

THE EFFECT OF PROCESSING ON INTERFACIAL SHEAR PROPERTIES OF COMPOSITE MATERIALS

W.G. McDonough, J.P. Dunkers, G.A. Holmes
and R.S. Parnas

National Institute of Standards and Technology
100 Bureau Drive, Stop 8543
Gaithersburg, Maryland 20899

INTRODUCTION

A driving force for promoting the use of polymeric composites is a clearer understanding of the influence that processing conditions can have on the final properties of fabricated parts. For example, as we reduce the processing time of composites, we may reach a point where we start to adversely affect properties such as interfacial strength. Because of the role that the interfacial region has in determining mechanical properties and long-term durability of composites, there is a need for appropriate methods to assess changes in the strength and stability of the interface. Consequently, micro-mechanical test techniques such as the single fiber fragmentation test (SFFT) have been developed to reduce the complexity of events that confound interfacial failure analysis.

In the SFFT, a dogbone specimen is made with a resin having a high extension to failure and a single fiber embedded down the central axis. The sample is pulled in tension and stress is transmitted into the fiber through the fiber-matrix interface. Since the fiber must have a lower strain to failure than the resin for the test to work, eventually the fiber breaks at its weakest flaw as the strain is increased. This process of fiber breakage continues until the remaining fiber fragments are all less than a critical transfer length. This critical transfer length is the length below which the fragments are too short for sufficient load to be transmitted into them to cause failure. Fragmentation of E-glass fibers during interfacial adhesion tests of an epoxy SFFT specimen have been shown by Holmes et al. [1] to occur when the matrix is exhibiting nonlinear viscoelastic behavior. Their model has been used in this study to calculate interfacial shear properties.

Because of its processing versatility, vinyl ester reinforced with glass fibers is a composite system of particular interest to industries such as automotive and infrastructure. Thus, for this study, we varied the processing times for a vinyl ester/E-glass fiber

composite system and used the SFFT to assess changes in interfacial properties.

EXPERIMENTAL

Materials and Specimen Preparation

The resin system used was a vinyl ester resin containing a mass fraction of 0.45 styrene. Polymerization was carried out using various formulations containing methyl ethyl ketone peroxide (MEKP) as the catalyst, and dimethyl aniline and cobalt naphthenate as a promoter package. The fibers used were E-glass fibers with a proprietary epoxy size.

We chose to modify an existing mold used for resin transfer molding [2,3]: a ten-cavity aluminum insert was placed inside the main spacer plate. A tow of fibers was cut from a spool of E-glass fibers, and then individual fibers were separated from this tow and placed in the mold insert cavities. Before the mold was placed in the press, a thick-walled rubber hose was attached between the outlet port of the mold assembly and a pressure source to supply back pressure to the mold. The platens were then closed to apply enough pressure to the mold to prevent leakage when the resin was injected. Subsequently, the platens and mold were heated to 80 °C, and the temperature of the mold was allowed to equilibrate for 1 h.

We chose MEKP as our catalyst to obtain gel times that were far enough apart to determine if there were measurable differences in mechanical properties. We found that when containing a mass fraction 0.02 catalyst was added, we achieved a gel time of approximately 45 min (procedure A). We also repeated procedure A and extended the postcure time to a total of 7 h in an effort to increase the glass transition temperature (T_g) (procedure B). When we added containing a mass fraction 0.10 MEKP, we achieved a gel time of approximately 8 min (procedure C). We also wanted to achieve a gel time of under 2 min, but this goal could not be achieved by simply adding more MEKP. We found that if we used containing a mass fraction of 0.02 MEKP and added containing a mass fraction of 0.002 dimethylaniline and containing a mass fraction of 0.001 cobalt naphthenate to serve as the promoter package, we achieved a gel time of 2 min (procedure D).

