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Annual Performance Report

Performance Period: 7/14/97 to 6/30/98

RAPID PROTOTYPING OF COMPOSITE STRUCTURES

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Introduction

This progress report for the project *Rapid Production of Composite Structures* covers the period from July 14, 1997 to June 30, 1998. It will present a short overview of the project, followed by the results to date and plans for the future.

The goal of this research is to provide a minimum 100x reduction in the time required to produce arbitrary, laminated products without the need for a separate mold or an autoclave. It will accomplish this by developing the science underlying the rapid production of composite structures, specifically those of carbon fiber-epoxy materials. This scientific understanding will be reduced to practice in a demonstration device that will produce a part on the order of 12" by 12" by 6".

Work in the past year has focussed on developing an understanding of the materials issues and of the machine design issues. Our initial goal was to use UV cureable resins to accomplish full cure on the machine. Therefore, we have centered our materials work around whether or not UV cureable resins will work. Currently, the answer seems to be that they will not work, because UV light cannot penetrate the carbon fibers, and because no "shadow" curing seems to occur. As a result, non-UV cureable resins are being investigated. This has resulted in a change in the machine design focus. We are now looking into a "dip and place" machine design, whereby a prepreg layer would have one side coated with a curing agent, and then would be placed onto the previous layer. This would lead to cure at the interface, but not to the top of the layer. The formulation of the resins to accomplish this task at room or slightly elevated temperatures is being investigated, as is the machine design needed to apply the curing agent and then cure or partially cure the part. A final, out-of-autoclave, post-cure may be needed with this strategy, as final cure on the machine may not be possible, as it was for the initial UV cure strategy.

The remainder of this report details the progress in the materials and machine design areas.

Materials Development

The material system must be designed to fulfill the following requirements: to reduce the time and labor requirements of typical cure cycles; to reduce the thermal stresses developed during conventional heat curing; and to develop a structure that the build sequence requires. In order to accomplish these goals, there have been parallel tracks of investigation. One area has tested photopolymerizable (ultraviolet (UV) curable) materials and combinations of these materials with standard heat curing resins. The second area has investigated resins that cure rapidly at room or low heat temperatures. The main goal of these investigations has been to identify a system that will rapidly set or cure at room temperature during a tape lay-up process and hold its structure during a post-cure cycle.

To date, resin testing has focused on characterizing several cationic photopolymerizable resins (Table 1). The tests were designed to determine the way that the resins act in the presence of UV light and heat and how these resins differed from each other. These tests showed some of the problems that must be addressed before proceeding. Table 2 presents the test conditions and results. Resins supplied by UCB, Union Carbide, and Sartomer were exposed to UV light for varying times to analyze their response. The resins cured rather slowly and, most noticeably, formed a "skin" on the surface that grew in thickness over time as surface layers of resin cured leaving resin underneath unchanged. All of the resins took much longer to cure completely through than expected. These same resins were subjected to heating which only caused a decomposition of the resins rather than curing. The results of the heat cure tests are presented in Table 3.

Tests were performed to study the "shadow" curing of the UV resins in combination with carbon fibers to see if curing can occur under carbon fibers. Figure 1 graphically shows the tests that were performed. The carbon fiber acted to absorb and scatter light and caused the resin to remain, for the most part, uncured. The only curing that occurred was under spread out, single tows of carbon fibers. The results of these tests showed that "shadow curing" does not seem to be an option to pursue.

These initial tests and discussions with several scientists in the UV resin field revealed that the power used for testing these resins was inadequate. Currently, UV curing equipment is being evaluated in order to purchase a more powerful curing unit. The shadow cure experiments will be performed again, for completeness, with the more powerful UV lamp. Different results are not anticipated. It also was learned that cationic resins tend to have a much slower through cure than free radical resins. Further tests will be performed on both the initial cationic resins and new free radical and hybrid (cationic/free radical, UV/heat curable) systems. This results will be supplemeted with data gathered through DPC (differential photocalorimetry-basically DSC with a UV light) and DSC to determine cure speeds, cure times, and degree of cure at varying stages. The following questions must be answered about these resins:

1. How much light/heat is needed to fully cure material?
2. How much cure will still allow for consolidation of layers during build?
3. How many layers of carbon fiber/epoxy can UV light penetrate?
4. What are the effects of combining UV and heat curable materials?

