

# Surface Preparation for Adhesive Bonding of Polycyanurate-Based Fiber-Reinforced Composites Using Atmospheric Plasma Treatment

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**ABSTRACT:** In this article, the effects of atmospheric plasma treatment on the microstructural, chemical, and mechanical behavior of epoxy-bonded polycyanurate composites are investigated. Adhesive bond strength of plasma-treated specimens exhibited strength increases of over 35% to that of peel-ply and solvent-wiped surface preparation techniques. The improvements were as much as 50% greater than those obtained using abrasive surface preparation techniques. X-ray photoelectron spectroscopy analysis showed an increase in the surface concentration of oxygen as a function of plasma treatment passes. However, the levels were substantially lower than that of epoxy composites treated under identical conditions. In addition, the concentration of carboxyl groups ( $\text{O}-\text{C}=\text{O}$ ), which have been associated with improved adhesive strength in

epoxy-based composites, was shown to saturate in cyanate ester composites after a much lower exposure period than what was observed when treating epoxies. The effect of plasma surface treatment on the surface morphology of the cyanate ester composite was also studied using scanning electron microscopy and atomic force microscopy. Atomic force microscopy analysis showed a progressive increase in surface roughness with treatment; however, this increase only translated into a marginal increase in surface area and is not believed to contribute significantly to adhesive strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 921–931, 2011

**Key words:** atmospheric plasma; cyanate ester; bonding; composites; surface preparation

## INTRODUCTION

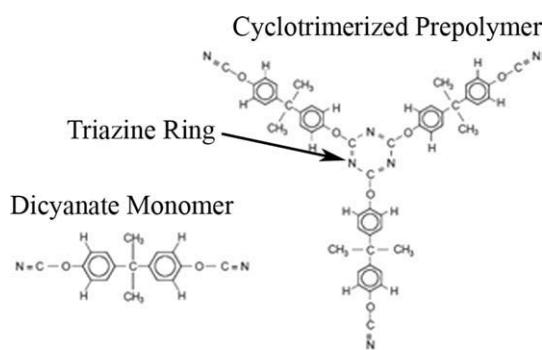
Composite manufacturers rely on well-controlled processes to create consistent, high-performance bonded joints. Current standards for preparing the surface of a composite for bonding use either mechanical roughening or peel ply techniques.<sup>1,2</sup> Recently, there have been a number of articles that have evaluated the use of atmospheric plasma treatment as an alternate method over currently accepted techniques. The recent availability of plasma sources that operate at atmospheric pressure and relatively low temperatures has made atmospheric plasmas a promising alternative to vacuum plasmas.<sup>3</sup> The atmospheric plasma treatment process uses a capacitive discharge at atmospheric pressure to produce a uniform high density of mix of ions, electrons, and free radicals. The reactive species impinge on the surface of the composite resulting in both microstructural and surface chemistry modifications that improve adhesive bonding.<sup>4</sup> Unlike abrasion, the atmospheric plasma

treatment is noncontacting, requires minimal operator intervention, and can be applied to complex shapes. Additionally, secondary contamination is expected to be greatly reduced compared with abrasion techniques. Plasma treatment has been applied to a number of polymer systems<sup>5</sup> as well as to a few structural composite material systems<sup>6</sup> with promising results. However, the improvements vary depending on the substrate treated.

Over the last decade, polycyanurate composites have become the structural composite material of choice for most space applications. Developed as a drop-in replacement for epoxy systems in the early 1990s, cyanate ester resins have the advantages of lower moisture absorption,<sup>7</sup> with a corresponding high-dimensional stability, increased glass-transition temperatures,<sup>8</sup> and improved fracture toughness.<sup>9</sup> Polycyanurate resins are typically synthesized by the polymerization of cyanate ester monomers. The addition of heat and/or a metal catalyst allows three dicyanate ester monomers to come together by a cyclotrimerization reaction, forming an intermediate-molecular-weight prepolymer as shown in Figure 1.

The prepolymer material is further cured and ultimately forms a highly cross-linked network connected with triazine rings. There is very limited work with respect to the use of plasma treatment of

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**Figure 1** Schematic showing the polymerization of cyanate ester monomers forming a triazine ring.

cyanate ester-based composites. The majority of the work that has been performed to date focuses on the plasma surface treatment of the fiber reinforcement before its incorporation within the cyanate ester matrix material rather than the treatment of the cured composite.<sup>10</sup> Even though cyanate ester composites are processed and used for similar applications to that of epoxy composites, the difference in chemical structure may affect the manner in which they respond to atmospheric plasma.

In this article, the effect of atmospheric plasma treatment on the bonding behavior of a widely used carbon fiber-reinforced polycyanurate composite is investigated. As described in a previous publication, many of the improvements observed in the adhesive bond strength of plasma-treated graphite epoxy composites are a result of the formation of active chemical species incorporated onto the surface of the substrate.<sup>11</sup> As the surface concentration of carboxyl species increases, the subsequent bond strength is also shown to increase. It is postulated that this improvement in performance is primarily a result of these activated groups on the substrate reacting with the epoxy adhesive during cure and subsequently forming strong bonds. However, in this investigation, the matrix material used in the composite substrate varies sufficiently in chemistry from epoxy resins to warrant a complete microstructural and chemical surface analysis. Developing an understanding of how the plasma treatment affects the chemical and surface structure of cyanate ester materials and how these changes translate to the mechanical behavior of the treated bond surfaces will allow an assessment of the suitability of this technique as an alternative to current industrial practices.

## EXPERIMENTAL

### Materials

The composite materials investigated in this study were manufactured using Tencate's (Benicia, CA) RS3C cyanate ester resin with Toray's M55J PAN-

based carbon fibers. The RS3C resin system is based on a dicyclopentadienyl dicyanate ester monomer. The laminates consisted of eight prepreg plies laid up in a unidirectional configuration. The laminates were cured in an autoclave at 121°C under a pressure of 0.69 MPa (100 psi) and subsequently post-cured to 177°C for 2 hr. The ramp rate was maintained for all processes at 1°C/min. The baseline specimens were manufactured on a polished aluminum mandrel with a 0.127-cm FEP release film. No other release agents were used during processing. The peel ply specimens were manufactured exactly the same as the baseline specimens, with the addition of one layer of Precision Fabrics (Greensboro, NC) polyester peel ply (60001) adjacent to the tool side surface during processing.

