



Co-Injection Resin Transfer Molding of Vinyl-Ester and Phenolic Composites

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Abstract

Vacuum-assisted resin transfer molding (VARTM)-type processes have been proven cost-effective manufacturing techniques for large composite structures. However, their use has been limited to a single resin system. Many composite structures require multiple resins to serve different purposes while being integrated into a single structure. Co-injection resin transfer molding (CIRTM) is a new manufacturing process developed by the U.S. Army Research Laboratory (ARL) with the University of Delaware that enables the user to manufacture multilayer hybrid composite parts in a single processing step. In this report, CIRTM is used to manufacture a dual-layered structure consisting of a vinyl-ester layer for structural integrity and a phenolic layer for fire, smoke, and toxicity protection. The two resins are simultaneously injected into a mold filled with a stationary fiber bed and are co-cured. Resin separation is maintained by a 1-mil-thick polysulfone film sandwiched between two layers of 6.5-mil-thick adhesive. A differential scanning calorimeter (DSC) is used to select the optimum cure cycle for all of the materials. Mechanical testing is used to evaluate the performance of the interphase formed between dissimilar materials. Experimental results show that co-injected, co-cured materials offer equivalent properties, or, in some cases, more superior properties than those provided by single-injection resin composites. This case is used to develop and present a methodology that can be followed to co-inject different resins.

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1. Background and Motivation

Composite materials have a number of advantages over traditional materials. Some of these advantages are light weight, high stiffness-to-weight ratio, improved signature management, and resistance to corrosion. In most cases, one material cannot serve all of these functions, but different materials can be easily layered to serve multiple tasks while being integrated in a single structure. For example, vinyl esters are low-cost resins that offer good mechanical properties, room-temperature cure, and reliable processing. However, they are extremely flammable and produce toxic smoke upon combustion. This limits their use in a variety of applications where material flammability is a concern. Phenolic resins offer low cost but poor mechanical properties due to the evolution of water during cure. However, they offer outstanding fire, smoke, and toxicity protection [1]. Using co-injection resin transfer molding (CIRTM) [2], a single structure can be manufactured with a thick layer of vinyl ester to take advantage of its mechanical properties and a thin layer of phenolic to act as a fire, smoke, and toxicity barrier.

Pike, McArthur, and Schade [3] have shown that vacuum-assisted resin transfer molding (VARTM) processes are cost-effective methods to manufacture large structures. CIRTM takes advantage of these methods and improves them by enabling them to manufacture multilayer structures in a single processing step. Prior to CIRTM, each layer would typically be manufactured individually and then bonded together. This approach requires multiple steps, including surface pretreatments and adhesive bonding, which can introduce additional defects into the part. CIRTM eliminates all of these additional steps, lowers costs, and can improve quality and performance of the part due to the co-cure feature of the process. The fundamentals of CIRTM are investigated in detail by Gillio [4] and by Gillio et al. [5]. In this present study, the CIRTM process is described and used to fabricate glass-reinforced vinyl-ester/phenolic hybrid composites. Parts are subject to a variety of tests to characterize mechanical properties and durability of the interphase formed during co-injection and co-cure.

2. Manufacturing Procedure

2.1 Processing. In the vast majority of structural applications, the vinyl-ester layer would be considerably thicker than the phenolic layer. However, in this research, the co-injected preforms were of equal thickness. This was done because the mechanical tests performed to evaluate the interphase properties require that the interface between the dissimilar materials be located at the geometric midplane. Additionally, the Mode I interlaminar fracture double cantilever beam (DCB) test and the wedge test require that the precrack be placed at the midthickness between two cantilever beams of comparable stiffness. Therefore, under the assumption that the modulus is a fiber-dominated property, the panels were manufactured with the same fiber reinforcement throughout the thickness. Sublaminates infiltrated with each type of resin were assumed to have the same modulus.

Figure 1 shows the experimental setup used to manufacture the co-injected specimens. Seven layers of S2-glass twill-weave, 18-oz/yd² fabric were used for the phenolic and vinyl-ester preforms. The vinyl ester used in this study was Dow Derakane 411-350, which is a room-temperature vinyl ester with a gel time of approximately 30 min. The phenolic used was J2027/L manufactured by British Petroleum and cures at approximately 140° F. An impermeable separation layer was used between them to demonstrate the feasibility of this method for large composite structures. The need for an impermeable separation layer was investigated by Gillio et al. [6]. The setup used in this study is typical of the Seemann composite resin infusion molding process (SCRIMP) [7]. The distribution medium placed on each side of the preforms is a high-permeability material that helps carry the flow along the length and width of the part while the resin flows through the thickness of the preform. The distribution media drastically reduces fill times and enables thick section parts to be impregnated under vacuum only. The resins were simultaneously injected from the two injection locations shown in the figure. Once the part was infused and the resin had cured, the distribution medium was removed.

