulk resin system for the purpose of curing the epoxy resin, but the cure time is much longer.

- The degrees of cure were sufficiently high for the laminates to be handled or processed after the cure process was finished because all the degrees of cure are above 96%.

- No degradation of interlaminar shear strength could be found when compared with pre-mixing method. That is because the epoxy pre-catalyzing layer disappeared after the bulk resin system is applied on the fabric. Unlike the polystyrene, the epoxy layer is not in a rigid form, and it can diffuse into the resin matrix easily. The interface between the matrix and fiber should be very similar with the pre-mixing method. The only difference is that a small amount of epoxy resin is mixed into the large amount of bulk vinyl ester resin system The glass fiber used in this study is sized with volan, and this binding agent is able to securely attach not only to the vinyl ester, but also to the epoxy resin. That is why the ILSS almost had no changes.

- The acetone can dissolve the epoxy resin very fast, only several minutes are needed for hand stirring. Since acetone can evaporate faster than toluene, only 2 days are needed for completely drying the pre-catalyzed fabric. The most

important aspect is that acetone is much less toxic than toluene, and has less influence to people's health and environments.

Through the study for both kinds of pre-catalyzing methods, it can be concluded that the pre-catalyzing method can significantly reduce or eliminate the peak exotherm whether the polystyrene or epoxy resin is used as the catalyst binder. But the method using the epoxy resin has the advantage over the method using the polystyrene to overcome the degradation of the interlaminar shear strength. In this improved method, the experiment with the lowest content of MEKP and Epon 828 (1.4% MEKP and 1.4% Epon 828 as compared to 100 parts of glass fabric) is optimum. It can not only restrain the exothermal temperature (only 39°C) and keep ILSS not decreasing, but also save on the pre-catalyzing materials (MEKP and Epon 828).

Contributions

This work has found a new method for the manufacture of thick composites. The contribution in this study is using epoxy as catalyst binder instead of polystyrene. This method can:

- Provide very low exothermic temperature and good interlaminar shear strength.

- Clear away a big application obstacle of this technique in industry by using acetone as the solvent in catalyst solution instead of toluene because of the toxicity of toluene.

- Shorten the time of pre-catalyzing process greatly by using acetone instead of toluene because of short stirring time and short drying time of pre-catalyzed fabric.

The penalty of this method is that the time for curing is longer. This can increase the product cycle for manufacturing thick composites.

Future work

The following related works are recommended for future study:

- The catalyst can be mixed with the binding agents of glass fiber, such as volan and silane coupling agent. With this mixture, the pre-catalyzing process can be finished together with the sizing process in the manufacturing of the glass fiber. The related temperature profiles, the degree of cure and mechanical properties should be investigated.

- Future study can be done by choosing other resin systems, catalysts and manufacture processes with the pre-catalyzing technique.

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