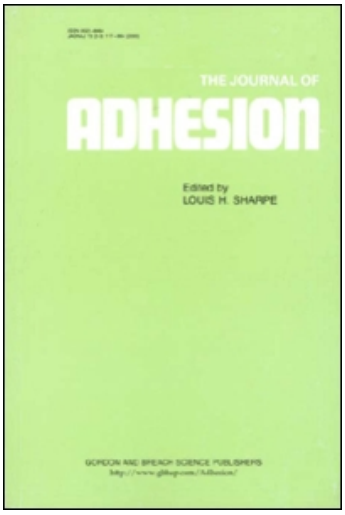

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Characterization, properties, and processing of larc peti-5® as a high-temperature sizing material: III. Adhesion enhancement of carbon/BMI composites

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Online publication date: 08 September 2010

To cite this Article Cho, Donghwan , Choi, Yusong and Drzal, Lawrence T.(2003) 'Characterization, properties, and processing of larc peti-5® as a high-temperature sizing material: III. Adhesion enhancement of carbon/BMI composites', The Journal of Adhesion, 79: 1, 1 — 22
To link to this Article: DOI: 10.1080/00218460309559
URL: http://dx.doi.org/10.1080/00218460309559

The Journal of Adhesion, 79: 1–22, 2003
0021-8464/03 $12.00 +.00
DOI: 10.1080/00218460390147906

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CHARACTERIZATION, PROPERTIES, AND PROCESSING OF LARC PETI-5® AS A HIGH-TEMPERATURE SIZING MATERIAL: III. ADHESION ENHANCEMENT OF CARBON/BMI COMPOSITES

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A phenylethynyl-terminated imide oligomer (LaRC PETI-5®) with a number average molecular weight of 2500 g/mol has been applied onto the surfaces of PAN-based carbon fiber tows and woven carbon fabrics as a sizing material to introduce an interphase between the fiber and matrix in carbon/BMI composites. The adhesion between the fiber and matrix was enhanced by the presence of a properly processed LaRC PETI-5® interphase. The results showed that when LaRC PETI-5® was sized and processed at 150°C, the interfacial shear strength (IFSS) of

Received 8 September 2001; in final form 22 May 2002.

This research was sponsored by the Air Force Office of Scientific Research, Air Force Material Command, USAF, under grant number F49620-98-1-0377, Dr. Charles Lee, Program Director. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government. We wish to thank Dr. John W. Connell of the NASA-Langley Research Center for supplying the samples of LaRC PETI-5.®

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unidirectional IM7/BMI composite measured by using a microindentation technique and the interlaminar shear strength (ILSS) of a carbon/BMI composite measured by short beam shear test were markedly improved by about 35% and 66%, respectively, in comparison with the unsized counterparts. The adhesion enhancement strongly depends not only on the presence or absence of LaRC PETI-5® sizing interphase but also on the temperature profile applied to the sizing before composite fabrication. Both of these factors critically influence the physical and chemical state of the sizing material. Scanning electron microscopic observations of the composite fracture surfaces support the improved interfacial property of carbon/BMI composites.

Keywords: Phenylethynyl-terminated imide oligomer; Sizing; Fiber-matrix interphase; Interfacial shear strength; Interlaminar shear strength; Carbon/BMI composite

INTRODUCTION

Carbon fiber/bismaleimide (BMI) composite materials are currently utilized for commercial and military aircraft and aerospace applications [1]. However, these materials have some critical concerns such as brittleness and property loss due to microcracking and thermal degradation. Fiber-matrix adhesion has been measured using a variety of adhesion tests in a carbon/BMI composite, and the conclusion is, in general, that the adhesion is very low [2]. The interfacial shear strength values of carbon/BMI composites measured using a microindentation test were less than 10% of the values obtained for standard carbon/epoxy composite systems. The interlaminar shear strength as demonstrated by the midplane shear failure of flexure composite specimens was very poor. Achieving better adhesion by providing enhanced interfacial properties has attracted attention in carbon/BMI composites [3, 4].

Adhesion or interfacial strength between fibers and matrix is critically important in a carbon/polymer composite material because the ultimate mechanical properties of the material strongly depend on it [10]. There have been considerable efforts to improve the interfacial properties of carbon fiber-reinforced polymer matrix composites. They include changes in fiber surface energy [5], surface morphology [6], surface chemistry [7] and resin chemistry [8], and fiber sizing [9]. A number of studies have been focused primarily on surface-treating carbon fibers rather than on sizing them in order to improve the fiber-matrix adhesion. However, it has been reported that the probability of significantly increasing adhesion in carbon/BMI system *via* fiber surface treatment appears low [2, 4]. As an alternative, use of a sizing material to design an interphase between the fiber and matrix may be a useful, practical approach. Sizing is normally applied to provide

better adhesion between fibers and matrix in a composite system [11] as well as to improve the handleability and to reduce fiber damage during fabrication of the prepreg and composite [12].

When interfaces in a material are subjected to severe environmental attack, failures may take place at the interface between the constituents. The adhesive performance critically depends upon the interphase between adhesive and substrate, specifically between BMI matrix and carbon fiber reinforcement in a carbon/BMI composite. The interphase, which is a third distinctive phase placed between a bulk fiber region and a bulk matrix region, transfers the load occurring between the two bulk phases [13]. The addition of an interphase has great potential because its composition and properties can be tailored to provide adhesion to the fiber, miscibility with the matrix resin, and improvement of overall composite properties, independent of the bulk matrix properties. This is particularly important for high-temperature applications, where it has been shown that processing at temperatures above 300°C can remove all of the functional groups that are created on the carbon fiber surface during surface treatment [32]. The selection of a proper sizing material with high thermal stability and durability is desirable because a beneficial interphase may be created if appropriate miscibility between the sized material and matrix resin is possible. An optimization of the sizing interphase and sizing process is, of course, necessary to obtain desired ultimate properties of a composite.

In general, the experimental methods used to characterize the fiber-matrix interphase have been based on single fiber-matrix interfacial measurements such as the single-fiber fragmentation test, the single fiber pull-out test, or the microbonding test or the direct interfacial measurement in a real composite laminate, such as the transverse tensile test, short-beam shear test, or microindentation test. The latter methods can provide some advantages over the former from the viewpoint that they allow *in situ* measurement of debonding force and interfacial probing in the real environment. Excellent review articles describing experimental methods for the measurement of fiber-matrix adhesion in composites have been published elsewhere [10, 14, 15].