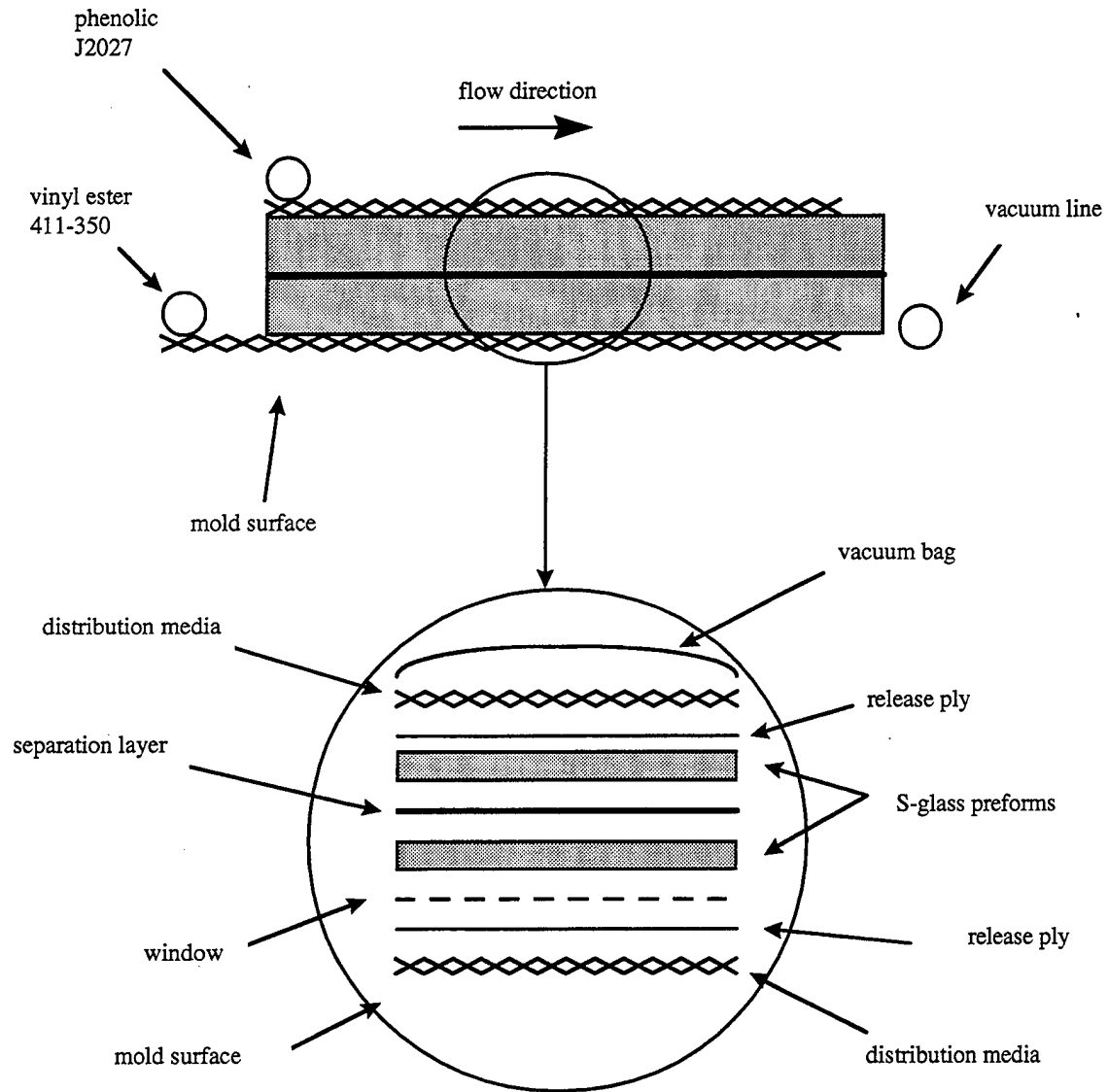


Figure 1. Experimental Setup Used to Manufacture the Co-Injected Specimens.

The impermeable separation layer was formed of a polysulfone film sandwiched between two layers of epoxy-based adhesive. This solution exploits the diffusion-enhanced adhesion (DEA) [8–10] mechanisms where epoxy and the amine curing agent diffuse and react in the polysulfone barrier layer. A 1-mil-thick polysulfone film was selected to go into solution quickly with the epoxy and to toughen the interphase during cure. Additionally, the phenolic is co-cured with the

compatible epoxy. The approach provides a toughened co-cured interphase between materials that would not be compatible otherwise.

