

# Coupling Carbon Fibers to Epoxy Matrices with Grafted Side-Chain Liquid-Crystal Polymers

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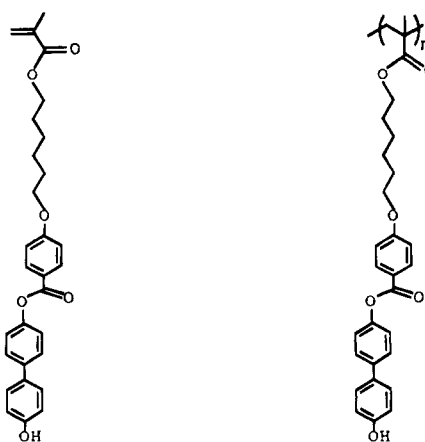
This work investigated the interfacial adhesion between carbon fibers grafted with liquid-crystalline compounds and an epoxy matrix using the "single-fiber tensile test". The liquid-crystalline monomer and its side-chain liquid-crystalline polymer contain phenolic groups and can therefore bond covalently to both carbon fibers and epoxy matrices. Their mesogenic nature also offers the possibility of forming highly ordered interfacial structures. Epoxy specimens containing a single carbon fiber embedded along their length were loaded in tension and observed in transmission by polarized light microscopy. Both stress birefringence due to plastic deformation of the epoxy and the fiber's critical fragmentation length,  $l_c$ , were measured. Relative to specimens with ungrafted fibers or monomer-grafted fibers, those containing fibers grafted with the self-ordering polymer revealed the greatest plastic deformation in the matrix possibly caused by strong interfacial adhesion. Measurements of critical fragmentation lengths suggest the grafted liquid-crystal polymer causes toughening of the carbon fiber/epoxy interface.

## Introduction

Composite materials containing epoxy matrices reinforced by carbon fibers are used as engineering materials in applications such as structural components for aircrafts, space vehicles, and marine deep-submergence pressure vessels. Their mechanical properties and environmental stability depend critically on interfacial adhesion at fiber/matrix interfaces. Establishing the advantages of forming covalent bonds at these interfaces has been an issue of interest for many years.<sup>1,2</sup> Research groups have investigated fiber/matrix chemical interactions and coupling agents mostly in connection with glass fibers and concluded that durable bonds form at the fiber/matrix interface.<sup>3-6</sup> Since the surfaces of carbon fibers are less reactive than those of glass fibers much less is known about their interfacial chemistry in composites. Surface oxidation and coating fibers with a monomeric precursor were the only treatments that resulted in some significant improvement of adhesion at the interface.<sup>7</sup> Usually the monomeric coatings consist of thin films (100-200 nm thick) of un-cross-linked epoxide precursors deposited on fiber surfaces from dilute solutions. Their function is usually to protect the fiber surface from mechanical damage, improve wetting of fiber surfaces by matrix-forming

materials and to protect fiber surfaces from chemical contamination.<sup>8,9</sup> Drzal et al.<sup>10</sup> studied the effect of oxidizing surface treatments on carbon fibers and concluded that the contribution to interfacial adhesion of covalent bonds formed between carboxylic or phenolic groups present on oxidized fiber surfaces and epoxide groups in the matrix was relatively small. They also studied the behavior of an epoxy-based coating on the fiber/matrix interface.<sup>11</sup> The conclusion of this study was that even though the coating increases interfacial shear strength creating a brittle interphase between the fiber and matrix, it does so creating a failure mode which is no longer interfacial. It is widely recognized that only specially designed chemistries in both fiber surfaces and matrices would be an effective approach to interfacial adhesion. This concept has indeed motivated this work which investigates a functionalized liquid-crystal polymer and its corresponding monomer as coupling agents of carbon fibers to epoxies.