Phenylethynyl-terminated imide oligomers (LaRC PETI) have had considerable attention in aircraft and aerospace applications for use as composite matrices and adhesives as well as a potential high-temperature sizing material since they were reported by the NASA Langley Research Center in 1994 [16–18]. Among a series of LaRC PETI polymers, it has been known that LaRC PETI-5®, of molecular weight 2500 g/mol, has an excellent combination of processibility, high glass transition temperature, high toughness, and mechanical, physical, chemical, and thermal properties and adhesion at elevated

temperature [19]. Research has been devoted to studying adhesive properties of phenylethynyl-terminated oligomers as a structural adhesive [16], as a matrix in a carbon fiber composite system [17], and in a polyimide/metal substrate adhesive system [20].

In our previous reports [18, 21, 22], we have characterized the fundamental properties of LaRC PETI-5® chemically, physically, and thermally and also found thermal processing conditions for the application of PETI-5 as a potential high-temperature sizing material. Fourier Transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) techniques were used to understand the bulk processing and properties of PETI-5. Consequently, the goal of the present study is to improve fiber-matrix interfacial properties in carbon/BMI composites by introduction of a LaRC PETI-5® interphase as a high-temperature sizing material. In this paper, we report the interfacial shear strength (IFSS) and interlaminar shear strength (ILSS) of LaRC PETI-5® sized carbon/BMI composites measured by a microindentation technique and short beam shear test, respectively.

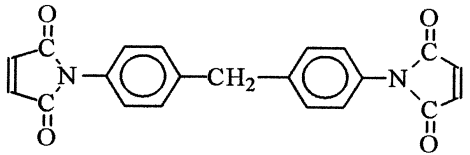
EXPERIMENTAL

Materials

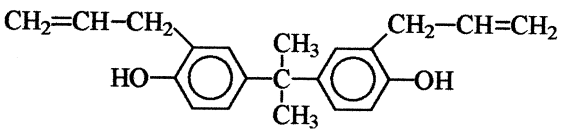
The PAN-based carbon fiber (IM7) tows used for unidirectional composite specimens in the present work were supplied by Hexcel, Inc. (Salt Lake City, Utah) with a proprietary surface-treatment level of 100%, which is the standard commercial treatment, and without sizing. PAN-based woven carbon fabrics (ACELAN TZ-307) with 6000 filaments and 8-harness satin weave, manufactured by Tae Kwang Industries Co., Korea, were used as reinforcement of 2-directional composite specimens. The fabrics supplied were surface-treated by a proprietary method and unsized.

Bismaleimide (BMI, Matrimid® 5292) used as matrix resin in this work and supplied by Ciba-Geigy Co., (Vantico, Inc., East Lansing, MI), is composed of two components, 4,4′-bismaleimidodiphenyl methane (BMPM) and *O,O′*-diallyl bisphenol A (DABPA). Each component was used "as-received" throughout the work without any modification before thermal treatment. Before mixing, both components were stored in a freezer prior to use. The mixing ratio of BMPM to DABPA was 1:0.86. The chemical structures of each component and a representative reaction of BMPM and DABPA are illustrated in Figure 1a and 1b, respectively.

Phenylethynyl-terminated imide oligomer (LaRC PETI-5®) used as high-temperature sizing material was synthesized and supplied as a



4,4′-bismaleimidodiphenyl methane
(BMPM)



0,0′-diallyl bisphenol A
(DABPA)

(a)

(b)

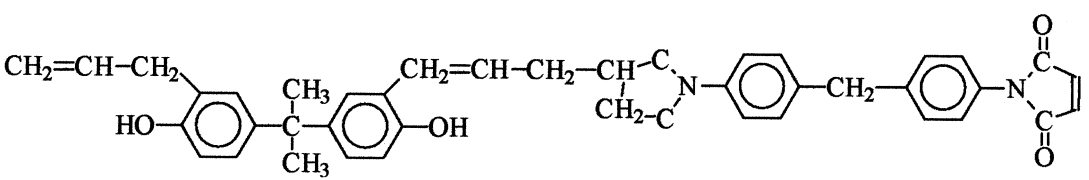


FIGURE 1 The chemical structures of (a) Matrimid® 5292 components and (b) a representative reaction occurring between each component.

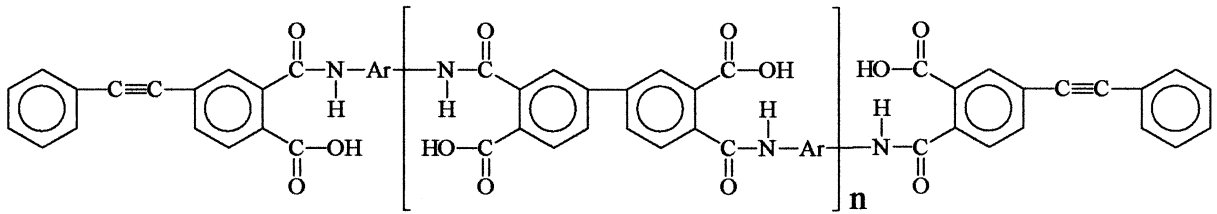
liquid amic acid by Imitec, Inc. (Schenectady, NY). The LaRC PETI-5® oligomer is a random copolymer with a number average molecular weight of 2500 g/mol. It has a solids content of about 35 wt% in *N*-methyl-2-pyrrolidinone (NMP). The LaRC PETI-5® amic acid oligomer is thermally cyclodehydrated to the LaRC PETI-5® imide oligomer and subsequently transformed into the corresponding polyimide. Figure 2 represents the chemical structures. The synthesis and chemistry of LaRC PETI-5® have been described in detail elsewhere [23–25]. The "as-received" oligomer was kept in a freezer and warmed to ambient temperature for only a couple of hours immediately prior to use. The sizing was applied by a dipping method. The sizing concentration was 1.0 wt% in NMP for all the composite specimens for both the microindentation test and the short beam shear test. The sizing was processed at various temperatures of 150°C, 250°C, and 350°C for 1 h each after application and before fabrication into composites.

Composite Specimen Preparation for Microindentation Testing of Fiber–Matrix Adhesion

Unidirectional IM7/BMI composite specimens were prepared by placing 75 mm lengths of the IM7 carbon fiber tows in a high-temperature silicone mold with multiple rectangular cavities. The dimensions of the mold cavity were 75 mm in length, 12 mm in width, and 3 mm in depth. The tows were either unsized or sized with LaRC PETI-5® at different temperatures for comparison before being placed in the mold. BMI resin was heated to about 120°C, degassed in a vacuum oven, and then poured over the preheated mold. The mold was then placed in the vacuum oven and degassed again to facilitate wetting of the fibers by the BMI resin. The mold was then placed in an air-circulating oven and heated at 177°C for 90 min. After this cycle, the cured specimens were removed from the mold and subjected to the standard postcure cycle of 200°C for 2 h and 250°C for 6 h. An unsized IM7/LaRC PETI-5® specimen was also prepared by compression in a metal mold using a Tetrahedron Press because it cannot be successfully made in a silicone mold. LaRC PETI-5® normally requires applied pressure above 1 MPa to mold [23]. The composite specimens obtained were cut into coupons approximately 15 mm long for analysis. Two pieces of each were cold-mounted in epoxy and finely polished for interfacial testing system (ITS) testing.