The manufacturing took place in the following steps. First, the mold surface, a flat steel plate, was cleaned and mold release was applied to it. Then, the distribution medium was placed on the plate. On top of it, an impermeable layer was placed in which a window had been cut approximately 1 in smaller than the preform on each side. The purpose of this window was only to avoid edge effects, and it was removed, together with the distribution media, after the process was complete. A layer of release film was placed on top of these two layers so that they could be removed. The first seven layers of S2-glass were then placed on top of the release film so that the distribution media would extend out from underneath the preform on one side. Then, the separation layer was placed on top of the fiber preform. Generally, the polysulfone film was sandwiched between the epoxy adhesive before the part was laid up. Once the separation layer was in place, seven layers of S2-glass were placed on top of the preform followed by another layer of release ply and a layer of distribution media. At this point, the lay-up was complete. Two inlet tubes were used. One was placed on top of the preform, and the second one on the part of the bottom distribution media that extended out from underneath the preform. The vacuum tube was placed at the opposite end of the preforms. This whole assembly was then placed under a vacuum bag and sealed, and the vacuum was applied. The vacuum serves three purposes: (1) it compacts the fabric; (2) it removes the air, thus reducing the number of voids in the composite; and (3) it creates a pressure difference that drives the impregnation of the resin into the spaces between the fibers.

A number of baseline panels were manufactured and tested, and the results from all specimens were compared. Two single-resin baseline panels were manufactured: one with a vinyl-ester matrix and one with a phenolic matrix. The main purpose of these baselines was to assess the performance of the co-injected parts. It would not be expected that the co-injected specimens would perform better than the weaker of the two constituent materials. Finally, a panel was manufactured in a three-step process to simulate the current multistep procedure used to manufacture multilayer structures. Two panels were manufactured: one using phenolic and the other using vinyl-ester resins. Then,

they were bonded together using the same adhesive film used in co-injection. In order to limit the number of variables, the polysulfone film was used together with the adhesive in an effort to compare manufacturing techniques.

2.2 Materials. One of the primary challenges presented by co-injection is the selection of a cure cycle. During co-injection, two or more polymers co-cure together. Therefore a cure cycle must be selected, which allows the successful cure of all polymers. Since this application of CIRTTM is designed for large structures, the goal in selecting the materials was to maintain the cure cycle below 200° F (95° C). The vinyl ester used was Dow Derakane 411-350, which cures at room temperature using 0.2% by weight of cobalt naphthenate as the accelerator and 2% by weight of Trigonox 239A (organic peroxide) as the initiator. The phenolic was British Petroleum's J2027/L, a low-viscosity resole phenolic that was catalyzed using 5% by weight Phencat 381. This phenolic must be cured at approximately 140° F in order to limit void formation due to the water present in the phenolic resin. Two adhesive films were selected for this study. The first was 3M's AF-163-2OST, which is an amine-cured epoxy-based adhesive. This adhesive is designed to cure at 225° F or higher. However, Figure 2 shows that it is possible to cure it as low as 200° F if the time periods are extended significantly. Another adhesive, a phenolic-epoxy (PH/EP), was selected due to its better compatibility between the adhesive and the bulk phenolic. This resin is manufactured by Cytec-Fiberite as a film adhesive, HT 424. The compatibility is believed to be improved with this adhesive because PH/EP has a similar curing reaction to the bulk phenolic resin, whereas the epoxy adhesive has a much different curing reaction. As in the previous case, the PH/EP is designed to cure at elevated temperatures, 350° F, but, again, it is possible to lower the cure temperature by increasing the cure time.

The infusion of the part takes place at room temperature to facilitate the manufacturing process, particularly when this technology will be used to manufacture large composite structures. After the infusion, the part is cured at 140° F (60° C) for 4 hr to cure the phenolic. It is necessary to go through this slow cure cycle to limit the formation of voids in the phenolic layer.

