

ULTRA-THICK CROSS SECTION FIBER REINFORCED COMPOSITES

Project Code: F98-D04

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ABSTRACT

We developed a thermo-chemical computer model that is capable of approximating the heat transfer that occurs within a composite as it cures. The model is easily adjustable to different fiber/resin systems. An intensive study using a pre-catalyzed fabric procedure for the fabrication of ultra-thick composites was carried out. In our examination of the precatalyzed fabric process, it was found that the exotherm created during the curing process is controllable by alternating the number of catalyzed and uncatalyzed plies. Whether or not this technique will adequately reduce the exotherm in thicker composites or if their material strength will be comprised is still unknown. The fabrication of 120-ply composites, as well as, material testing procedures are currently being developed to answer these questions.

PROJECT OBJECTIVE

The overall objective of this study is to perform a fundamental examination of the basic fiber and resin material parameters that are important in the manufacture of thick cross-section composites. Advanced fabrication methods will be used such as in-situ consolidation, non-autoclaving curing, and advanced fiber placement process for thermoset composites. The thickness range of interest is from 1.9 cm (0.75 inches) to 7.6 cm (3.00 inches), which would be useful in the construction of marine vessels and other load bearing engineering structures.

INTRODUCTION

In the first year the main goal of this project was to develop a better understanding of heat transfer that occurs during the curing of an ultra-thick composite. A comprehensive literature search was performed uncovering a few methods of producing such composites. Kim and White¹ for instance developed a method of staged curing in which thin composites are partially cured and then stacked until a desired thickness is reached. The staged curing procedure appears to be the most popular method for curing thick composites. Also, a thermo-chemical computer model was developed to accurately model the heat transfer that occurs during the curing process.

Thermo-Chemical Model for Glass Fabric / Epoxy Composite Curing

The computer model was developed using the heat transfer and cure kinetics equations 1, 2, and 3. These equations were non-dimensionalized as shown in our previous NTC Annual Report² and then compared with actual experiments we performed using glass/epoxy prepreg. Our

computer program is capable of representing many different resin and fiber combinations by simply changing the material properties and processing parameters. The results for a one inch thick epoxy resin/glass fabric composite (20cmW x 20cm L) comparing an experimental exotherm and our simulated exotherm can be seen in Figure 1. The experimental results followed the model equations 1, 2, and 3 fairly well.

$$\rho C \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \dot{Q} \quad (1)$$

$$\dot{Q} = \rho \gamma H_R \frac{\partial c}{\partial t} \quad (2)$$

$$\frac{\partial c}{\partial t} = Z \exp\left(\frac{-\Delta E}{RT}\right) (1-c)^n c^m \quad (3)$$

Where ρ , C , k , q , γ , H_R , Z , ΔE , R , and c are density, specific heat, thermal conductivity, rate of volumetric heat generation, resin mass fraction, heat of reaction, frequency factor, activation energy, universal gas constant, and degree of cure, respectively.

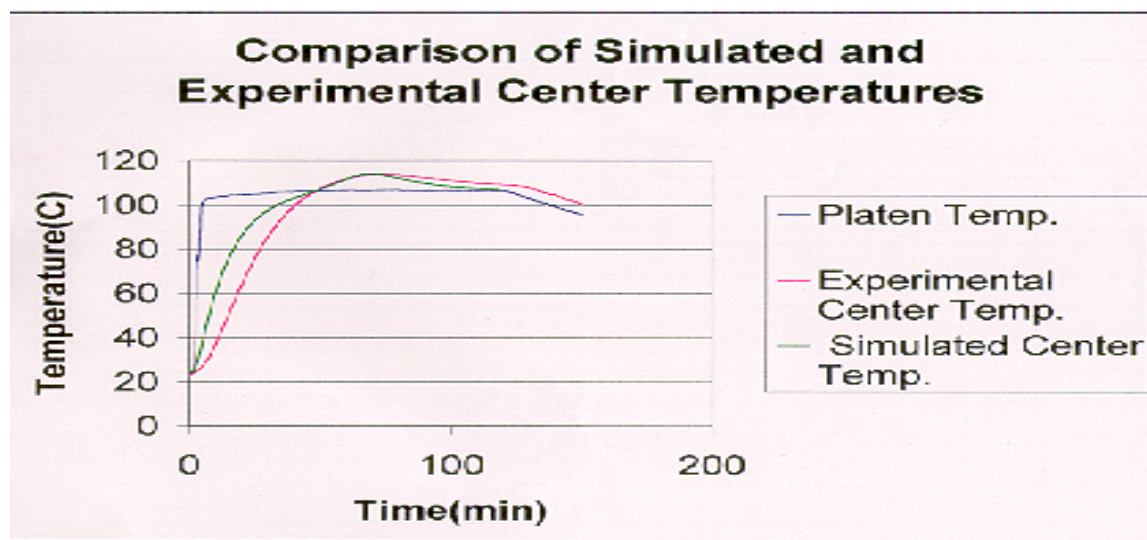


Figure 1: Comparison Between Simulated and Experimental Results for Epoxy Resin/Glass Fiber Composites.