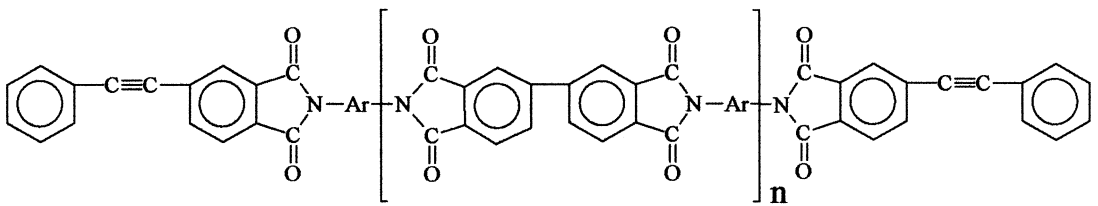
Composite Specimen Preparation for Short Beam Shear Test

Two-directional (2-D) carbon fabric/BMI prepregs were prepared with the resin content of about 50% by weight. About 25 plies of the



Phenylethynyl-Terminated Amic Acid Oligomer

(a)



LaRC PETI-5

(b)

FIGURE 2 The chemical structures of an (a) LaRC PETI-5® amic acid oligomer and (b) the corresponding polymer.

prepregs cut into proper size were stacked by a hand lay-up method in a metal mold 50 mm × 50 mm in size. Any air possibly entrapped between the stacked plies was removed by repeated pressing and depressing cycles every five plies before molding. Finally, 2-D carbon/BMI composites sized with LaRC PETI-5® at different temperatures were obtained by a compression molding method with a time-temperature profile at 177°C for 90 min, 200°C for 2 h, and 250°C for 6 h. The pressure applied was 0.6 MPa. An unsized 2-D carbon/LaRC PETI-5® composite was also processed with a time-temperature profile at 150°C for 1 h, at 250°C for 1 h, and at 350°C for 2 h for comparison. The pressure applied was 1 MPa. The thickness of each composite obtained was about 7 ~ 8 mm. An unsized 2-D carbon/BMI composite was prepared according to an identical process for comparison. Each specimen was cut using a low-speed saw (Isomet, Buehler) for the short beam shear test.

Microindentation Measurements with the Interfacial Testing System (ITS)

The ITS apparatus measures the adhesion between fiber and matrix in real composite specimens by loading the polished faces of fibers with a hemispherical diamond indenter as depicted in Figure 3. During the test, the specimen is moved toward the microindenter tip using stepper motors in 0.04 μm increments. The applied load is measured using a Sartorius balance interfaced with the controlling computer. The balance has a resolution of 0.01 g. The debonding load is determined by using incremental loading steps and visually checking for a debond between each loading using an attached light microscope. Here, failure is defined as a debond of at least 90° ~ 120° around the fiber. Figure 4 is a view of a carbon fiber filament surrounded by several neighboring fibers in the matrix at the identical location, indicating the debonding phenomenon occurring during the ITS test. The IFSS is calculated within the ITS software using a formula obtained from a finite element analysis of this loading condition [2]. The formula takes into account the distance between the tested fiber and its nearest neighbor as well as the tensile modulus of the fiber, shear modulus of the matrix, and failure load. In this experiment, a 5 μm tip was used throughout the testing. Five fibers were selected for testing in a specimen. The fibers to be measured are ones that are surrounded by 5 ~ 6 neighboring fibers distant from each other within the fiber diameter as depicted in Figure 4.

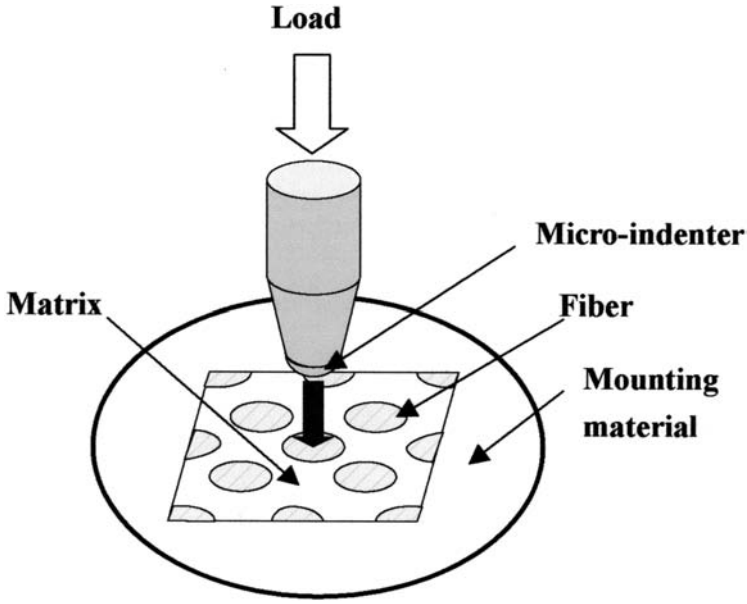


FIGURE 3 Fiber loading in the interfacial testing system (ITS).

Short Beam Shear Test

A universal testing machine (Instron 4467) was used to perform the short beam shear test and to measure the interlaminar shear strength of composites unsized and sized with LaRC PETI-5® at different temperatures according to ASTM D-2344 [26]. The dimensions of a specimen were 40 mm long, 6.5 mm thick, and 6.4 mm wide. The span-to-depth ratio of the specimen was 4:1. A 30 KN load cell was used, and the crosshead speed was 1.3 mm/min. Ten specimens were used in the test.

Microscopic Observations

The sizing surfaces for IM7 and the fractured surfaces for IM7/BMI composite specimens were observed using an environmental scanning electron microscope (SEM) (ElectroScan 2020 ESEM®). Fracturing was done applying a 3-point bending load in a universal testing machine. The applied load was uniform for all the specimens to be fractured. After the short beam shear test, the interlaminar debonding patterns occurring between the cross-plies for each specimen were observed using a conventional SEM (Hitachi S-2400).