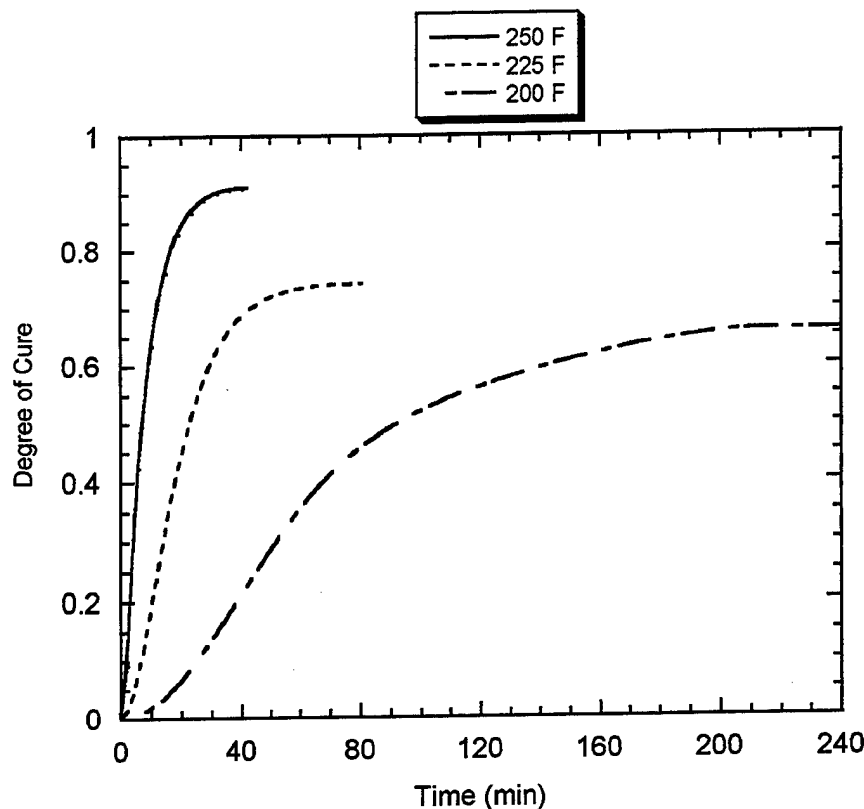


Figure 2. Degree of Cure of the Epoxy Adhesive at Different Temperatures.

After the 4-hr cure of the phenolic, several variations of adhesive cure times were investigated. Two separate cases were investigated for the materials with 3M epoxy adhesive. The first was 4 hr at 200° F, which provided adequate cure when tested in the differential scanning calorimeter (DSC) (Figure 2). In addition, another set was cured at 200° F for an additional 24 hr. This time length was chosen as a maximum limiting time for the epoxy to co-cure with phenolic at 200° F. This cure cycle was investigated because there is a reaction between the acidic curing of the resole phenolic resin and the basic amine curing agent in the epoxy film adhesive. It was anticipated that this reaction could retard the cure of both resins in the interphase region. Therefore, an extended cure cycle was investigated to determine whether this retardation of the reaction could be compensated for by increased cure time. The goal of this new cycle schedule was to fully cure the adhesive while minimizing cure temperature for manufacturing of large structures. The materials using the PH/EP

film adhesive used the same 4-hr, 140° F cure cycle to cure the phenolic and were then cured for 4 hr at 200° F to cure the adhesive.

3. Results and Discussion

3.1 Short Beam Shear. The American Society for Testing Materials (ASTM) short beam shear test (ASTM 2344) is an extremely popular test due to its simplicity. This makes it a good tool to compare shear strength and overall quality of different composite specimens. Specimens were cut using a diamond-coated saw blade based on the dimensions dictated by the ASTM standard. Crosshead speed was set at 0.05 in/min (1.27 mm/min), and at least 10 specimens were tested for each type of specimen. The apparent shear strength was obtained using the following formula:

$$S_H = 0.75 \frac{P_B}{bd}, \quad (1)$$

where S_H is the apparent shear strength, P_B is the failure load, b is the width of the specimen, and d is the thickness. The majority of failures occurred at the interphase between dissimilar materials. Table 1 summarizes the results obtained. Results discussed in the text incorporate statistical variation (mean minus 3 standard deviations [σ]). The vinyl ester performed considerably better than all of the materials with shear strength of 5.0 ksi. The phenolic sample exhibited significantly lower shear strength (2.9 ksi) than the vinyl-ester baseline. The multistep and 8-hr cure co-injection panels using the amine/epoxy adhesive (2.7–2.8 ksi) were slightly lower than the phenolic baseline. Notable improvements in shear strength are achieved with co-injected panels using the 28-hr extended cure amine/epoxy adhesive (4.2 ksi), as well as the 8-hr cure PH/EP adhesive (3.2 ksi). Short beam shear tests show the potential for co-injected parts to provide equivalent or improved properties when cure cycles are optimized. Further research is required to fully optimize the process and performance.

Table 1. Short Beam Shear Results

Material	Apparent Shear Strength (psi)	Apparent Shear Strength [Mean Minus 3σ] (psi)	Failure Type and Location
Vinyl-Ester 411-350	$5,360 \pm 120$	4,990	Brittle, Midplane
Phenolic J2027/L	$3,280 \pm 120$	2,930	Brittle, Midplane
Multistep Process	$3,420 \pm 230$	2,720	Adhesive
Co-Injected With Amine/Epoxy Adhesive (8-hr Cure)	$2,970 \pm 70$	2,760	Cohesive, Phenolic Side
Co-Injected With Amine/Epoxy Adhesive (28-hr Cure)	$4,470 \pm 100$	4,170	Cohesive, Phenolic Side
Co-Injected With PH/EP Adhesive (8-hr Cure)	$3,450 \pm 80$	3,210	First Ply Phenolic