### Plasma treatment

A Surfex Technologies (Culver City, CA) AtomFlo-250 atmospheric plasma unit was used to treat all samples investigated in this study. The control unit uses helium gas as the carrier and oxygen as the active gas. All gases are of 99.9% purity. The plasma wand (Surfex PS02129) used a 25 mm linear beam. Plasma conditions were fixed at 96 W of radio frequency (13.56 MHz) power, 0.450 L/min of oxygen as the active gas, and 30 L/min of helium as the carrier gas. During treatment, the samples were placed on a stationary stage and a robotic arm holding the plasma head was scanned at a constant rate across the specimen face. A LABVIEW program was used to control the robotic arm, and a scan rate of 24.5 mm/sec was used for all specimen treatments. The working distance was held fixed at 1.0 mm from the source. Before surface treatment, all specimens were cleaned with deionized water and then wiped with isopropanol. Samples were typically bonded within 48 hr of plasma treatment unless otherwise stated. Plasma exposure is defined in terms of the number of passes by the plasma head over the test surface. The plasma exposures used in this study were 0, 1, 3, 6, 12, 16, 24, and 48 passes. Details have been described in a previous publication.<sup>12</sup>

### Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed on specimens directly after plasma treatment to identify any variation in the glass-transition temperature because of degradation or cure advancement of the resin system. Single-ply (0.127-cm thick) specimens were cured using the process described previously for the baseline specimens and used for this series of DMA testing. We believe that the thinner specimens would be more susceptible to changes caused by the plasma because the surface-to-volume ratio of the tested specimen would be increased. A

TA Instruments (Yorba Linda, CA) 2980 DMA Analyzer was used for all testing. The samples were scanned from room temperature to 300°C at a rate of 10°C/min. The samples were tested in a single cantilever mode at a frequency of 1 Hz and a maximum strain of 20  $\mu\text{m}$ . The glass-transition temperature ( $T_g$ ) was identified as the maximum in loss modulus.

### Contact angle wetting experiments

A Rame-Hart (Netcong, NJ) Advanced Automated Digital Goniometer was used for all contact angle measurements. The test unit uses DROPimage Advanced software for resolving all contact angle measurements and surface energy analysis. 25  $\times$  25 mm composite specimens were cut, cleaned using isopropanol, and plasma treated at the aforementioned plasma conditions to evaluate the effect of plasma treatment on the wetting angle. Specimens were compared with solvent-wiped specimens as well as conventionally hand-abraded specimens.

### Scanning electron microscopy

A JEOL (Pleasanton, MA) scanning electron microscope was used to analyze the surface microstructure of the composite samples after plasma treatments. The specimens were gold coated and viewed shortly after treatment using a voltage of 15 kV.

### X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) system Surface Science Instruments (SSI) (Bend, Oregon) using an Al K $\alpha$  source was used for surface chemical analysis as a function of plasma treatment. Analyzer pass energies of 150 and 50 eV were used for wide scans and high-resolution spectra, respectively. The XPS analysis chamber was pumped by an ion pump and had a base pressure of  $1 \times 10^{-10}$  Torr.

### Atomic force microscopy

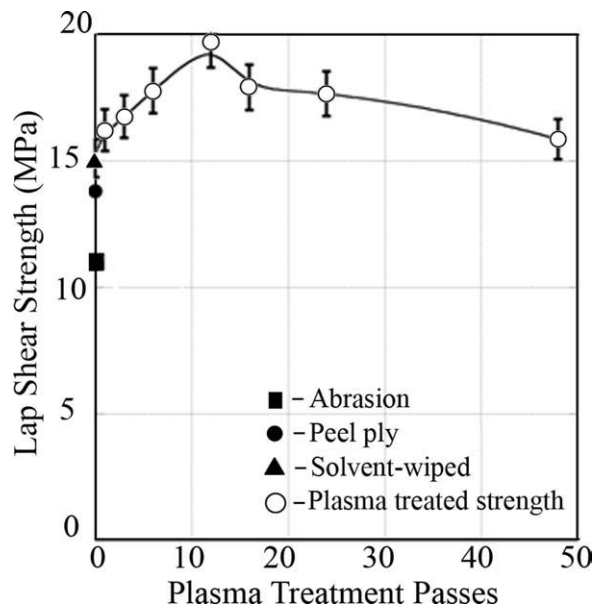
An AGILENT (Santa Clara, CA) 5500LS atomic force microscope was used for analysis of the surface morphology of the composite specimens. The tool side of composite specimens were treated and analyzed. The tool side of the composite is typically much smoother than the bag side, which provides a better baseline surface when trying to detect small variations. A number of 10  $\times$  10  $\mu\text{m}$  scans were obtained and compared as a function of plasma treatment condition. The root mean square and surface area difference were also measured as a function of treatment condition. Surface area calculations were obtained by selecting an identically sized area, 5  $\times$  5  $\mu\text{m}$  (25  $\mu\text{m}^2$  of projected area) from each image frame.

### Mechanical testing

Composite-to-composite single lap shear testing was performed per ASTM D 3165 to assess the effectiveness of plasma treatments for enhancing bond strength. All composite adherends tested in this investigation were postcured at 177°C. E-glass/epoxy doublers having the same thickness as the RS3C/M55J laminates (1.5 mm) were bonded to one side of the 150  $\times$  150-mm laminates. The 65-mm-long doublers were bonded to the grip end on the same side of the laminates as the bond area, ensuring that the laminates did not fail in the grip area and minimizing bending stresses on the bond area. The doublers were bonded using an ambient-temperature-cure adhesive, Hysol EA 9359.3. The doublers were bonded to the laminates before plasma treatment to minimize post-treatment handling.

After the doublers were cured, the bond area for each adherend was wiped with isopropanol and plasma treated. The two adherends were bonded together within 48 hr of treatment with no post-treatment cleaning. Bondline control wires (0.13 mm diameter) were placed parallel to the 15.2 mm-long lap area at five equally spaced locations across the width of one laminate. The wires extended beyond the lap area and were secured with tape. Polyethylene film was placed across the width of both laminates along the edge of the bond area. Hysol EA 9394 epoxy paste adhesive was used for all bonding and was applied to the bond area on both adherends. The two laminates were placed together, positioned with a 15.2-mm lap, and taped in place to prevent relative motion. Clamps were applied at the center bondline control wire and midway between the outer wires. Excess adhesive squeezed out at the ends of the lap, but was prevented from bonding to the laminates by the polyethylene film. Thus, a controlled lap length of 15.2 mm was maintained. The Hysol EA 9394 adhesive was cured at ambient temperature over 24 hr, followed by an oven cure at 80°C for 2 hr. The oven cure was used to ensure that the adhesive was fully cured for all lap shear coupons. Following the oven cure, five lap shear specimens were cut from each bonded assembly using a water-cooled diamond saw. The lap shear specimens had a nominal width of 25.4 mm. For lap shear strength (LSS) testing, the specimens were secured in wedge grips along the full length of the doublers. They were tested to failure at a crosshead displacement rate of 2.5 mm/min in an Instron Universal Testing machine equipped with a 44.5-kN load cell.