For each of the procedures used, the mixing and molding procedures were similar. The catalyst (and promoter package used in procedure D) were added to the vinyl ester and mixed with a stirrer for 1 min. We covered the resin with aluminum foil and allowed the resin to degas for 30 min at atmospheric pressure to reduce the chance of forming voids. Following this

step, we poured the resin into tubes that were then attached to an injection gun. Then, through the thick-walled hose that had been attached to the inlet port, we connected the injection gun to the apparatus. Subsequently, we injected the resin into the mold cavity, sealed off the inlet valve, and turned on the back pressure (103 kPa over atmospheric pressure). We then kept the mold at 80 °C for the anticipated gel time plus an additional 15 min. This temperature was chosen to speed up the gelation times. Next, we ramped the temperature to 90 °C and then held the pressure for 2 h (or 7 h for procedure B). Afterwards, we turned off the heat and back pressure and allowed the mold to cool down to room temperature slowly overnight. Finally, the mold was opened and the samples removed.

Testing

After processing, two marks were placed on the specimen surface approximately 1 cm apart and perpendicular to the axis of the specimen and were used to measure the strain in the specimen during the test. The fragmentation tests were carried out on a hand operated testing apparatus such as that described by Drzal and Herrera-Franco (1990) [4]. This apparatus was attached to a polarizing microscope. The stationary grip of this apparatus was attached to a load cell, the details of which are given in Holmes et al. [1]. During the test, small step strains were applied manually by turning a knob attached to the movable grip of the apparatus. The strain increments are of the order of 0.1 % strain. After the strain increment, there was a delay of 10 min before the next step-strain.

After each strain increment, the number of fragments and the strain were recorded, and this routine was followed until the fragmentation process ceased. After each test was completed, the specimens were unloaded and allowed to relax until no residual stress was observed in the specimen. Then, the fragment lengths were measured using a video micrometer. These data were used to calculate the interfacial shear strength values. The relative standard uncertainty in the interfacial shear stress measurement of the sample is 6 %. The standard uncertainty in the strain measurement is 3 % of the measured value. The standard uncertainty in the measurement of the fiber fragments at the critical length was 0.005 mm.

Near Infrared Spectroscopy

The Fourier transform near infrared spectra were collected from (7900 to 4000) cm^{-1} using a bench equipped with a white light source, calcium fluoride beamsplitter, and indium antimonide detector. Transmission spectra were collected on the SFFT

specimens using 16 scans with a 4 cm^{-1} resolution, referenced to air. A (6300 to 5600) cm^{-1} region of the spectrum was analyzed to determine the consumption of the vinyl groups belonging to the vinyl ester (VE) at 6164 cm^{-1} and the styrene (STY) at 6134 cm^{-1} . Peaks attributed to the vinyl ester group and styrene group in the resin used in this study were determined by analyzing the area of the VE and STY peaks. The internal standard (STD) peak used for these calculations is a carbon-hydrogen stretch overtone present at 5667 cm^{-1} . To calculate remaining species, the area attributed to either the VE or the STY was divided by the area of the STD of each SFFT specimen. This ratio was then normalized to the corresponding VE/STD or STY/STD for the unreacted resin to obtain the fractional remaining species.

Differential Scanning Calorimetry

The glass transition temperatures (T_g 's) were estimated using a differential scanning calorimeter with software provided by the manufacturer. Specimens were scanned at 10 °C/min from 40 °C to 160 °C.

RESULTS AND DISCUSSION

Processing Results

Table 1 shows the stiffness of the cured properties of the systems examined in this paper. The 2 % catalyst specimens cured with promoter (Procedure D) provided a very strong, tough matrix (higher Young's Modulus, E) with residual strains (ϵ_r) after testing of 0.2 %. The 2 % and 10 % unpromoted specimens that had a 2 h postcure (Procedures A and C, respectively) were very ductile and had residual strains of approximately 3 %. The properties of the 2 % catalyst specimens without the promoters eventually approached those of the promoted specimens when they were given a longer post cure (7 h) (Procedure B).

The T_g 's for the specimens made by procedures A, B, C, and D were 85 °C, 92 °C, of 55 °C, and 99 °C respectively, with a standard uncertainty of 2 °C.