EXPERIMENTAL

Background

This year our focus has shifted to the use of glass fabric pre-catalyzed with benzoyl peroxide in the creation of polyester resin based ultra-thick composites. We believe there may be several advantages to pre-catalyzing a fabric prior to adding the resin. The technique involved “sizing” the glass fabric with a toluene solution of benzoyl peroxide and polystyrene. The polystyrene served as a binding agent for the catalyst onto the surface of the glass fabric yarns. First, in laying up a thick composite using unsaturated polyester / styrene resins one major obstacle is the "pot life" of the polyester resin-hardener mixture. While applying the resin and hardener to a large number fabric plies the mixture will begin to cure long before you can complete your task. This causes a waste of precious materials and makes it very difficult to lay-up thick composites. We believe that by pre-catalyzing the glass fabric, the curing will occur after the lay-up is complete. Another advantage is that the exotherm can be controlled by changing the number of pre-catalyzed plies in the composite lay-up. Precatalyzing alternate plies could possibly save materials, shorten lay-up time, and lower the reaction's exotherm during cure. These features would also lower manufacturing costs.

Fabric Catalyzation Procedure

A procedure for catalyzing glass fabric that would cure with a polyester resin was developed.

A) Catalyzing the glass fabric:

Materials:

- 1) Benzoyl Peroxide
- 2) Toluene Solute
- 3) Polystyrene
- 4) Glass fabric (Fibreglast: Style 7715, 7 Oz./Sq. Yd., .008" Thick, Plain Weave Construction)

Procedure:

- 1) 6 grams of benzoyl peroxide is added to 100 ml of the 5% polystyrene in toluene solution and stirred.
- 2) The glass fabric is then impregnated with the solution and hung up to dry over night.

B) Fabrication of the laminate:

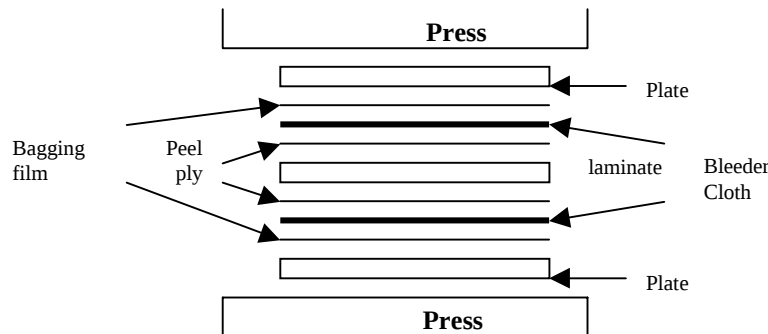
Materials:

- 1) Polyester resin (Evercoat Marine Premium Resin 100553)
- 2) Precatalyzed glass fabric (Ten - 8" x 8" pieces)
- 3) Porous release film (Fibreglast 582)
- 4) Nylon bagging film (Fibreglast 578)
- 5) Bleeder cloth (Fibreglast 579)

- 6) Release spray (Fiberlease-one step mold release)
- 7) Metal plates
- 8) Platen press (For pressure only)
- 9) Type K thermocouple

Procedure:

- 1) Apply the uncatalyzed polyester resin with a brush onto the precatalyzed fabric.
- 2) Place a thermocouple between the fifth and sixth ply in order to monitor any rise in temperature.
- 3) Lay-up the laminate as seen in Schematic 1.
- 4) Use the data acquisition system to record the temperatures.
- 5) Apply 7.8 psi of pressure to the laminate.



Schematic 1 : Lay-up Scheme of the Trial Laminate

RESULTS AND DISCUSSION

After developing the catalyzation procedure and producing a fully cured room temperature composite, we decided to speed up the process by producing our next composites using a heated flat-platen press. Here pre-heated platen temperatures (80 °C) were used. Also, by curing the composite under higher than room temperature conditions, it becomes much easier to determine whether adjusting the number of catalyzed plies changes the exotherm event. The first two composites, only 8 and 10 plies, cured quickly (under 30 minutes). No increase in the center temperature was observed. A 60-ply composite (approximately 0.5625 inches), however produced a large exotherm, and showed a rather significant temperature increase. This is shown in Figure 2.