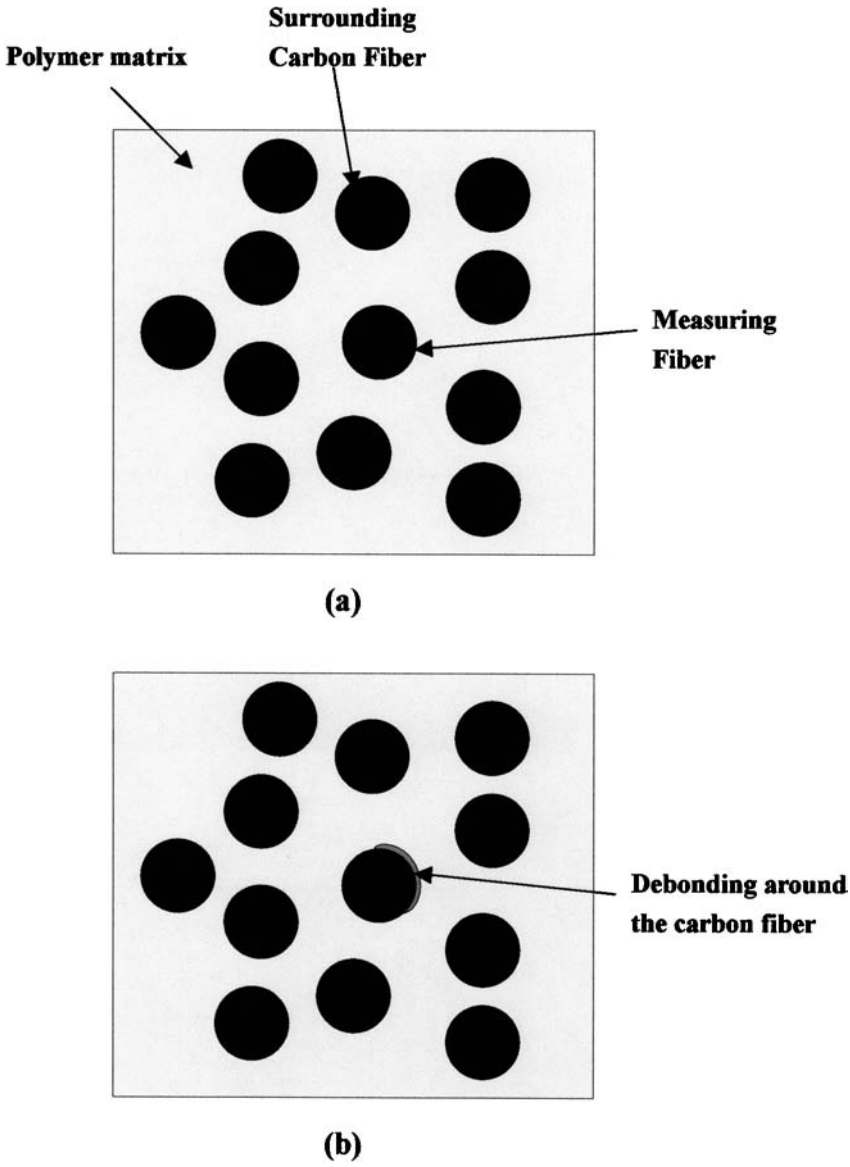


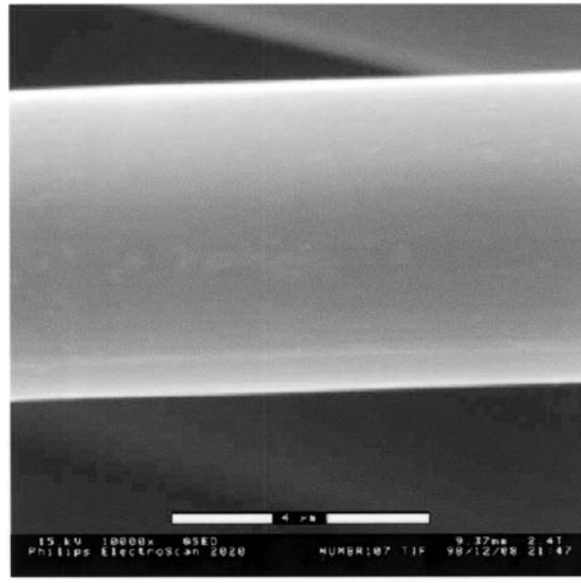
FIGURE 4 Representative views of a measuring fiber surrounded by neighboring fibers in the ITS testing, (a) before debonding and (b) after debonding. A fanlike area along the circumferential direction of a measuring fiber indicates debonding between fiber and matrix in a composite.

RESULTS AND DISCUSSION

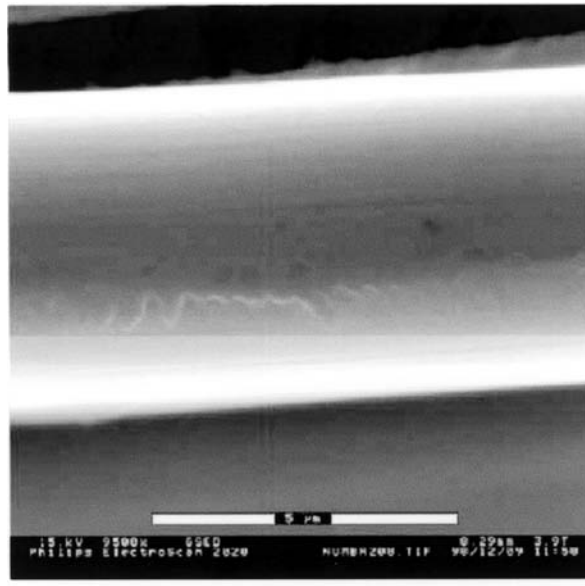
Figure 5 shows scanning electron microphotographs for the 100% surface-treated IM7 carbon fiber before and after sizing with LaRC PETI-5® amic acid oligomer of 1.0 wt% in NMP. Sizing does not alter significantly the appearance of the surface when it is done at 150°C, where LaRC PETI-5® is partially imidized and uncured [16]. Most of the solvent was removed from the surface. The sizing thickness is expected to be less than 0.1 μm. With increasing sizing temperature, the surface chemistry may be changed due to full imidization of LaRC PETI-5® at 250°C and full cure at 350°C [18], although the appearance of the surfaces does not change significantly.

Figure 6 represents the effect of the presence and absence of LaRC PETI-5® sizing and the processing temperature on the IFSS of IM7/BMI composites fabricated according to a cure and postcure cycle. The IFSS values were measured using microindentation with the ITS system. An unsized IM7/BMI composite was also measured for a control and has a lowest IFSS value of 23.5 MPa. As can be seen, the IFSS value of the unsized IM7/BMI composite is significantly enhanced by sizing the carbon fiber with LaRC PETI-5® and is dependent on the sizing processing temperature. The highest improvement is about 35% in the case of the composite sized at 150°C. The IFSS value is approximately 31.4 MPa. The value decreases with increasing sizing temperature.