In addition to the plasma-treated specimens, two sets of control LSS coupons were prepared. For one set of control coupons, the bond area of the as-fabricated laminate surface was wiped with isopropanol immediately before bonding. For the second set, the bond area was sanded across the width of the bond



**Figure 2** Lap shear strength for plasma-treated composites is shown as a function of treatment.

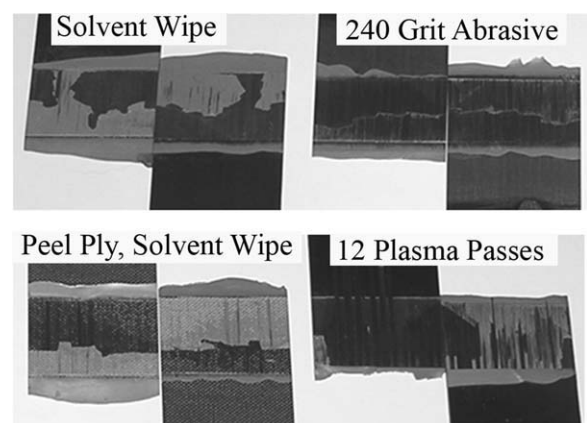
area with 280-grit silicon carbide abrasive paper, water cleaned, wiped with isopropanol, and bonded.

## RESULTS AND DISCUSSION

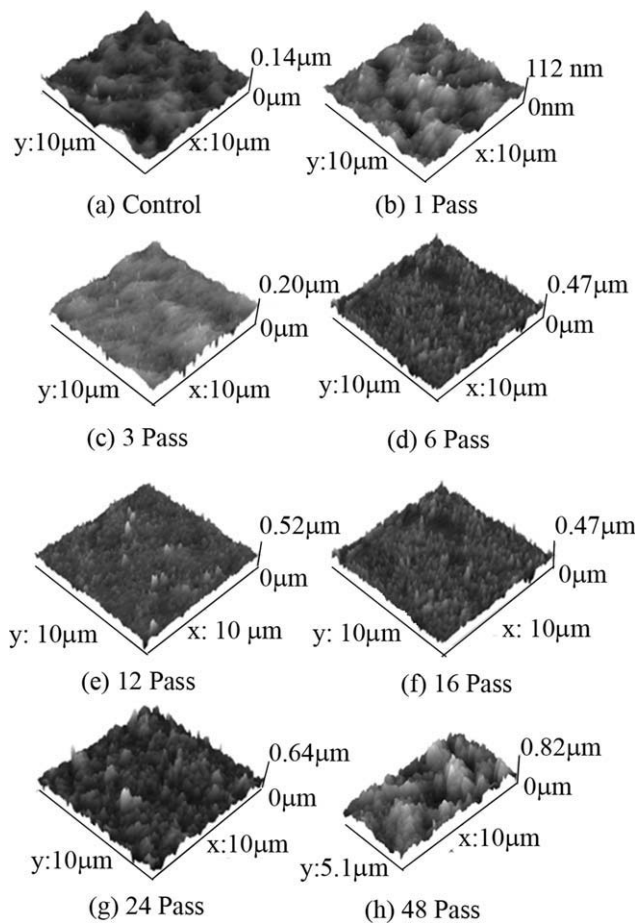
The bond strength behavior of epoxy-bonded plasma-treated polycyanurate composites was investigated and is shown in Figure 2. The plot shows the LSS as a function of plasma treatment passes. In addition, three separate surface preparation conditions (abrasion, peel ply, and solvent wipe) were included for comparison purposes. As shown, the LSS for the abrasion-treated sample is approximately 10.8 MPa. The average strengths for the solvent-wiped and the peel ply specimens were approximately 15.3 and 13.7 MPa, respectively. The low strength for the abrasion-treated specimens is a result of the fair degree of fiber damage that occurs during the abrasion process. Even though the primary purpose of abrasion is to remove outer surface contaminants and promote mechanical interlocking, the degree of degradation that can be observed can be quite pronounced when using higher-modulus carbon fibers. Composites surfaces manufactured adjacent the mandrel surfaces tend to also be more prone to this type of damage. The peel ply preparation technique removes the need for abrasion; however, several studies<sup>13,14</sup> have shown that a degree of contamination is always evident and may result in reduced bond performance. Even though the degree of surface roughness is considerably greater with the peel ply process, the very smooth solvent-wiped specimens generally resulted in higher average adhesive bond strengths.

As shown in Figure 2, the average LSS of our composite increases as a function of plasma treatment condition and maximizes after 12 passes. The strength at this point is approximately 30% stronger than the solvent-wiped specimen and over 75% stronger than that of the abrasion-treated specimen. The peel-ply specimen strengths also fall about 40% below this value. Further plasma treatment causes a gradual decrease in bond strength. However, even after 48 passes, the bond strength still remains above values for the other surface preparation techniques.

Examples of the fracture surfaces for the corresponding specimens are shown in Figure 3. Both sides of the fractured lap shear coupons are shown for four different surface conditions. At first glance, failure for the solvent wipe condition seemed to be primarily adhesive. However, closer inspection revealed a thin layer of surface resin from the composite adhered to the EA9394 adhesive. Thus, failure was dominated by a mixed-mode cohesive failure at the surface of the composite between the surface resin and first ply and within the first ply. Only about 10% of the fracture surface failed adhesively. A similar failure mode occurred with the peel ply, except, in this case, a thick surface resin layer was present because of the peel ply. Cohesive failure occurred within this surface resin and between the resin and first ply. Fracture surfaces of all of the plasma-treated specimens' exhibited 100% cohesive failure within the composite. For the lower strength plasma-treated conditions, a majority of the failure was the mixed mode mechanism between the surface resin and first ply. For the higher strength conditions, a higher fraction of the fracture surfaces exhibited failure deeper within the first ply. The abraded specimens exhibited primarily interlaminar



**Figure 3** Fracture surfaces of different surface-treated polycyanurate composite specimens (solvent wipe, 85% mixed mode + 5% first ply + 10% adhesive; 240-grit abrasive, >95% first ply + <5% adhesive; peel ply, 100% adhesive or cohesion within peel ply resin layer; and plasma 12 passes, 50% mixed mode + 50% first ply).