The conversion of VE, STY, and VE and STY together is presented in Figure 1 for the processing conditions used in this study. Note that less than three spectra were used in the calculation of conversion for processing procedure D, therefore, no bars indicating relative standard uncertainty were used in the calculation of conversion for this procedure. For the 2 % and 10 % MEKP with a 90 °C postcure (Procedures A and C, respectively), the VE reacted more than the STY. For 2 % MEKP with a 7 h postcure (Procedure B), the conversion of VE increased when compared to the 2 h

postcure. The STY did not cure appreciably, resulting in a small increase in the total conversion of vinyl groups. For the 10 % MEKP, the STY were more reacted than the 2 % cases which led to an overall higher conversion of vinyl groups. When the promoter was added (Procedure D), STY groups underwent more reaction than the VE groups. The total reaction of vinyl groups for the system with promoter was about 5 % higher than for the 2 % MEKP without promoter.

Single Fiber Fragmentation Test Results

We can see from the results of the fragmentation test in Table 1 that the promoted and long post cure unpromoted specimens had the highest modulus values (procedures D and B, respectively). The stiffer matrices can be expected to transfer more stress into the fibers and, consequently, have more fragments at the end of the test. The number of fragments at saturation is reflected in the value for the average critical length, l_c , in the strain in the matrix at the critical length, and thus, in the estimated value for the strength of the fiber at the critical length.

Interface damage zones

An interesting aspect of the failure or fragmentation process was the damage zones around the breaks in the fiber. In glass-fiber, epoxy matrix systems and glass-fiber, polyisocyanurate fragmentation samples, when breaks occurred they had small damage or debond zones, and these zones either remained along the interface or extended into the matrix. With the vinyl ester samples used in this study, we saw larger debond regions that indicated a poorer interface bond. What was of particular interest, however, was the appearance of large discolored regions at the fiber-matrix interfacial region surrounding a break that developed upon relaxation (See Figure 2). We have not observed such behavior in other resin systems, however, we do observe this behavior with the vinyl ester system with unsized and vinyl ester sized E-glass fibers.

CONCLUSIONS

Based on the results of the fragmentation test, it would appear that we can achieve similar mechanical properties whether we use promoters or not. However, there was no clear correlation between the mechanical properties and the conversion of vinyl groups as measured by FT-IR. This suggests the possibility of different chemical networks, and the impact of these differences need to be explored further.

REFERENCES

1. G. A. Holmes, R. C. Peterson, D. L. Hunston, W.G. McDonough, Proc. 21st Adhesion Society, 175, (1998).
2. J. P. Dunkers, K. M. Flynn, R.S. Parnas, Composites Part A, 28A, 163, 1997.
3. D. L. Woerdeman, J. K. Sporre, K. M. Flynn, R. S. Parnas, Polymer Composites, 18, No. 1, 133, 1997.
4. L. T. Drzal, P. J. Herrera-Franco, Engineered Materials Handbook: Adhesives and Sealants, 3 (ASM International, Metals Park, Ohio), 391, (1990).

Table 1

Results from the Single Fiber Fragmentation Test

Procedure	E, GPa	l_c , μm	ϵ_f , %	τ , MPa
A	1.9	845	3.0	72.4
B	3.1	674	0.3	96.0
C	1.4	1084	3.0	44.3
D	2.9	607	0.2	104.6

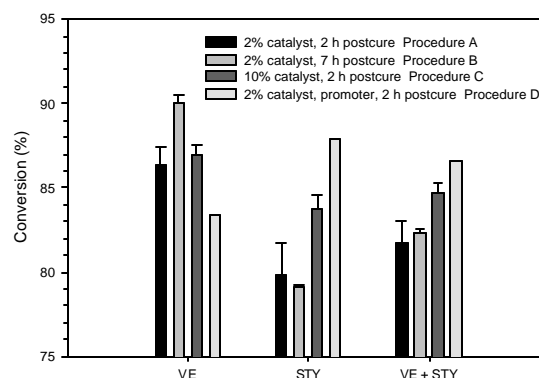


Figure 1: Conversion of vinyl ester, styrene, and total vinyl groups for procedures A, B, C, and D, respectively as determined from near IR spectra.



Figure 2: Failure zone at the fiber-matrix interface.