During the composite fabrication process, the uncured matrix resin is uniformly distributed over the sized carbon fiber surfaces. Meanwhile, wetting of the surfaces leads to an intimate contact at the interfaces between the uncured resin and the sized interphase. Diffusion or interpenetration may occur between the two molecular chains across the interface. Also, it may be possible that covalent bonding between the diffused molecules can occur if the materials are further processed at higher temperature, where both molecules can react with each other. The term "coreaction" may be used to distinguish the chains reacted at the interface and in the bulk matrix region. Therefore, the adhesion enhancement by introduction of the LaRC PETI-5® sizing interphase between carbon fiber and BMI matrix may be the result of possible interdiffusion at the interface between the LaRC PETI-5® and BMI during carbon/BMI composite processing. The interdiffusion of molecular chains through the interface between two similar polymer layers is not easy to access directly unless one polymer chain is chemically or spectrally distinguishable from the other chain. In an indirect and destructive manner, measuring the interfacial strength of the specimens as a function of processing



(a)



(b)

FIGURE 5 Scanning electron microphotographs for the 100% surface-treated IM7 carbon fiber (a) before sizing ("as-received") and (b) after sizing with LaRC PETI-5® at 150°C.

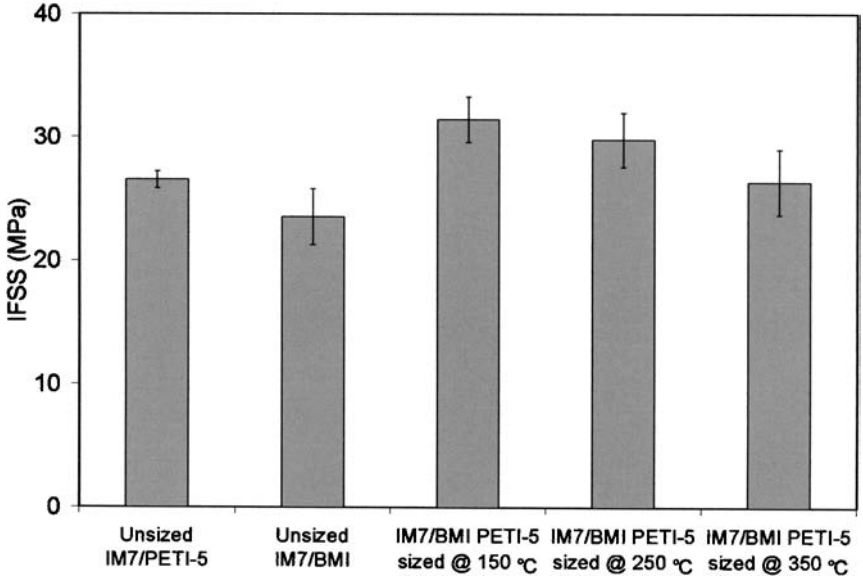


FIGURE 6 A comparison of the interfacial shear strengths measured for IM7/BMI composites unsized and sized with LaRC PETI-5® at different temperatures and an unsized IM7/LaRC PETI-5® composite.

conditions can be a useful way to explore the interdiffusion phenomenon [27], as was done in the present work.

In earlier studies, we demonstrated the interdiffusion by means of dynamic mechanical analysis [28] for immiscible LaRC PETI-5®/BMI blends and fluorescence spectroscopy [29] for thin LaRC PETI-5®/BMI layers. In a previous report [22], we also confirmed that the LaRC PETI-5® sized on a braided glass substrate is partially imidized at 150°C, fully imidized but partially cured at 250°C, and fully cured at 350°C. Therefore, it was concluded that physical interdiffusion was highest at 150°C, may partially occur at 250°C, and only slightly occurs at 350°C. In addition to this, two interdiffused molecules between the LaRC PETI-5® and BMI may be chemically coreacted at the interface during processing of the composite.

To fabricate an IM7/LaRC PETI-5® composite successfully, the final cure temperature of 350°C should be used for complete consolidation. The IM7/BMI composite sized at 350°C shows an IFSS value of 26.4 MPa, which is the lowest among the sized specimens, for the reasons cited above. This value is similar to that of an unsized IM7/LaRC PETI-5® composite. For the case of processing the sizing at 350°C, the fiber-matrix adhesion between the IM7 and fully cured

LaRC PETI-5® matrix may be similar to adhesion between the IM7 and LaRC PETI-5® interphase, producing a low IFSS value of 26.5 MPa, similar to the IM7/BMI composite having a sized but fully-cured interphase.

The fracture surfaces of IM7/BMI composites unsized and sized with LaRC PETI-5® at different temperatures were also examined to see if the microscopic observations agreed with the fiber-matrix adhesion results. Figure 7 shows scanning electron microphotographs

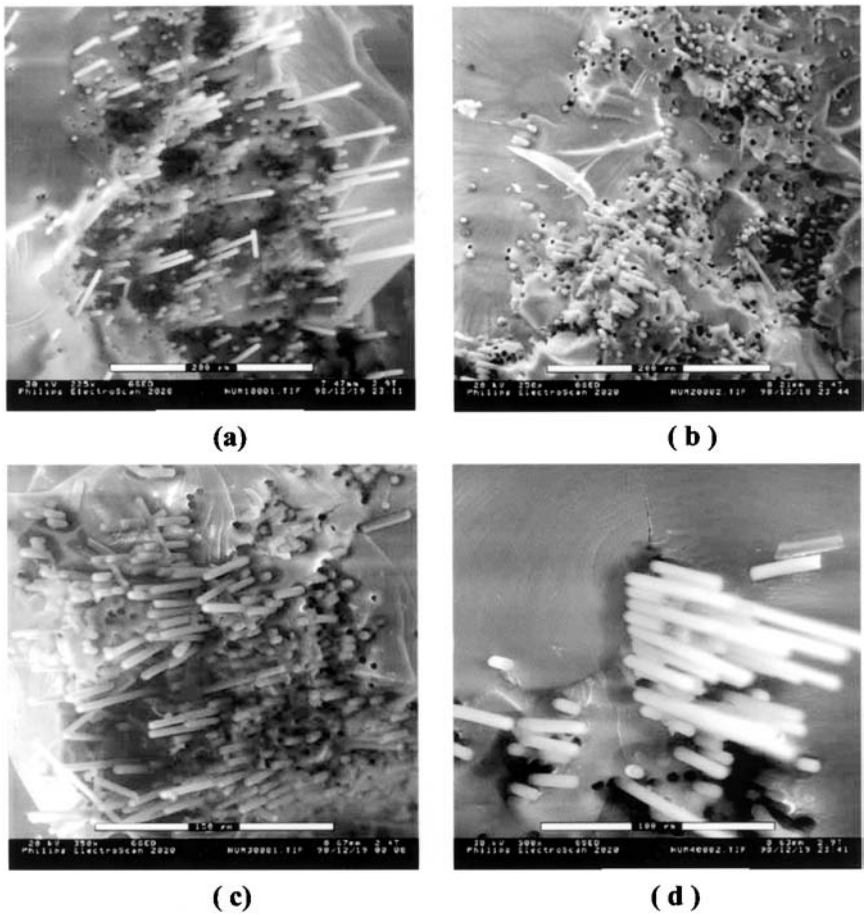


FIGURE 7 Scanning electron microphotographs showing the fractured surfaces of IM7/BMI composites (a) unsized and sized with LaRC PETI-5® at (b) 150°C, (c) 250°C, and (d) 350°C.