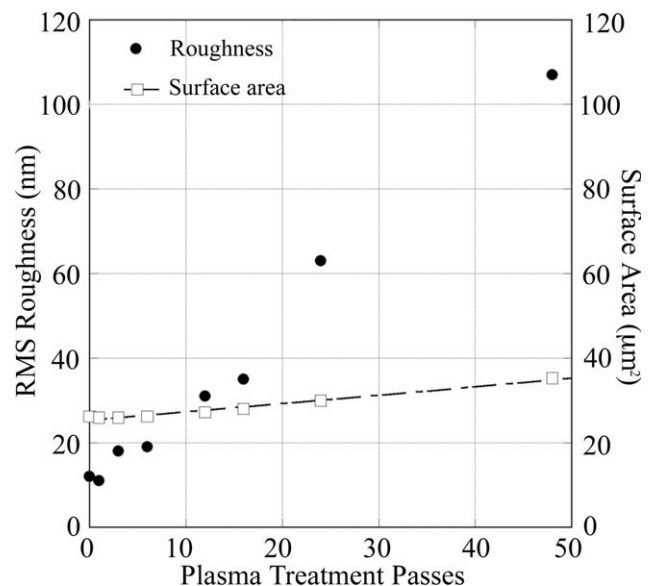
**Figure 4** AFM scans of polycyanurate composites showing surface morphology as a function of plasma treatment. (a) Control, (b) 1-pass, (c) 3-pass, (d) 6-pass, (e) 12-pass, (f) 16-pass, (g) 24-pass, and (h) 48-pass.

failure at a shallow depth within the first ply. This type of failure is consistent with ply damage caused by the abrasion process. The failure mechanisms exhibited by the polycyanurate matrix composites are similar to those observed in the earlier work for an epoxy matrix composite system. However, the higher bond strengths with the epoxy system caused failure to occur deeper within the composite.

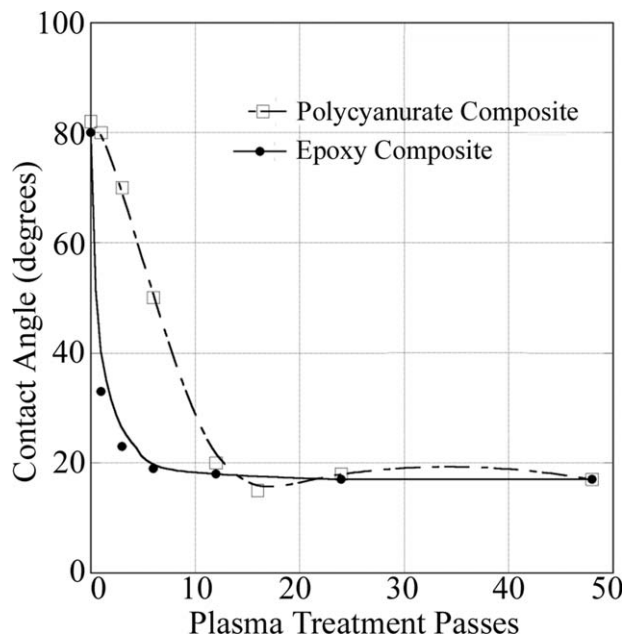
In a previous publication, it was shown that with each additional plasma-treatment pass on an epoxy-based composite, a corresponding increase in adhesive strength was achieved.<sup>11</sup> Even though the adhesive bond strength of the tested polycyanurate composite laminates improved with plasma treatment, they did not show the same magnitude or continuous improvement with additional exposure as the previously tested epoxy substrate system. To better understand how the mechanical properties of polycyanurate materials are affected by the plasma treatment, a number of microstructural and chemical characterization techniques were applied.

It is believed that surface roughening contributes to the interfacial bonding by increasing surface area.

Atomic force microscopy (AFM) was performed on the surface of the treated polycyanurate laminates to identify changes in surface morphology. Figure 4(a–f) shows qualitative changes in surface roughness with increasing plasma treatment. For example, the untreated surface [Fig. 4(a)] exhibits a low-frequency periodicity between troughs and high points. The 1-pass specimen appears nearly identical. However, subsequent passes clearly modify the surface morphology. The surface no longer exhibits the wide undulating profile of the control specimen but seems to have an increased periodicity or frequency in the surface profile. Root mean square surface roughness was measured for each plasma condition and plotted in Figure 5, which shows a linear increase in surface roughness, from 13 nm for the untreated to 110 nm for 48 passes. This change seems substantial; however, it is clearly inadequate to explain the lap shear test results in Figure 2, which does not exhibit linear and continuous increase with plasma treatment. It should be noted that interfacial bonding is more directly related to surface area when purely mechanical interaction is assumed. Calculations were done, which showed that the relative changes in surface area measured with AFM translate into very small changes in micrometer-scale surface area. Even after 12 plasma treatment passes, a virtually negligible increase of 4% was measured. Additionally, above 12 passes, the adhesive strength of the bonded joint shows an inverse relationship with increases in surface area. These results suggest that even though the changes in nanoscale roughness seem significant at first, contributions from mechanical



**Figure 5** Surface roughness and calculated surface area of plasma-treated polycyanurate composites as a function of plasma passes.



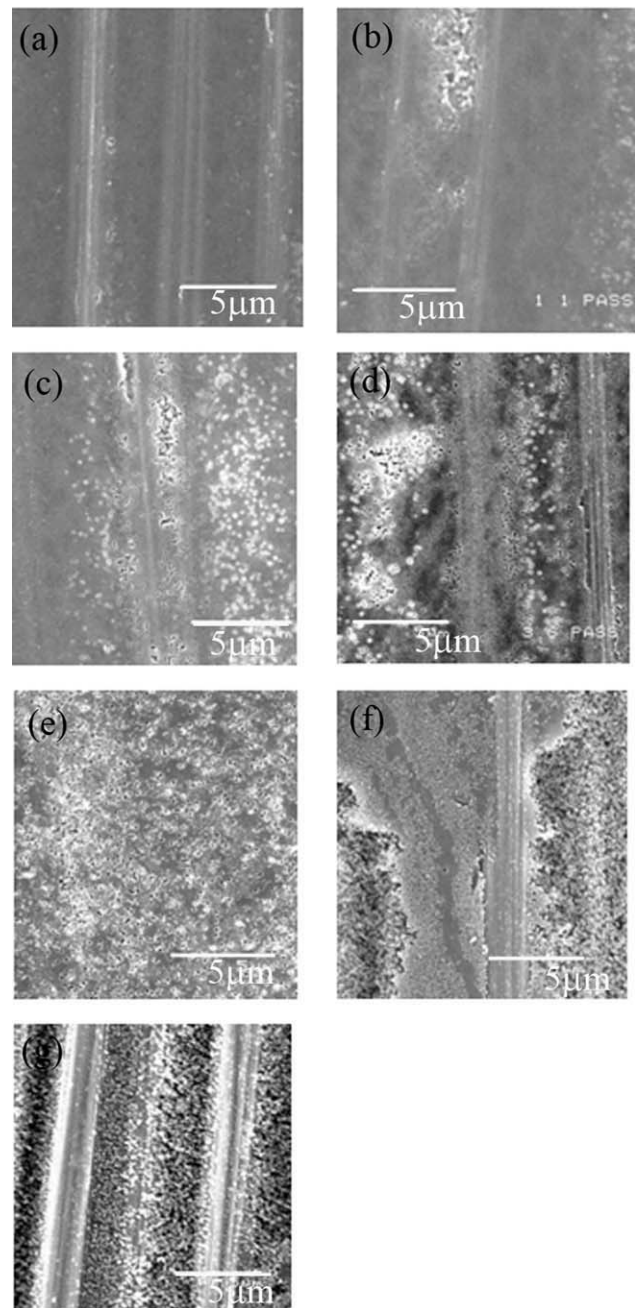
**Figure 6** Contact angle versus plasma treatment passes for a polycyanurate and epoxy-based composite.