3.2 DCB Testing. DCB measures Mode I fracture toughness, which is a measure of the resistance of the material to delamination within the interphase. The DCB test (ASTM D-5588) directly loads the interphase formed during processing. The DCB test is expected to be more sensitive to the performance of the various interphases created than the SBS test. In the DCB specimen, an artificial flaw of known dimension was manufactured into the composite in the form of a precrack. The specimens were then cut from the composite panel. The specimens were approximately 24 mm wide and 300 mm long. Two blocks were then bonded to the end of the specimen where the precrack was located to allow loading of the specimen. One of the sides of the specimen was carefully painted, and evenly-spaced marks were placed 5 mm apart. The crosshead speed was set at 0.5 mm/min. The specimens were placed in the fixture, and the load was applied. As the load was applied, the crack tip propagated along the specimen. During the test, the critical load, P_{cr} , and the crosshead displacement, v_{cr} , were recorded at every crack tip location.

These data were then used to obtain the fracture toughness of the material using the experimental compliance method, also known as Berry's method [11]. The benefit of this method is that it enables G_{Ic} vs. a to be determined and, consequently, the R-curve effects to be quantified through the following relationship:

$$G_k = \frac{nP_{cr}v_{cr}}{2Wa}, \quad (2)$$

where the critical load and the crosshead displacement are measured during the test; n is the power law index relating compliance to crack length and fit to the data based on

$$C = Ka^n. \quad (3)$$

The results of the DCB tests are summarized in Table 2 and presented in Figure 3. The vinyl-ester specimens provided the highest fracture toughness (980 J/m^2) followed by the co-injection panel using the PH/EP adhesive (730 J/m^2). The other two co-injection panels exhibited fracture toughnesses similar to the phenolic panel ($530\text{--}560 \text{ J/m}^2$). The multistep process exhibited significant scatter in the results and yielded the lowest performance at 360 J/m^2 . All of the co-injected specimens showed cohesive failure. Note that the samples that used a PH/EP adhesive had the highest fracture toughness of any multiple resin material tested. The high Mode I fracture toughness of this material is most likely due the chemical compatibility between the film adhesive and the phenolic resin. Additionally, the precrack was placed both between the phenolic and the epoxy and between the epoxy and the vinyl ester, but this did not appear to effect the results. In most of the DCB samples, the failure was between the epoxy adhesive and the phenolic. It should also be noted that the specimens manufactured through a multistep process exhibited undesirable adhesive failure.

The co-injected specimens that used an epoxy/amine adhesive and were cured for only 8 hr exhibit a unique behavior; the fracture toughness decreases with increasing crack length. Additionally, during the tests, it was noted that the failure that occurred in the epoxy adhesive was always extremely ductile, displaying a behavior that indicated that the epoxy had not fully cured. This stimulated the development of the 24-hr cure cycle. A viscoelastic response exhibited by partially cured thermoset resins would be expected to exhibit this behavior. It is difficult to characterize the local effects on cure and viscoelastic behavior that evolves during processing and

Table 2. Summary of DCB Results

Material	Fracture Toughness (J/m ²)	Fracture Toughness [Mean Minus 3 δ] (J/m ²)	Comments
Vinyl-Ester 411-350	1,220 $\pm$ 80	980	mostly brittle fracture at surface
Phenolic J2027/L	730 $\pm$ 60	550	high void content
Multistep Process	720 $\pm$ 120	360	fails at adhesive/phenolic interface
Co-Injected (Amine, 8-hr Cure)	860 $\pm$ 100	560	failure in adhesive on phenolic side; ductile behavior suggests material not fully cured
Co-Injected (Amine, 28-hr Cure)	740 $\pm$ 70	530	cohesive failure in epoxy on phenolic side, cracks developed in first ply of phenolic
Co-Injected (PH/EP, 8-hr Cure)	940 $\pm$ 70	730	cohesive failure PH/EP adhesive