of the unidirectional composite coupons that have been fractured in a bending mode. As can be seen, the average fiber pull-out length after fracturing is shorter in Figure 7b for the composite sized at 150°C than the unsized one in Figure 7a and the ones sized at a higher temperature in Figure 7c. In Figure 7b many fibers were broken leaving very short fibers protruding from the fracture surface, in comparison with Figures 7a, c, and d. The fiber pull-out length is observed to be longest in the unsized composite. The carbon fiber surfaces look clean, especially in Figures 7a and d, indicating relatively poor adhesion between the fiber and matrix. These two composites have the lower values of fiber-matrix adhesion. The BMI matrix in the composite was fractured, showing brittle deformation in all the specimens. Close inspection of Figure 7b shows that there is some roughness in the appearance of the fracture surface of the matrix resin surrounding the broken or pulled out fibers which was not seen in the other specimens. This is ascribed to improved adhesion between the IM7 and BMI matrix by a LaRC PETI-5® interphase sized at 150°C. The microscopic examination of the IM7/BMI composite sized with LaRC PETI-5® at 150°C shows the best adhesion between the IM7 carbon fiber and BMI matrix among the specimens. The results also qualitatively support the difference among the IFSS values for the composites given in Figure 6.

Composite Results

The short beam shear test has been one of the most popular methods to determine the interlaminar bond quality of fiber-reinforced polymer composite materials due to the simplicity of the test methods and sample preparation [14]. It has been most frequently used to study the effect of surface-treatment and sizing in a real composite laminate system. Figure 8 shows the typical variations of the applied load as a function of displacement during short beam shear tests for unsized and sized carbon/BMI composites. The loading was stopped as soon as shear failure at the midplane occurred with a simultaneous load drop. The maximum applied load (P_{max}) was used to calculate the interlaminar shear strength (ILSS, τ_{max}) of the tested specimens with the following equation [26],

$$\tau_{max} = 3P_{max}/4b \cdot t$$

where b is the specimen width and t is the thickness. In general, different commercial sources and types of matrix resin and carbon fiber

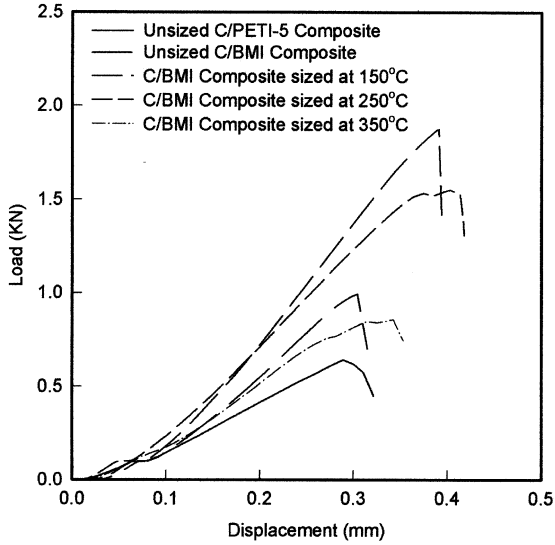


FIGURE 8 Plots of the applied load as a function of displacement occurring during short beam shear tests.

importantly influence the interlaminar properties of a composite laminate. In addition, the interlaminar performance critically depends on fiber texture, fiber alignment, fiber content, and fabrication method.

The ILSS values obtained in the present work for carbon/BMI composite specimens are lower than those obtained by other research groups [30] for carbon/BMI composites with different commercial sources of BMI resin and carbon fiber. Their values reported fall into the range of 100 to 150 MPa for unidirectional carbon/BMI composites at room temperature. It is generally known that unidirectional composites have a higher ILSS value than do 2-directional woven fabric composites. Shin and Morgan reported that carbon/BMI composites with $[0/90]_{4S}$ and $[90/0]_{4S}$ balanced symmetric laminates have short beam shear strength of about 40 MPa [31]. Therefore, the ILSS values for woven fabric composites examined in the present study are primarily useful for comparing the sizing effect on carbon/BMI composites. Figure 9 represents the ILSS values for various 2-directional woven carbon/BMI composites, unsized and sized with LaRC PETI-5® at different sizing temperatures.

The carbon/BMI composite sized at 150°C shows the highest ILSS value followed by that sized at 250°C. The carbon/BMI composite

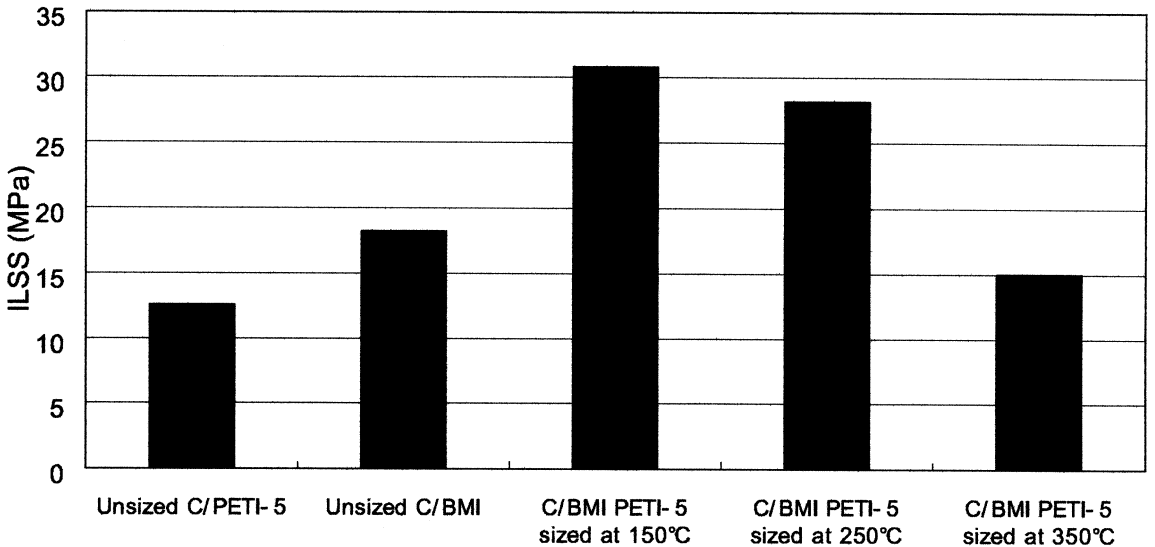
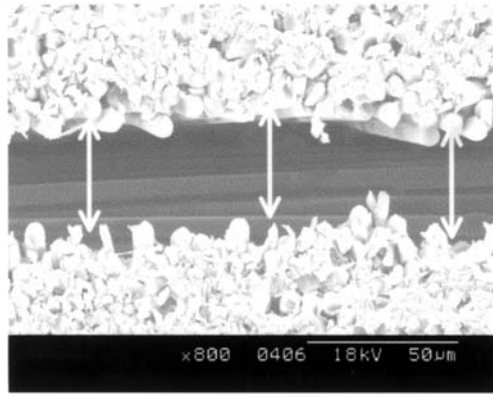