interlocking on the bond strength seem to be a minor component because of limited changes in the surface area.

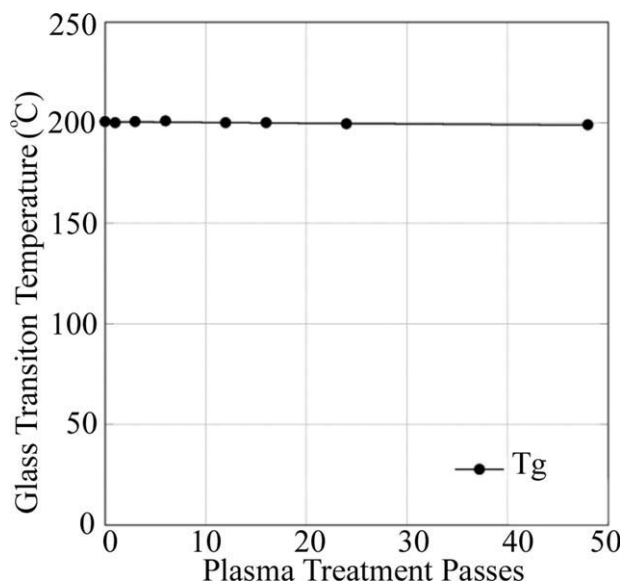
Contact angle measurements provide insight on the wetting characteristics of a substrate after plasma treatment because of chemical modification of the surface.<sup>15</sup> Figure 6 shows a plot of contact angle as a function of plasma treatment passes for the polycyanurate composite investigated in this study. The wetting characteristics for an epoxy-based composite as a function of similar plasma treatment are included for comparison. The contact angle is approximately 80° for the untreated polycyanurate composite sample, which indicates a fairly poor degree of wetting. As the number of plasma treatment increases, the contact angle is shown to decrease. The changes in contact angle for the polycyanurate composite are more gradual in nature than the epoxy composite for the same treatment conditions. After 12 passes, the contact angles for both composite systems are approximately 20°, which indicates good wetting for this material. Further plasma treatment of both resin systems specimen exhibited no further reduction in contact angle. This behavior suggests that there is a critical concentration of polar functionality necessary to obtain maximum hydrophilicity. These wetting results are in agreement with our previous results with epoxy composites as well as with the behavior of other polymers investigated in the literature where an oxygen plasma was utilized.<sup>16</sup>

Scanning electron microscopy (SEM) of the treated surfaces provides a few additional details. As shown

in Figure 7(a–g), there is observable evidence of oxidation even after a 1-pass, and, after 12 passes, the surface matrix material appears pitted to a fair degree. After 12 passes, some of the carbon fibers start to approach the surface of the treated composite as a consequence of matrix recession. The 24-pass specimen shows a fair distribution of bare carbon filaments approaching the surface of the treated specimen. It is surprising that the bond performance is still fairly high compared with conventionally



**Figure 7** SEM micrographs of polycyanurate composites showing surface morphology as a function of plasma treatment. (a) Control, (b) 1-pass, (c) 3-pass, (d) 6-pass, (e) 12-pass, (f) 24-pass, and (g) 48-pass.



**Figure 8** Glass-transition temperature of a polycyanurate composite as a function of plasma treatment passes.

prepared surfaces for these extreme plasma treatment conditions. After 48 passes, the appearance of ash particulates can also be observed throughout the surface of the higher plasma-treated specimens.

To better evaluate how the plasma treatment affects the matrix material, DMA of 1-ply polycyanurate composites was performed. DMA allows us to determine the glass-transition temperatures ( $T_g$ ) of the matrix material within the composite as a function of treatment. A significant decrease in  $T_g$  would be attributed to degradation of the polymer network, whereas an increase in  $T_g$  would be caused by additional cross-linking. It should be noted that this resin is only 90% cured using the manufacturer's recommended standard cure schedule used in this investigation. Figure 8 shows a plot of  $T_g$  as a function of plasma treatment passes. The initial control specimen has a  $T_g$  of approximately 195°C. Additional plasma treatment of the treated parts shows very little change in the  $T_g$ , even after 48 passes. This indicates that the material does not seem to change considerably with treatment or that any changes observed are localized to the very outermost surface layers. The oxidized material observed by SEM is either localized to such a small segment of the composite thickness or the damaged material is entirely removed, therefore resulting in no observable changes as measured using DMA.