We reported previously on the grafting chemistry to carbon fiber surfaces of the monomer and polymer shown here:<sup>12</sup>



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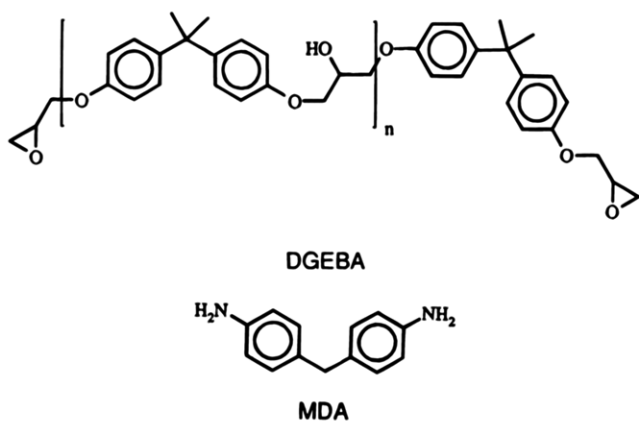
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The phenolic functionality at the terminus of the mesogenic structure can react with carboxyl groups present on functionalized carbon fiber surfaces and form ester bonds. Our previous work offered evidence for this postulated grafting. Furthermore, phenolic groups which do not react with fiber surfaces may react with oxirane rings in epoxy matrices, thus completing the molecule's covalent coupling function. This strategy enables us in principle to covalently bond carbon fibers to the epoxy matrix. The liquid-crystalline nature of these compounds also offers the additional possibility of forming highly ordered and dense boundary zones around fibers. These interfaces could improve environmental stability and physical properties of processed composites. In this work we studied interfacial adhesion between functionalized carbon fibers grafted with these novel liquid crystalline compounds and an epoxy matrix. These studies were carried out using the single fiber tensile test.<sup>10,13</sup>

### Experimental Section

**Materials.** The carbon fibers used were obtained from Hercules, Inc. (AS4 12K). These fibers have been oxidized, and some were grafted in our laboratory with a liquid-crystal monomer or polymer as described in a previous publication.<sup>12</sup> Control fibers for those grafted with monomer were prepared by subjecting the fibers to identical conditions without using a critical reagent for the grafting reaction, and control fibers for those grafted with polymer were prepared similarly but without polymer in the reaction medium. The epoxy was based on the diglycidyl ether of bisphenol A and was obtained from Shell Chemical Co. (DGEBA, Epon 828). 4,4'-Methylenedianiline (MDA, curing agent Y, Shell Chemical Co.) was used as curing agent for the epoxy in the amount of 27 parts per hundred. The matrix around carbon fibers is formed through chain extension and cross-linking using DGEBA and MDA.



All reagents were used as received and were kept in closed dry containers away from direct light. The room-temperature vulcanizing (RTV) silicone molding rubber used for fabricating dogbone molds was obtained from General Electric Company (Silicones, RTV 11-012).

**Preparation of Tensile Test Specimens.** A single fiber, carefully handled with tweezers, was mounted across a specially made U-shaped "fiber holder". Before the fibers were

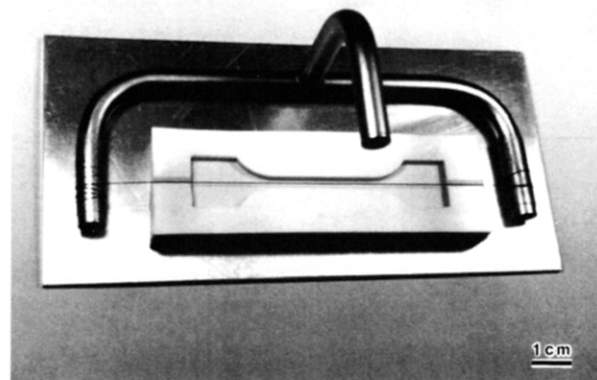


Figure 1. Fiber axially aligned in RTV silicone mold.

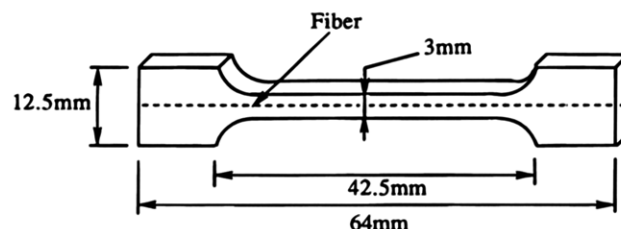


Figure 2. Dimensions of single-fiber specimens for tensile deformation.

brought in contact with the holder, its ends had been covered with double-sided adhesive tape. The fiber was then aligned axially in the cavity of the RTV silicone mold as illustrated in Figure 1. The screws at the end of the dogbone mold helped keep the fiber centered. Eliminating small air bubbles from the molding while casting the epoxy resin around the fiber was very important in order to avoid premature failure of the whole specimen. Therefore the resin mixture was degassed in a vacuum oven at 80 °C and then was injected slowly into the mold using a micropipette. The specimens were cured for 2 h at 80 °C and then for 3 h at 150 °C. The fiber holder was left in place during the cure cycle in order to keep the fiber in centered position and then removed without disturbing the embedded fiber once the resin was cured. Great care was taken in order to avoid fiber contamination in the region embedded in the epoxy matrix. The dimensions of the dogbone sample are given in Figure 2.