FIGURE 9 A comparison of the interlaminar shear strengths for carbon/BMI composites unsized and sized with LaRC PETI-5® at different temperatures and an unsized carbon/LaRC PETI-5® composite. Here, carbon indicates woven carbon fabrics.

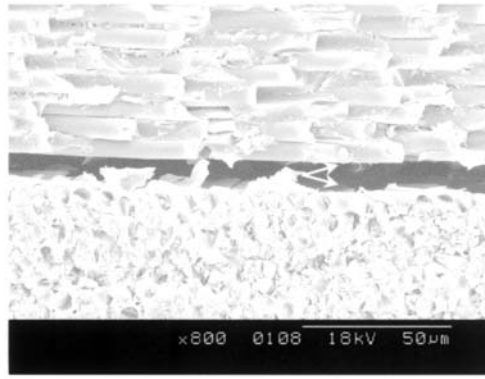
sized at 350°C exhibits the lowest ILSS among the sized composites. The unsized carbon/LaRC PETI-5® composite shows the lowest ILSS. It is very noticeable that the ILSS is improved by about 66% for the carbon/BMI composite sized at 150°C, comparing with the unsized counterpart. The LaRC PETI-5® interphase sized at 250°C is fully imidized but partially cured. Therefore, there may be some possibility of interdiffusion and coreaction with the BMI matrix, as described earlier. However, the possibility is less than that of the carbon/BMI composite sized at 150°C. The composite sized at 350°C shows lower ILSS than the unsized composite. This can be explained by the fact that the LaRC PETI-5® sized and processed at 350°C is fully cured and the surface of the carbon fiber will be coated with thin solid LaRC PETI-5®, which will not interdiffuse into the BMI matrix. Therefore, there is little possibility of reaction between the sizing and the BMI matrix. Consequently, it can be concluded that the improved fiber-matrix adhesion and ILSS values for the carbon/BMI composites sized with LaRC PETI-5® at 150°C may be due to physical interdiffusion and chemical coreaction at the interface between the LaRC PETI-5® interphase and the BMI matrix resin.

Figure 10 shows scanning electron microphotographs observed for each composite specimen after the short beam shear test. The photos were taken at the same magnification of 800 ×. Interlaminar failure was microscopically verified by the failure pattern of sized and unsized composite specimens. The unsized carbon/LaRC PETI-5® composite exhibited the weakest interlaminar failure with many cracks, and the cracks propagated in various directions. Some intralaminar failure with large cracks was also found, as shown in Figure 10a, as indicated by arrows. Such intralaminar failure patterns were not observed in Figures 10b, c, and d. This type of failure may be caused by poor adhesion between the carbon fiber and matrix, resulting in the low ILSS values in Figure 9. On the other hand, the unsized and sized carbon/BMI composites showed crack formation between the cross-plies, as typically expected from the short beam shear test. The interlaminar cracks were formed along the ply direction, as indicated by arrows in Figures 10b, c, and d. The carbon/BMI composite sized at 150°C results in the highest ILSS and IFSS with a large amount of the resin adhered to the carbon fibers compared with the other composite specimens. The microscopic results qualitatively support improved fiber-matrix adhesion being responsible for the improved interlaminar properties in the carbon/BMI composite by introduction of a LaRC PETI-5® interphase at 150°C.

The combined results of IFSS and ILSS suggest that the interfacial strength depends on the extent of the interphase formed by the



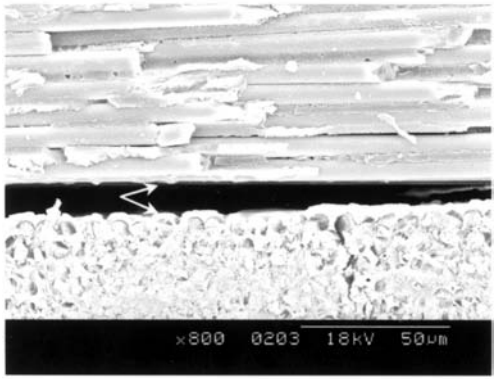
(a)



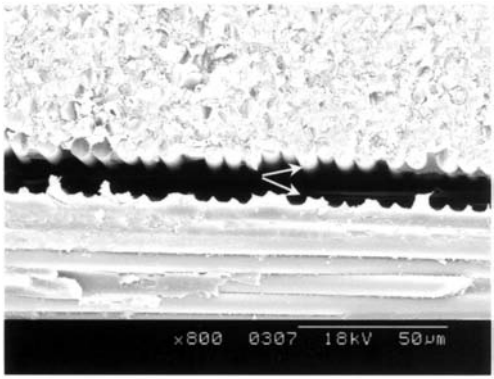
(b)

FIGURE 10 Scanning electron microphotographs (× 800) after the short beam shear test of (a) unsized carbon/LaRC PETI-5® composite, (b) unsized carbon/BMI composite. (Continued)

interdiffusion and/or coreaction of the molecules involved in the present composite system, which is temperature-dependent and time-dependent. Detailed experimental information supporting the interdiffusion behavior of the LaRC PETI-5® and BMI will be discussed in a future paper.



(c)



(d)

FIGURE 10 (Continued) Scanning electron microphotographs (× 800) after the short beam shear test of (c) carbon/BMI composite sized with LaRC PETI-5® at 150°C, and (d) carbon/BMI composite sized with LaRC PETI-5® at 250°C.