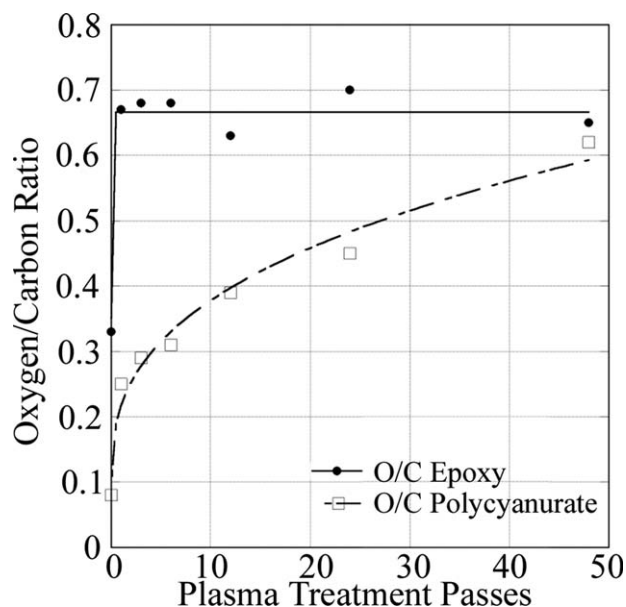
XPS was used to analyze what surface chemistry modifications occur to the substrate after treatment and how they contribute to the observed physical properties. Table I shows the elemental distribution on the composite surface as a function of treatment condition. As shown, there is an increase in oxygen content as a function of passes. This increase would

be expected to improve the wetting characteristics of the treated surface. The nitrogen content was also observed to increase steadily with an increased number of passes, though not as markedly as the oxygen. Others have shown that nitrogen-containing compounds can incorporate into the surface of resin when using an air plasma.<sup>17</sup> The surface silicon concentration was also identified to gradually increase as a function of treatment. This unexpected increase is most notable after the 48-pass treatment and is believed to be a consequence of the preferential removal of the organic portion of the matrix material, leaving behind the filler (cabosil), fumed silica, which is used as a viscosity modifier within the resin. The fluorine concentration was observed to markedly decrease as a function of plasma treatment, which would also contribute to an improvement in wetting. The initial fluorine content on the surface of the composite is a result of the high-temperature Teflon release film used in the manufacture of the laminates. Others<sup>18,19</sup> have shown similar effects during the manufacturer of polyphenylene sulfide-laminated composites. It was observed that these fluorinated release films used in the fabrication of composite hardware tend to emit low-molecular-weight fluorinated compounds onto the surface of the part, even at very low processing temperatures (<100°C) in vacuum. The majority of these fluorinated compounds diffuse during cure and are trapped and localized within the outer 1 nm of the laminate as verified by XPS (sputter depth) and cannot be removed with solvent rinses or thermal treatments. At least six passes of the plasma treatment were necessary to remove the majority of the fluorine from the composite surface.

Figure 9 shows the total oxygen content with respect to carbon (O/C) as a function of plasma treatment passes for a polycyanurate composite. In addition, the O/C ratio is also shown for an epoxy composite. A change in the O/C ratio is a good indicator of oxygen incorporation or oxidation of the matrix. As described in a previous publication, on plasma treatment, the O/C levels on the surface of an epoxy-treated specimen rise with only 1-pass and

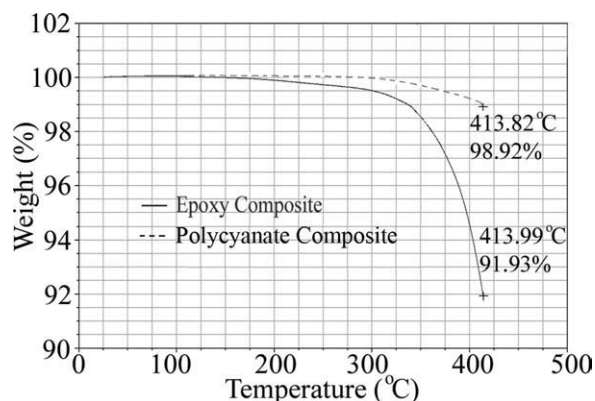
**TABLE I**  
Elemental Analysis of Composite Surface as a Function of Plasma Treatment Passes (atomic %)

	C 1s	O 1s	N 1s	F 1s	Si 2p
Control	66	6	3	26	0
Plasma 1 pass	62	15	4	18	<1
Plasma 3 passes	67	20	6	6	1
Plasma 6 passes	67	21	9	3	1
Plasma 12 passes	61	24	13	1	1
Plasma 16 passes	59	25	14	0	2.0
Plasma 24 passes	56	26	15	<1	3
Plasma 48 passes	47	30	19	0	5



**Figure 9** Oxygen-to-carbon ratio for both a polycyanurate and epoxy resin composite as a function of plasma treatment passes.

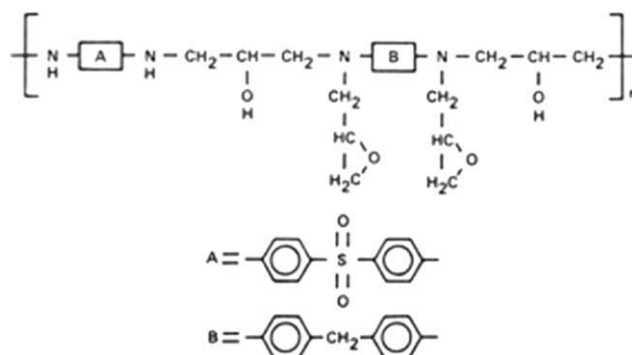
stabilize at these high levels. On the other hand, the polycyanurate resin seems to have a much greater resistance to surface oxidation with equal exposure. As shown, the O/C ratio slowly increases and only reaches similar levels to that of the epoxy after 48 passes. This trend follows a similar pattern to what was observed during the initial stages of our contact angle measurements. The epoxy composite exhibits a rapid increase in wetting with treatment, whereas the cyanate composite shows more of a gradual increase with passes corresponding with the observed changes in O/C levels. This behavior would again be in line with a system that is less susceptible to oxidation under similar conditions because of the inherent characteristics of its chemical structure.



**Figure 10** Thermogravimetric analysis of both an epoxy and polycyanurate composite as a function of temperature in flowing oxygen environment.

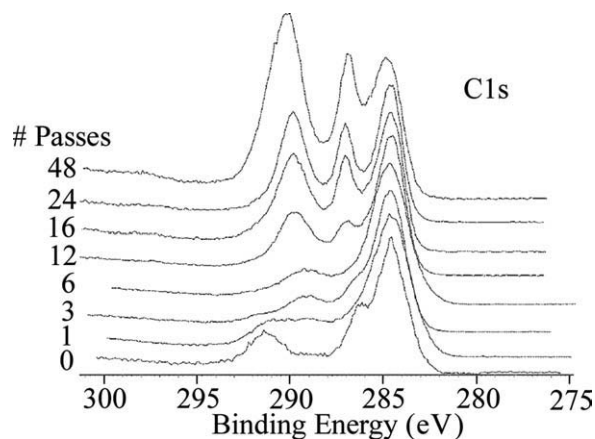
To verify the differences in the oxidation susceptibility for both of these systems, thermogravimetric analysis (TGA) was performed. TGA allows one to expose a material system to a thermal profile in a selected environment. The mass loss is then measured as a function of temperature for both systems. Even though plasma treatment is not performed at such elevated temperatures, a qualitative relationship can be established with regards to chemical structure and potential oxidation. Figure 10 shows a thermogravimetric profile for both an epoxy and a polycyanurate resin composite exposed in an oxygen environment. As shown, the epoxy resin is much more readily oxidized than that of the cyanate ester composite. Ramirez et al.<sup>20</sup> have shown that this class of thermosetting material has excellent thermal-oxidative behavior. The highly aromatic, cyclotrimerized chemical structure of the polycyanurate resin shown in Figure 1 makes it more resistant to attack by oxygen than that of the more aliphatic epoxy resin. As shown in Figure 11, the chemical structure of epoxy has a larger number of available sites, notably dangling hydroxyl groups that make it more prone to oxidation and thus more responsive to plasma treatment. Because increases in adhesive bond strength have been attributed to increases in the amount of oxygen-containing functional groups (i.e., carboxyl groups), we would expect that the total amount of oxidized chemical species on the surface of the polycyanurate composite would be considerably less than that of the epoxy system.