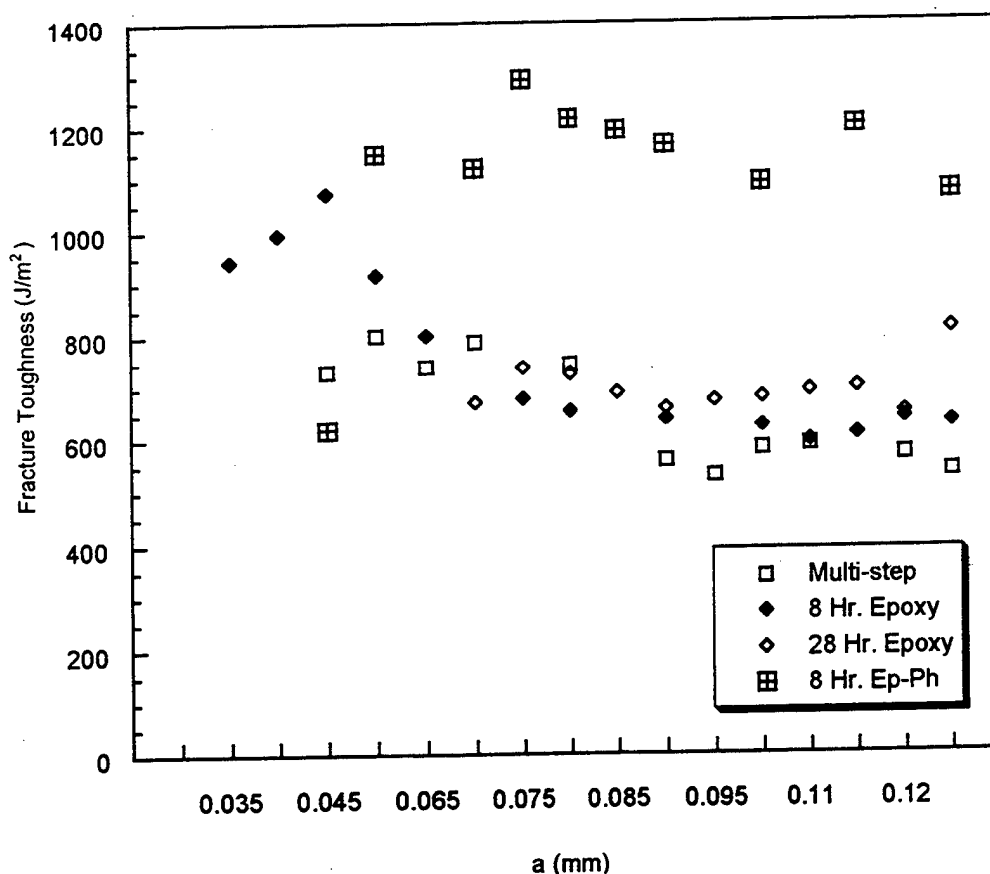


Figure 3. Typical Mode I Fracture Toughness vs. Crack Length.

interphase formation. Consequently, the DCB tests were conducted at higher rates to substantiate the mechanism.

Smiley and Pipes [12], as well as Gillespie, Carlsson, and Smiley [13] have studied the rate effects in the DCB test and can be quantified by defining a crack opening displacement rate as the opening displacement rate at a small arbitrary distance, ϵ , from the crack tip. The crack opening displacement rate, $\dot{y}_{ct}$, is a function of both the crosshead speed, $\dot{v}$, and the crack length, a . The expression they derive is:

$$\dot{y}_{ct} = \frac{3\dot{v}\epsilon^2}{2a^2}. \quad (4)$$

Figure 4 shows the change in crack opening displacement rate as a function of crack length for one of the co-injected specimens where $\dot{y}_{ct}$ changes by one order of magnitude as the crack propagates along the specimen. Specimens were retested at a rate 10 times the original crosshead speed (5 to 50 mm/min). Results are compared to the lower rate data and clearly show the rate effect on Mode I fracture toughness. The decreasing fracture toughness behavior is not present at the higher loading rate, as shown in Figure 5. It is apparent from the behavior in these co-injected specimens that the epoxy adhesive did not fully cure. The joint exhibited rate-dependent behavior in both the DCB and in subsequent durability tests. This finding confirms that, in co-injection, it is not sufficient to define the cure cycle of the final part by simply combining the cure cycles of the individual materials.

An additional proof of the fact that the viscoelastic behavior is caused by a partially cured interphase is that the extended cure cycle (28 hr) specimens did not exhibit any kind of viscoelastic behavior. These specimens had a slight reduction of Mode I fracture toughness as compared to the 8-hr cure specimens. The fracture toughness remained constant or increased with increasing crack length exhibiting a traditional R-curve behavior.