CONCLUSIONS

A phenylethynyl-terminated imide oligomer (LaRC PETI-5®), with a number average molecular weight of 2500 g/mol, has been applied onto the surfaces of PAN-based carbon fiber tows and woven carbon fabrics as a sizing material to introduce an interphase between the fiber and matrix in carbon/BMI composites. The adhesion between the

fiber and matrix was largely enhanced by the LaRC PETI-5® interphase. The carbon/BMI composites coated with the LaRC PETI-5® sizing material processed at 150°C produced the highest IFSS (35%) using a microindentation technique and the highest ILSS (66%) measured by the short beam shear test. Processing of the sizing at 250°C produced improved results, but not as good as for the 150°C process. The results showed the interfacial properties decrease with increasing sizing temperature up to 350°C. Therefore, it is concluded that the adhesion enhancement strongly depends on sizing temperature as well as on the presence or absence of LaRC PETI-5® sizing interphase.

Based upon earlier dynamic mechanical analysis and fluorescence spectroscopy, the improved interfacial properties of carbon/BMI composite resulting from the introduction of a LaRC PETI-5® interphase can be explained by the physical interdiffusion and chemical coreaction occurring at the interface between the LaRC PETI-5® and the BMI matrix resin during composite processing. The sizing processing temperature critically influences the physical and chemical state of LaRC PETI-5®. Scanning electron microscopic observations qualitatively support the improved fiber-matrix adhesion resulting from the use of the LaRC PETI-5® sizing processed at 150°C.

REFERENCES

[1] Lincoln, J. E., Morgan, R. J., and Shin, E. E., *J. Adv. Mater.*, **32**(4), 24–34 (2000).
[2] Wilenski, M. S., *The Improvement of the Hygrothermal and Mechanical Properties of Bismaleimide and K3B/IM7 Carbon Fiber Composites Through a Systematic Study of the Interphase*, PhD dissertation, Michigan State University (1997).
[3] Heisey, C. L., Wood, P. A., McGrath, J. E., and Wightman, J. P., *J. Adhesion*, **53**, 117–147 (1995).
[4] Wilenski, M. S., and Drzal, L. T., *Improvement of BMI/IM7 properties*, unpublished results (2000).
[5] Nardin, M., Asloun, E. M., and Schultz, J., *Polym. Adv. Tech.*, **2**, 115–122 (1991).
[6] Jangchud, I., Eby, R. K., Serrano, A. M., and Meador, M. A., *J. Adv. Mater.*, Oct., 19–25 (1996).
[7] Donnet, J.-B., Wang, T. K., Peng, J. C. M., and Rebouillat, S., *Carbon Fibers* (3rd ed.), (Marcel Dekker, Inc., New York, 1998).
[8] Wilkinson, S. P., Ward, T. C., and McGrath, J. E., *Polymer*, **34**, 870–884 (1993).
[9] Drzal, L. T., *Vacuum*, **41**, 1615–1618 (1990).
[10] Herrera-Franco, P. J., and Drzal, L. T., *Composites*, **23**, 2–27 (1992).
[11] Drzal, L. T., Rich, M. J., Koenig, M. F., and Lloyd, P. F., *J. Adhesion*, **16**, 133–152 (1983).
[12] Blackketter, D. M., Upadhyaya, D., King, T. R., and King, J. A., *Polym. Compos.*, **14**, 430–436 (1993).
[13] Drzal, L. T., Rich, M. J., and Lloyd, P. F., *J. Adhesion*, **16**, 1–30 (1982).

[14] Kim, J.-K., and Mai, Y.-W., *Engineered Interfaces in Fiber Reinforced Composites* (Elsevier Science Ltd., London, 1998), Chapter 3.
[15] Drzal, L. T., Herrera-Franco, P. J., and Ho, H., "Fiber-Matrix Interface Tests," In: *Comprehensive Composite Materials*, Kelley, A. and Zweben, C., Eds (Elsevier Science Ltd., London, 2000), Chapter 5.
[16] Jensen, B. J., Bryant, R. G., Smith, Jr., J. G., and Hergentother, P. M., *J. Adhesion*, **54**, 57–66 (1995).
[17] Rommel, M., Konopka, L., and Hergenrother, P. M., *28th Int'l SAMPE Tech. Conf.*, Society for the Advancement of Materials and Processing, Baltimore, MD, pp. 1–13 (1996).
[18] Cho, D., and Drzal, L. T., *J. Appl. Polym. Sci.*, **75**, 1278–1287 (2000).
[19] Smith, Jr., J. G., Connell, J. W., and Hergenrother, P. M., *43rd Int'l SAMPE Symp.*, Society for the Advancement of Materials and Processing, Long Beach, CA, pp. 93–105 (1998).
[20] Tan, B., Vasudevan, V., Lee, Y. J., Gardner, S., Davis, R. M., Bullions, T., Loos, A. C., Parvatrareddy, H., Dillard, D. A., McGrath, J. E., and Cella, J., *J. Polym. Sci., Part A: Polym. Chem.*, **35**, 2943–2954 (1997).
[21] Cho, D., and Drzal, L. T., *J. Appl. Polym. Sci.*, **76**, 190–200 (2000).
[22] Cho, D., Choi, Y., and Drzal, L. T., *Polymer*, **42**, 4611–4618 (2001).
[23] Hergenrother, P. M., and Smith, Jr., J. G., *Polymer*, **35**, 4857–4864 (1994).
[24] Hergenrother, P. M., Bryant, R. G., Jensen, B. J., and Havens, S. J., *J. Polym. Sci.: Part A: Polym. Chem.*, **32**, 3061–3067 (1994).
[25] Connell, J. W., Smith, Jr., J. G., and Hergenrother, P. M., *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C40**, 207–230 (2000).
[26] ASTM D-2344, *Test Method For Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short-Beam Method* (1989).
[27] Ruch, F., David, M. O., and Vallat, M. F., *J. Polym. Sci.: Part B: Polym. Phys.*, **38**, 3189–3199 (2000).
[28] Choi, Y., *Dynamic Mechanical Properties of Larc PETI-5 Polyimide, The Blends and the Composites*, MS Thesis, Kumoh National University of Technology, Korea (2001).
[29] Cho, D., Yang, G., and Drzal, L. T., *Polym. Mater. Sci. Eng.*, **87**, 283 (2002).
[30] Pater, R. H., *SAMPE J.*, **30**(5), 29–38 (1994).
[31] Shin, E. E., and Morgan, R. J., *Proc. ANTEC '93*, 1357–1363 (1993).
[32] C. L. Weitzsacker, Xie, M., and Drzal, L. T., "Using XPS to Investigate Fiber/Matrix Chemical Interactions in Carbon Fiber Reinforced Composites", *Surf. Interf. Anal.*, **25**, 53–63 (1997).