**Tensile Test.** The cured dogbone-shaped specimens were mounted in a specially constructed and hand-operated tensile testing machine. This device was then secured to the stage of a transmitted light-polarizing microscope (Leitz Laborlux 12 POL) in order to observe directly the interfacial response of tensile load application on the specimen. The load was applied until no further fiber fractures were observed with additional strain. A minimum of six specimens was tested for each type of fiber. Stress birefringence near the fiber was recorded photographically during testing and was quantified using the image processing program NIH Image 1.47 (Wayne Rasband, NIH) which is public domain software on Macintosh computers. The fractured fiber fragment lengths were measured in situ with a calibrated eyepiece.

### Results and Discussion

Two methods commonly used to investigate fiber/matrix adhesion are the fiber pull-out test and the single-fiber tensile test. The fiber pull-out test<sup>14,15</sup> has been common because of its simplicity, but the clamping and alignment of fibers can be difficult and it is questionable what is the proper fraction of fiber that should be

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embedded. It is best suited for glass fibers and is difficult to use with the brittle and thin carbon fibers. Data from single-fiber tensile tests are more difficult to interpret, but in principle more information can be obtained from a single test. Moreover the test itself simulates well the actual interfacial shear stress conditions of composites. In this work we chose and adapted the single-fiber tensile test to evaluate adhesion at carbon fiber/epoxy matrix interfaces.

Our test is an adaptation to polymer composites of a method originally developed by Kelly and Tyson.<sup>16</sup> These authors studied the tensile behavior of single-fiber test coupons made from tungsten and molybdenum fibers embedded in a copper matrix. Their work described that as a tensile load is applied to the specimen it is transferred to the fiber through shear forces at the fiber/matrix interface. Since the maximum strain of the fiber is much smaller than that of the matrix, the fiber fractures into small fragments within the matrix until a critical fragment length,  $l_c$ , is reached which is too short to allow the transfer of stress equal or greater than the fiber tensile strength,  $\sigma_c$ . They derived an expression relating  $l_c$ ,  $\sigma_c$ , the shear yield stress of the matrix  $\tau_c$ , and the fiber diameter  $d$ :

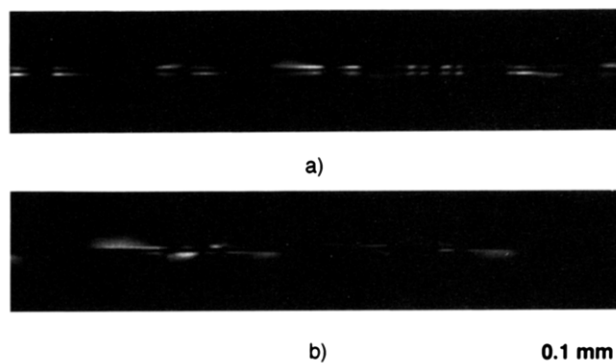
$$\tau_c = \sigma_c d / 2l_c \quad (1)$$

which is obtained from the equilibrium condition

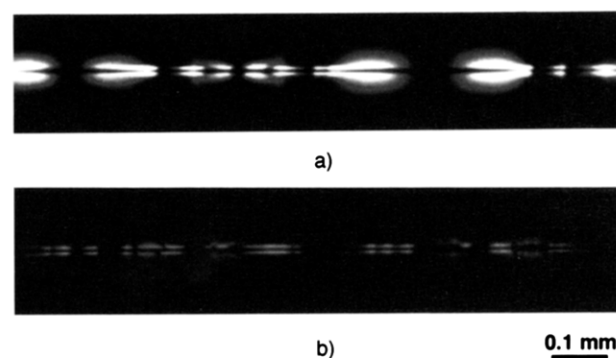
$$1/4 \pi d^2 \sigma_c = 1/2 \pi d l_c \tau_c \quad (2)$$

Many investigators working on polymer composites have used eq 1 to calculate  $\tau_c$ , which is identified as the fiber/polymer matrix interfacial shear strength obtained from  $l_c$  measurements.