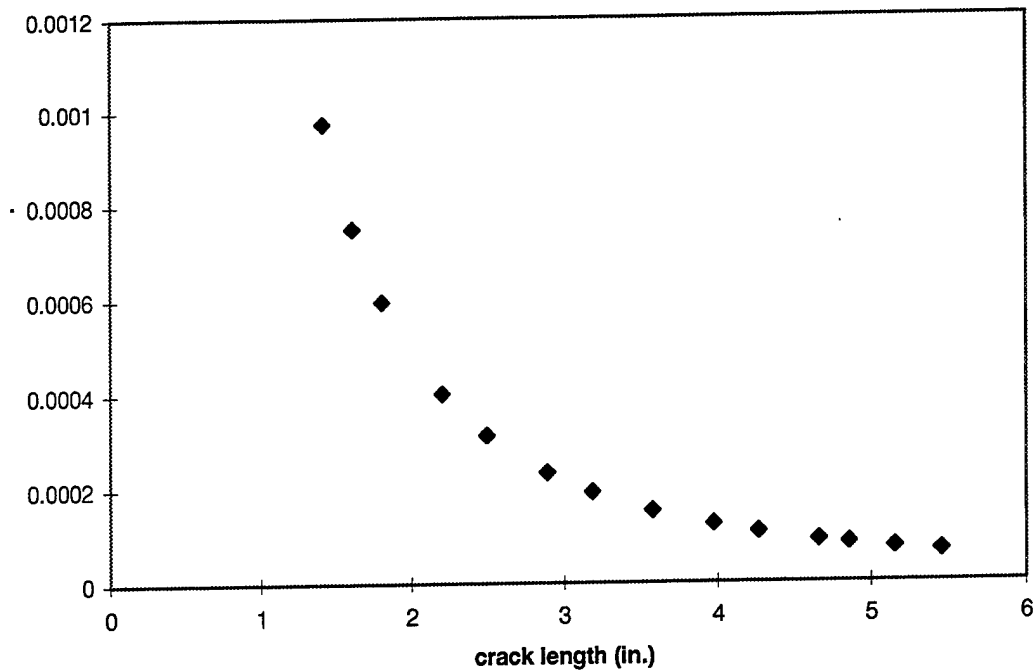


Figure 4. Crack Opening Displacement Rate vs. Crack Length. Data Are Normalized With Respect to the Crosshead Speed.

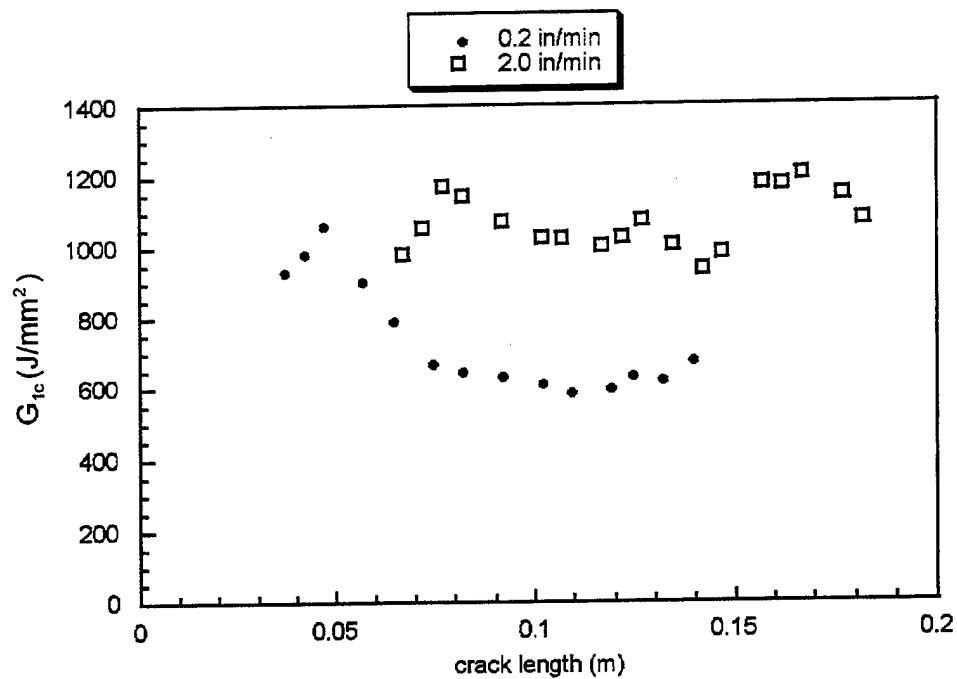


Figure 5. Fracture Toughness vs. Crack Length for Co-Injected Specimens Tested at Different Crosshead Speeds.

3.3 Durability Tests. The final test conducted on the specimens was a durability test. The wedge test (ASTM 3762) was used to evaluate the performance of the interphase under adverse environmental conditions. The wedge test is performed on the same type of specimens used for the DCB. A wedge was inserted into the precrack to initiate a crack. The entire specimen was then inserted in water to simulate an adverse environment, and the crack propagation was recorded at regular time intervals. In this test, the highly stressed crack tip was continuously exposed to room-temperature water, and, therefore, its long-term durability could be evaluated. Figure 6 shows a graph of crack propagation vs. time for all phenolic/vinyl-ester hybrid samples. Under initial wedge insertion, cracks propagated and arrested to the distance at time = 0 in Figure 6. The cracks are then measured at given time intervals over a testing period of 2 weeks. The crack in the co-injected specimen that uses the epoxy/amine adhesive and the short cure cycle, on the other hand, keeps propagating for longer times, exhibiting reduced durability. This is consistent with the viscoelastic behavior observed in the DCB tests. All other materials demonstrate superior durability in this environment.