Sixty-Ply Composites :

Two samples of 60 ply composites (20cm W x 20cm L) were produced using the same procedure described for the 8 and 10 ply laminates. The only difference was the number of precatalyzed fabric layers used. The first composite was produced using 100% precatalyzed fabric layers, while in the second composite precatalyzed fabric was used in alternate plies. When stacking the fabric in a partially catalyzed composite it is important to place a catalyzed layer on the outer

layers of the composite. The reason for this is the uncatalyzed plies would not get any resin placed on them. There is plenty of excess resin on the catalyzed plies that is distributed throughout the composite by the platens pressure. The lay-up is the same as Schematic 1. Thermocouple placement can be seen in Schematic 2 below. Figures 2 and 3 show the temperature profiles for these 60-ply thick composite curing cycles. As seen in Figure 2 and 3, the temperature spike is much lower in the alternate ply catalyzed composite. The oscillations in Figure 3 are caused by the thermocouple rubbing against the platens. The center temperature is quite smooth however and shows a much lower exotherm. Both composites appeared to be completely cured. However, mechanical testing of these sample composites has not yet been completed.

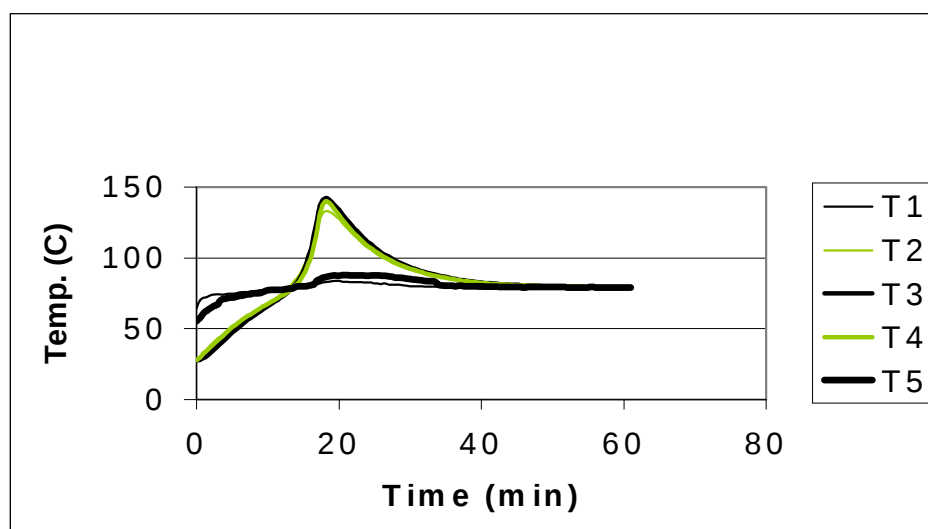
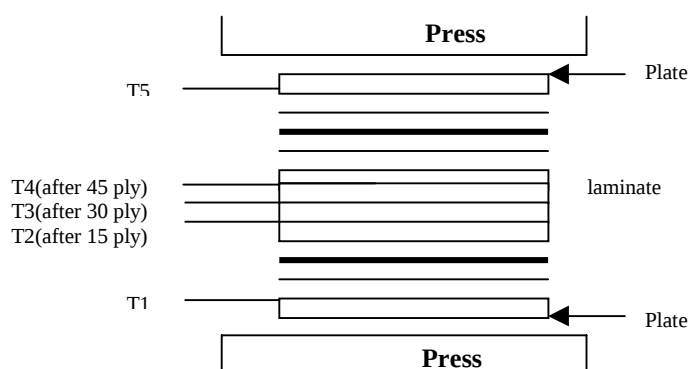


Figure 2 : Temperature Profile for 60-Ply Polyester Resin Curing Process Using All Precatalyzed Layers.