An important advantage of transparent polymeric matrices such as epoxies is that these materials can be investigated through direct observation of stress birefringence at the fiber/matrix interface using a polarizing microscope. Therefore during the tensile test used here, qualitative differences in the stress pattern can be correlated to different stress transfer mechanisms. In our experiments when dogbone specimens were deformed in tension photoelastic stress patterns were observed in the epoxy near the ends of fiber fragments. As we increased the tensile load, the photoelastic region rapidly expanded with increasing strain leaving a sheath of birefringence around the fiber. When we completely released the applied tension, part of the birefringence disappeared. Other authors have reported similar behavior.<sup>10,13</sup> In our fiber/matrix systems we expect the mesogenic molecules grafted on the carbon fibers to covalently bond to the epoxy matrix and thus produce good interfacial adhesion. On the basis of Bascom's observations,<sup>13</sup> we infer that the birefringence that persists in our experiments after removal of the tensile stress would be caused by plastic shear deformation of the resin caused by interfacial adhesion. The birefringence which disappears, on the other hand, would correspond to recoverable elastic strain presumably caused by frictional forces between fiber and matrix. In the case of poor fiber/matrix interfacial adhesion, stress relaxation would cause essentially all of the birefringence to vanish, whereas chemical adhe-



**Figure 3.** Polarized light micrograph of a deformed epoxy sample containing an embedded carbon fiber grafted with a functionalized liquid crystalline monomer (a). (b) Micrograph of a control sample (see text).



**Figure 4.** Polarized light micrograph of a deformed epoxy sample containing an embedded carbon fiber grafted with a functionalized liquid crystalline polymer (a). (b) Micrograph of a control sample (see text).

**Table 1. Ratios of Residual Birefringence around Grafted Fibers**

type of fiber	$\eta/\eta_c$
fibers grafted with liquid-crystalline monomer	0.96
fibers grafted with liquid-crystalline polymer	4.31

sion would lead to plastic deformation of the matrix, leaving permanent streaks of birefringence. Thus we used the amount of residual birefringence persisting after relaxation of the dogbone specimen as a direct measure of the quality of adhesion.

Figures 3 and 4 show permanent stress birefringence patterns at carbon fiber/epoxy interfaces after specimens were allowed to relax at room temperature for an hour following removal of the load. Figures 3 and 4 correspond to fibers grafted with monomer and polymer, respectively, and their control fibers. The fiber grafted with monomer and its control exhibit similar stress birefringence patterns. However, the intensity of residual birefringence around fibers grafted with polymer was greater relative to that observed for the control fibers. Ratios of the amount of residual birefringence,  $\eta$ , exhibited by grafted fibers to that of their control,  $\eta_c$ , are reported in Table 1. For fibers grafted with monomer, the birefringence ratio  $\eta/\eta_c$  is roughly equal to unity, suggesting that there has not been any significant improvement in adhesion between the fibers grafted with the liquid-crystal monomer and the epoxy matrix. However, a striking difference is observed in the case of fibers grafted with the liquid-crystal polymer. In this case the permanent birefringence obtained with grafted fibers is 4.31 times greater than that recorded with

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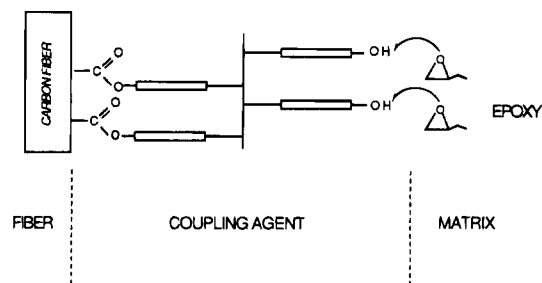
**Table 2. Values of Critical Lengths and Critical Aspect Ratios for Grafted Fibers**

fiber	$l_c$ (mm)	$l/d$
monomer-grafted control	$0.47 \pm 0.02$	$68.2 \pm 6.0$
monomer grafted	$0.50 \pm 0.02$	$72.5 \pm 5.4$
polymer-grafted control	$0.42 \pm 0.07$	$61.1 \pm 12.8$
polymer grafted	$0.60 \pm 0.04$	$86.1 \pm 8.6$

control fibers. This suggests that the strength of interfacial adhesion is increased greatly by the presence of grafted polymer at the fiber/matrix interface.