4. Conclusions

An application of CIRTM technology has been investigated for the purpose of producing large-scale composite structures with an integral fire barrier. Multilayer composite materials composed of a glass-reinforced vinyl-ester structural section and a glass-reinforced phenolic fire barrier section have been successfully manufactured using CIRTM processing. Mechanical characterization of these materials suggests that the choice of materials is critical to the success of the CIRTM process. A number of different alternatives were evaluated. Three different co-injected samples were evaluated in detail. Two used the same separation material, an epoxy/amine adhesive, but different cure cycle. One cycle was 8 hr, while the other was extended to 28 hr in order to ensure complete cure of the materials. The third samples were manufactured using a PH/EP adhesive to improve chemical compatibility with the phenolic resin. Investigations revealed that superior adhesion between the layers could be achieved through the use of the extended cure cycle or the PH/EP adhesive layer for the phenolic side of the part. Short beam shear tests show the potential for

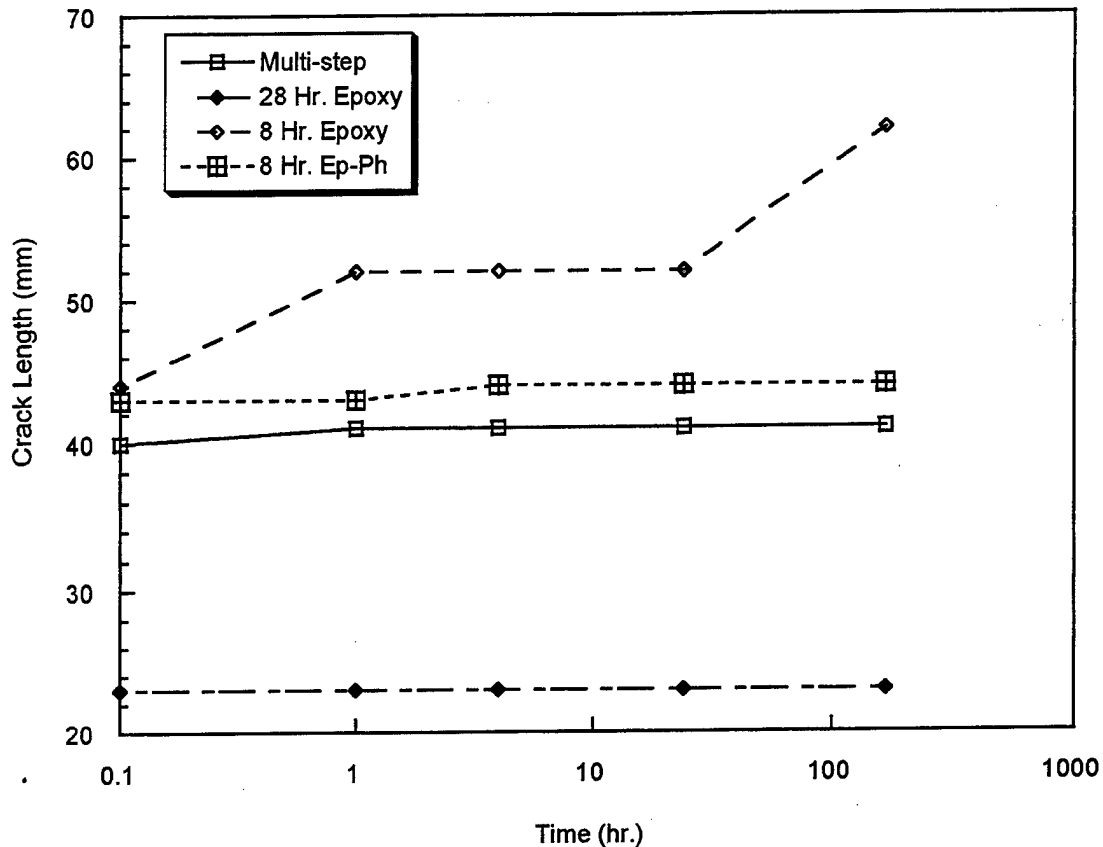


Figure 6. Crack Length vs. Time for All Materials Tested. The Crack Length at $T = 0$ Is the Crack Length After Initial Wedge Insertion. Note That Two Cracks Developed in the 28-hr Specimens and Only the Interface Crack Length Is Reported.

co-injected parts to provide equivalent or improved properties when cure cycles are optimized. However, the panel manufactured with the epoxy/amine adhesive and the short cure cycle exhibited inferior fracture toughness and durability and is attributed to the inhibition of cure at the PH/EP interphase due to acid-base interactions. Interlaminar shear strength values (mean minus 3σ) of 4.2 ksi and 3.2 ksi were measured for the extended cure cycle and PH/EP adhesive specimens, as compared to a value of 2.7 ksi for a panel made with the secondary bonding techniques. Although CIRTTM has provided superior properties and may reduce manufacturing costs, it is necessary to carefully consider the interactions between dissimilar materials to optimize interphase properties, structural performance, and cure cycles.

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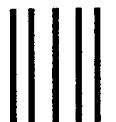
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