In previous studies, it was demonstrated that simple oxidation of the polymer matrix was inadequate to explain the changes in bond strength and that specific chemical functionality, i.e., carboxyl group, was identified and correlated with lap shear test results on epoxy-based composite system.<sup>11</sup> A similar chemical analysis was performed on the polycyanurate samples for this study. Figure 12 shows a compilation of C 1s X-ray photoelectron spectra as a



**Figure 11** Schematic showing typical high-temperature epoxy-amine chemical structure.





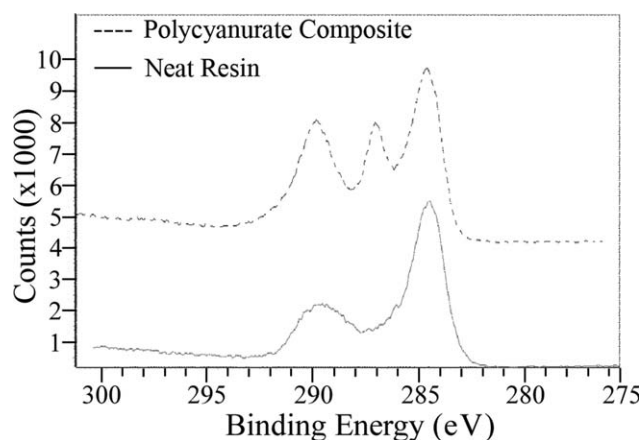
**Figure 12** X-ray photoelectron spectra showing the development of the C 1s as a function of plasma treatment passes.

function of increasing plasma treatment passes for the polycyanurate composite specimens. This analysis allows the growth and distribution of the functional groups that are created by this process to be tracked. Before the plasma treatment (0 pass), the main peak is at 284.6 eV, which is attributed to C—C or C—H in the backbone. C—F species is observed at 291.3 eV, and as discussed earlier, this is due to fluorinated release film that is removed with subsequent plasma passes. The plasma treatments also create new functional groups evidenced by new peaks. Up to six passes, the most notable peak growth is at 289.3 eV, which has been identified as a carboxyl group (O—C=O) in our previous studies. At 12 passes, two peaks emerge abruptly at 287.1 and 290.1 eV, and they both continue to grow with additional passes.

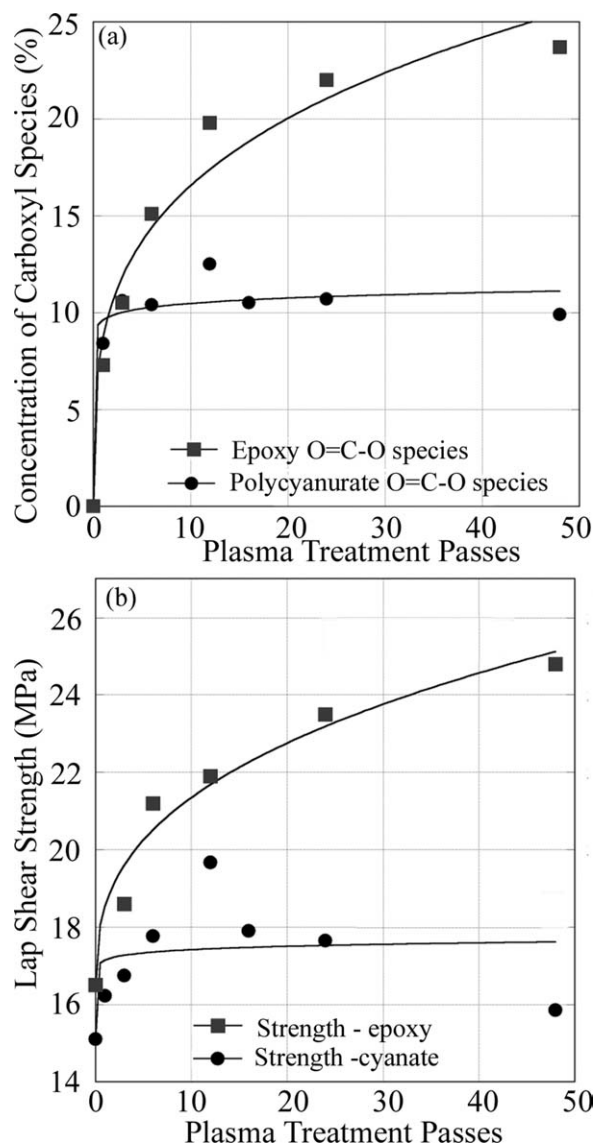
To identify these peaks, unreinforced resin with similar plasma treatment was investigated. Figure 13 shows a comparison of both a polycyanurate composite laminate and the neat resin after exposure to 16 passes of plasma treatment. As shown, the unreinforced resin specimen does not show the development of the 287.1-eV peak, strongly suggesting that it is associated with fibers exposed as a result of matrix recession. This is also consistent with both AFM and SEM results discussed previously. Bubert et al.<sup>21</sup> have shown that surface plasma oxidation of similar fibers causes the formation of ether groups functionality (C—OR) located at approximately 286.5 eV.