Currently, new resins are being obtained from Shell Chemical and Henkel to study the other area of interest: resins that cure rapidly at room temperature. These resins will be tested for their basic cure kinetics, as well as for effectiveness in the lay-up process. Samples will be made by hand to determine effectiveness, the amount of curing agent needed to completely cure part, the time for curing, and the effects of thermal post-cure. The following questions must be answered about these resins:

1. How much time and heat is needed to cure the material fully?
2. How much cure will still allow for consolidation of layers during build?

3. How should the curing agent be applied to maximize the curing?
4. How quickly and to what thickness does the curing agent penetrate after application?
5. What are the effects of a thermal post-cure?

Although thermally post-curing the composites after build is not desirable, it might be unavoidable at this stage in order to achieve the desired results. Therefore, it is important to develop a material system that will cure partially at room temperature and still maintain its firmness upon heating during post cure. A system which reaches desirable properties without being raised to the typical high curing temperatures, thereby avoiding some thermal stresses, also might be viable. Photopolymerizable materials might be able to form a structure among the layers of the composite and not move during heat post-cure. Materials that cure at room temperature might cure enough to hold shape when the temperature is raised just slightly enough to produce a complete cure with good material properties. These are the issues that will be addressed in the coming months.

Machine Design

The initial machine design issues involved with this project were the cutting of the carbon fiber prepregs to the shape of each laminate layer, the placement and the orientation of the layers, the consolidation of the laminates to remove voids and produce a well consolidated part, and the use of UV and thermal energy to cure the part. Figure 2 shows a schematic of the initial machine design.

Three companies were identified as having cutters that would be suitable for the needed application. Table 4 compares the various cutters. Lectra and Gerber have cutters with drag knives and American GFM has cutters with ultrasonic knives. All have cutters with comparable speeds. Lectra has a workshop facility in the Atlanta area that can be used if needed for making small parts at Georgia Tech. We will utilize the Lectra facility to prove out our system.

There will be no need for a delivery system for the initial machine because each layer will be placed manually. Some preliminary testing with a prestaged thermoset carbon-fiber epoxy towpreg was done on a filament winding machine to get an idea of the approximate pressures and speeds that will be needed to ensure that layers stick together.

A first generation machine is being designed and built. This machine will use the dip, place and cure idea. The curing agent will be added to one side of each prepreg layer just before placement onto the previous layer. This would lead to the curing of the interface, but not on the top of the layer. The machine will consist of a table that moves back and forth and a consolidation roller above it that will move up and down. Parts are on order for this machine.

The best means for delivering the catalyst needs to be determined. Possibilities include adding it with a roller after the prepreg layer has been placed on the table, spraying the catalyst on each layer either before or after it is placed on the table, or lowering each layer into a catalyst bath before it is placed. Heat and UV light may need to be used for on-line curing, so the best way of delivering each needs to be determined. Testing also needs to be done with the consolidation roller to determine the processing conditions needed to remove air and bubbles from the part.

Summary

We have made much progress in defining the key issues involved in the development of a Rapid Production of Composite Structures Machine. Our next steps are to build the machine to do a "dip and place" procedure or a spray variant, and to identify the epoxy system needed.

Table 1: UV Cationic Resins Tested

Union Carbide	(UVR6110, UVI 6990,6974)
Sartomer	(K 126, KI 85)
UCB	(Uvacure 1500, 1590)

Table 2: Initial UV Resin Screening Results

Wavelength: 365 nm Power: 400W total (10 bulbs @ 40W each)

		2 wt% Photoinitiator												3 wt% Photoinitiator											
	Resin	K 126				UVR 6110				UVR 6110				K 126				UVR 6110				UVR 6110			
Time	**Photoinitiator**	KI 85				UVI 6990				UVI 6974				KI 85				UVI 6990				UVI 6974			
(min.)																									
0.6														V1	C1			V1	C1				C2	S1	
1.2		V1	C1			V1	C1					S1	P1							S1	P1				P1
2.4								S1	P1	V1	C2			V2										S2	P1
4.8		V2										S2	P1					V2	C2	S2		V2	C3		
9.6				S1	P1	V2		S2			C3			V3		S1	P1				P2			S3	P2
19.2		V3		S2	P1		C2			V2		S3	P2	V4		S4	P3			S3	P2			S4	P2
38.4		V5		S5	P4	V3	C3	S3		V4	C4	S4	P2	V5		S5	P4		C3				C4		

V: Viscosity change Scale: 1 (lowest) - 5 (highest)
S: Skin formation Scale: 1 (thin) - 5 (thick)
C: Color change Scale: 1 (no change) - 5 (deep color)