In each test the load was applied until the fiber had fragmented fully and the critical fragment lengths were then measured. The variation in the  $l_c$  data was broad as expected,<sup>10,13</sup> so the data were treated statistically. It was not possible to measure the fiber tensile strength  $\sigma_c$  at short fiber length, so the  $l/d$  data was not converted to  $\tau_c$ . However, assuming that  $\sigma_c$  of the fibers being compared are similar, then the relative critical aspect ratio  $l/d$  is inversely proportional to the interfacial shear strength  $\tau_c$ . Since the grafted fibers and their controls were exposed to similar chemical treatments, the assumption of equal strength is reasonable. Table 2 lists values of critical lengths  $l_c$  and critical aspect ratio  $l/d$  measured for grafted and control fiber/matrix systems. The ratio  $l/d$  was measured for comparison between fibers having different diameters. Small variations in fiber diameter around a nominal value of  $7 \mu\text{m}$  contributed to the calculation of standard deviations of  $l/d$  values. The critical aspect ratio value determined for the fibers grafted with monomer is almost identical to the one for the control fiber. In the case of the fiber grafted with polymer, there is a 40% increase in the value of  $l/d$  compared to the control fiber.

Our experiments of single-fiber composites prepared with monomer grafted fibers do not reveal any improvement in interfacial adhesion. In this case there is a good correlation between the residual birefringence and the critical aspect ratio data. Samples prepared with polymer grafted fibers, on the other hand, reveal greater stress birefringence thus suggesting an improved fiber/matrix adhesion. This improvement may be attributed to the formation of covalent bonds between the grafted polyphenolic side-chain liquid-crystalline polymer and the epoxy matrix as depicted in Figure 5. One can argue that the improved properties obtained with the polymer-grafted samples might be simply due to enhanced wetting of the fiber by the epoxy at the interface. If this would have been the case, a similar improvement would be expected on monomer grafted fiber surfaces. The fundamental difference between the monomer and polymer grafted fibers is the ability of the latter to effectively couple fiber to matrix through covalent bonds. Our observations thus strongly suggest chemical reaction between phenolic and epoxide groups in the polymer-



**Figure 5.** Schematic of the side-chain liquid-crystalline polymer acting as coupling agent at the carbon fiber/matrix interface.

grafted samples. Moreover previous work in our laboratory<sup>17</sup> revealed that carbon fiber surfaces orient the phenolic mesogens over distances of microns. This could lead to dense anisotropic interfacial regions which may contribute to strong adhesion. However,  $l/d$  values for the grafted fibers were not lowered as one would expect for an increase of interfacial shear strength  $\tau_c$ . This may result from toughening of the fiber/matrix interphase by the grafted liquid-crystal polymer. Such toughening would decrease  $\tau_c$  and consequently increase  $l_c$ . We based this hypothesis on previous studies of interfacial behavior with different matrix systems. Drzal et al.<sup>11,18</sup> have studied the effect of interphases ranging from very brittle to tough on interfacial adhesion and the failure modes of composites. They concluded that creating a ductile interphase around the fiber decreases the interfacial shear strength, therefore increasing  $l_c$ . Similar behavior has also been observed by Kelly<sup>16</sup> on plastic/elastic metal matrices. In our polymer-grafted samples, during tensile loading, phenomena such as sliding of ordered liquid-crystalline layers and stretching of polymer backbones and aliphatic spacers are likely to occur and induce toughening of regions separating the fiber from the epoxy matrix.

## Conclusion

In our previous work we offered evidence for the grafting of a side-chain liquid-crystal polymer on functionalized carbon fiber surfaces. In this work such grafting was found to generate strong adhesion of carbon fibers to epoxy matrices. Furthermore, experimental data suggest the polymeric liquid crystalline zone at the fiber/matrix interface has a toughening effect during the fragmentation of fibers under a tensile stress.

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