As described earlier, the concentration of newly formed carboxyl groups contributes directly to the adhesive bond strength when using an epoxy adhesive after treatment. The likelihood for a chemical reaction between an activated carboxyl species and the epoxy monomer is quite favorable and has been established.<sup>22</sup> Figure 14(a) shows the concentration of carboxyl species as a function of plasma treatment

passes for both the cyanate ester and epoxy composites. As shown, the carboxyl concentration for epoxy continues increasing up to 48 passes. This implies that with each additional treatment there are numerous active sites that are oxidized and could serve as links with the adhesive through covalent bonding. On the other hand, the carboxyl concentration does not exhibit the same type of monotonic increase for the polycyanurate resin. In this case, the carboxyl species concentration saturates early at approximately 12% and shows no added increase with further treatment. This corresponds with the reduced susceptibility of the polycyanurate network to oxidation compared with the epoxy. Figure 14(b) shows the corresponding LSSs as a function of passes for both the polycyanurate and epoxy resin. As shown, the LSSs for both systems follow the trend observed for carboxyl species distribution. The strength for the epoxy system continues increasing with the number of plasma passes, whereas the cyanate ester system saturates at an earlier state as a consequence of its chemical structure. At very high plasma treatment passes (48), carboxyl concentration and LSS are not as well correlated. The strength is lower than that expected for the corresponding carboxyl concentration. It is believed that this is a consequence of the extensive matrix recession described earlier. Even though cyanate ester systems do not seem to oxidize as easily as epoxies, it seems that the limited available sites in the polycyanurate network may be more susceptible to chain scission of the back bone structure than those of the numerous corresponding hydroxyl groups available in the epoxy network. An understanding of the oxidation susceptibility of different plasma-treated resin systems will aid in correlating the bond performance improvements to chemical structure, as well as tailoring our treatments appropriately.



**Figure 13** X-ray photoelectron spectra showing the development of the C 1s peak after 16 plasma treatment passes for both a carbon fiber-reinforced composite and a neat resin.



**Figure 14** (a) Carboxyl concentration and (b) lap shear strength as a function of plasma passes.

## CONCLUSIONS

Atmospheric plasma treatment of epoxy-bonded polycyanurate composites was shown to improve the adhesive strength over that of conventional surface preparation techniques. The average shear strength of these composite was shown to increase as a function of plasma treatment condition and maximize after 12 passes. The strength was approximately 30% stronger than the solvent-wiped composites, 40% above peel ply-treated composites, and over 75% stronger than abrasion-treated composites.

Increases in surface roughness as a function of plasma treatment were observed using AFM. These increases in microroughness translated into negligible increases in surface area up to 12 passes, which

is over the range where the largest increases in strength are observed. This suggests that even though the changes in microroughness initially seem pronounced, at least on a relative scale, contributions from mechanical interlocking because of increases in surface area are limited and seem to be a secondary effect.

XPS analysis of treated polycyanurate composites shows large differences in oxidation susceptibility compared with epoxy composite systems. The O/C ratio as a function of plasma treatment shows more resistance to oxidation than epoxy composites. This behavior was corroborated with TGA and is consistent with a system that is less susceptible to oxidation because of the inherent characteristics of its chemical structure. This uptake behavior also follows a similar pattern to what was observed from contact angle measurements, which would be in line with a system that has a larger initial uptake of polar moieties. XPS analysis was also used to identify the surface carboxyl concentration as a function of plasma treatment passes for both epoxy and polycyanurate composites. The carboxyl concentration for epoxy continues to increase with each pass up to 48 passes, whereas the carboxyl concentration does not show the same type of monotonic increase for polycyanurate resin. Not only is the magnitude of carboxyl species concentration considerably lower than that of epoxy, but the amount of oxygen on the surface saturates at a relatively low number of passes. These concentrations were shown to best correlate with the adhesive bond strength for both systems.

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## References

- Davis, G. D. *Surf Interf Anal* 1993, 20, 368.
- Davis, H. J.; Bond, D. *Int J Adhes Adhes* 1999, 19, 91.
- Gonzalez, E.; Barankin, M.; Guschl, P. C.; Hicks, R. F. *Langmuir* 2008, 24, 12636.
- Jeong, J. Y.; Babayan, S. E.; Schütze, A.; Tu, V. J.; Park, J. Y.; Henins, I.; Selwyn, G. S.; Hicks, R. F. *J Vac Sci Technol A* 1999, 17, 2581.
- Kuwabara, A.; Kuroda, S.; Kubota, H. *Plasma Sci Technol* 2007, 9, 181.
- Kim, H. H.; Rhee, K. Y.; Kim, H. J.; Jung, D. H. *Mater Sci Eng A* 2007, 448, 269.
- Yeh, R.; Lin, P.; Lin, K. *J Polym Res* 2002, 9, 31.
- Fang, T.; Shimp, D. A. *Prog Polym Sci* 1995, 20, 61.
- Iijima, T.; Maeda, T.; Tomoi, M. *Polym Int* 2001, 50, 290.
- Marieta, C.; Schulz, E.; Mondragon, L. *Compos Sci Technol* 2002, 62, 299.
- Zaldivar, R. J.; Nokes, J.; Steckel, G. L.; Kim, H. I.; Morgan, B. A. *J Compos Mater* 2010, 44, p. 137–156.
- Zaldivar, R. J.; Kim, H. I.; Steckel, G. L.; Nokes, J. P.; Morgan, B. A. *J Compos Mater* 2010, 44, 1435–1454.

13. Hart-Smith, L. J.; Redmond, G.; Davis, M. J. In Proceedings of the 41st International SAMPE Symposium, March 24–28; 1996; pp 303–317.
14. Pocius, A. C.; Wenz, R. P. In Proceedings of the 30th National SAMPE Symposium, March 19–21; 1985; pp 1073–1087.
15. Wittenbeck, P.; Wokaun, A. *J Appl Polym Sci* 2003, 50, 187.
16. Gupta, B.; Hilborn, J.; Hollenstein, C.; Plummer, C.; Houriet, R.; Xantopoulos, N. *J Appl Polym Sci* 2000, 78, 1083.
17. Jiashen, L.; Jing, S.; Fei H.; Huili, D. *Chem J Internet* 2001, 3, 50.
18. Lonneman, W. A.; Bufalini, J.; Kuntz, R.; Meeks, S. A. *Environ Sci Technol* 1981, 15, 5.
19. Chin, J. W.; Wightman, J. P. *Compos Part A* 1996, 27, 419.
20. Ramirez, M.; Walters, R. N.; Savitski, E. P.; Lyon, R. E. Thermal Decomposition of Cyanate Ester Resins. DOT/FAA/AR-01/32; FAA William J Hughes Technical Center: Atlanta City, NJ, 2002.
21. Bubert, H.; Ai, X.; Heintz, M.; Bruser, V.; Pasch, E.; Brandl, W.; Marginean, G. *Spectrochim Acta Part B* 2002, 57, 1601.
22. Fedoseev, M.; Gurina, M.; Sdobnov, M.; Kondyurin, A. *J Raman Spectrosc* 1995, 27, 413.