Table 3: Initial Results of Heat Curing Tests

Resin: Union Carbide
Epoxy: UVR 6110
Photoinitiator: UVI 6974

Oven Temperature: 180°C

Time (min.)	2 wt% photo.	3 wt% photo.
2	C2	V2 C3 P1
4	V3 C3 P2	V5 C5 P5
8	V5 C5 P4	

Resin: Sartomer
Epoxy: K 126
Photoinitiator: KI 85

Oven Temperature: 230°C

Time (min.)	2 wt% photo.	3 wt% photo.
2	V1 C2 P1	V1 C2 P1
4	C3	C3
8		
16	V2 C4 P2	V3 C4 P2
32	V4 C5 P3	V5 C5 P5

Resin: Union Carbide
Epoxy: UVR 6110
Photoinitiator: UVI 6990

Oven Temperature: 230°C

Time (min.)	2 wt% photo.	3 wt% photo.
2	V1 C2 P1	V1 C2 P1
4	C3	C3
8		
16	V2 C4 P1	V4 C4 P3
32	V5 C5 P4	V5 C5 P5

V: Viscosity change — Scale: 1 (lowest) - 5 (highest)
C: Color change — Scale: 1 (no change) - 5 (deep color)
P: Surface broken when poked (cure depth) — Scale: 1 (easily broken) - 5 (impenetrable)

Table 4: Cutters

Company	Lectra	Gerber	American GFM
Knife	Drag	Drag	Ultrasonic
Max. Cutting Speed	328 ft/min.	225 ft/min.	200 ft/min.
Advantages	Workshop nearby Good edge quality	Good edge quality	Has robotic gripping system
Disadvantages	Need to find a way of placing material	Need to find a way of placing material	More expensive than other cutters

Figure 1: Test Set Up for Shadow Curing

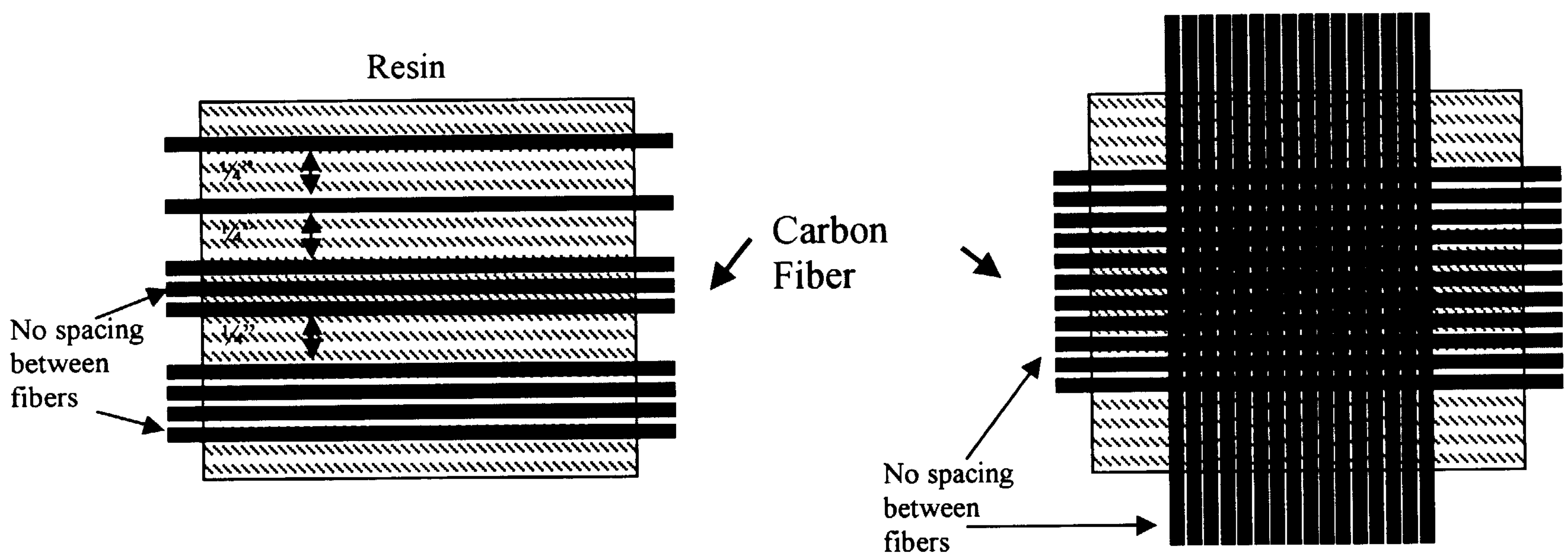

Figure 2: Initial Machine Design