Schematic 2 : Thermocouple Placement for 60-ply Thick Composite

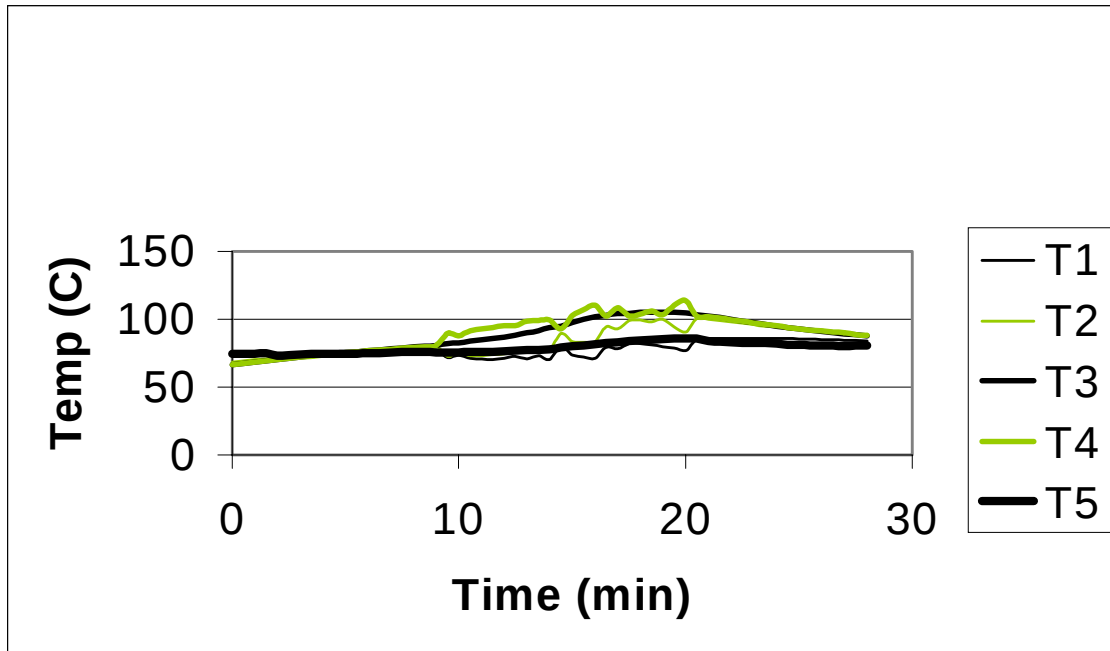


Figure 3 : Temperature Profile for 60-Ply Polyester Resin Curing Process Using Alternate Ply Precatalyzed Layers.

Experiments Currently Under Development

Our continuing work will now focus on the production of 120 ply composites using pre-catalyzed fabric. These samples will be for mechanical testing. The number of pre-catalyzed to uncatalyzed fabric layers will be varied. We have developed a technique based on the work of Kim and White³ that allows us to separate sub-laminates from the thicker composite with the use of a peel ply. This technique will be used to test these fabricated composites at various zones across the composite's cross-section thickness (sub-laminates).

Mechanical Testing:

The temperature at the center of each sub-laminate will be taken using thermocouples. The quality of each sub-laminate will be determined by testing longitudinal compression, interlaminar shear, transverse tension, and three-point bending. Standardized test procedures are going to be implemented for tensile testing (ASTM D3039)⁴, longitudinal compression testing (ASTM D3410)⁵, interlaminar shear (ASTM D3846)⁶, (ASTM D695M)⁷, and three-point bending (ASTM D2344)⁸ tests.

Future Work

After completing our examination of the precatalyzed fabric procedure for the fabrication of ultra-thick composites employing polyester resin matrices there are several other areas, which need to be studied. An advanced fiber placement process for thermoset composites will be addressed with the use of our computer controlled filament-winding machine. The filament-winding machine allows us to create ultra-thick tubular composites with a variety of fiber orientations. This process can be used with a number of different resin/fiber combinations, as well as, precatalyzed fibers. Also, a study needs to be done on the effect of varying platen temperatures with the various resin systems. Our thermo-chemical computer model has predicted that the exotherm can be greatly reduced by starting one of the platens cold and then increasing its temperature over time. Experiments verifying this effect need to be performed not only for epoxy resin systems, but also for other matrix resins (e.g., unsaturated polyester / styrene and vinyl ester resins). Finally, we need to develop an understanding of the dielectric, induction, and microwave curing of bulk fiber/resin mixtures in the context of fabricating ultra-thick composites.

CONCLUSION

We have successfully produced a thermo-chemical computer model that is capable of approximating the heat transfer that occurs within a composite as it cures. The model is easily adjustable to different fiber/resin combinations. We have begun an intensive study using a precatalyzed fabric procedure for the fabrication of ultra-thick composites. In our examination of the precatalyzed fabric process we have shown that the exotherm created during the curing process is controllable by alternating the number of catalyzed and uncatalyzed plies. Whether or not this technique will adequately reduce the exotherm in thicker composites or if their material strength will be comprised is still unknown. The fabrication of 120-ply composites, as well as, material testing procedures are currently being developed to answer these questions. After completing our analysis of the pre-catalyzed fabric procedure there are several other fabrication methods for ultra-thick composites to be studied.

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