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**EFFECT OF SURFACE ENGINEERING PROCESSES ON
THE SURFACE PROPERTIES AND ADHESIVE BONDING
OF GRAPHITE/EPOXY COMPOSITES (PREPRINT)**

F.J. Boerio, B. Roby, R.G. Dillingham, and R.H. Bossi

The Boeing Company

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EFFECT OF SURFACE ENGINEERING PROCESSES ON THE SURFACE PROPERTIES AND ADHESIVE BONDING OF GRAPHITE/EPOXY COMPOSITES

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ABSTRACT

The effect of surface engineering processes such as grit-blasting and plasma etching on the surface energy and composition of graphite/epoxy composites that were cured at 177°C was determined. As-tooled composites had about 73% carbon, 20% oxygen, and 5% nitrogen on the surface. Grit-blasting with 80- or 220-grit garnet resulted in an increase of several percent in the carbon concentration and a similar decrease in the oxygen concentration. However, grit-blasting with 220-grit alumina resulted in a decrease in the carbon concentration of a few percent and a similar increase in oxygen concentration. Etching as-tooled composites in O₂ plasmas resulted in a decrease in the carbon concentration and an increase in the oxygen concentration of about 10%. Derivatization of the composite surfaces with trifluoroacetic anhydride and pentafluorobenzaldehyde enabled the relative numbers of hydroxyl and amino groups on the surfaces to be determined and showed that the surface properties of the composites were dominated by the hydroxyl groups. As-tooled composites had a total surface energy of approximately 35 mJ/m²; the polar components were small, meaning that the surface energies were mostly dispersive. After grit-blasting with 80- or 220-grit garnet or 220-grit alumina, the polar component of the surface energy increased significantly and the total surface energy was approximately 50 mJ/m². Etching composites in oxygen plasmas had a similar effect on the polar component of the surface energy and the total surface energy. A good correlation was observed between the sum of the oxygen and nitrogen concentrations on the surface and the total surface energy of the composites and there was some indication that the polar component of the surface energy could be calculated from the atomic concentrations of various polar functional groups on the surfaces and the dipole moments associated with those functional groups. Grit-blasting and plasma-etching were both effective processes for surface engineering of composites. Thus, double-cantilever beam specimens prepared from as-received substrates failed at the interface between the adhesive and the composite but those prepared from grit-blasted and plasma-etched substrates failed cohesively within the composite.

KEY WORDS: Graphite Fiber Composites; Surface Preparation Materials/Processes; Characterization.

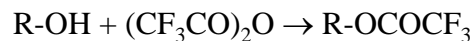
1. INTRODUCTION

The overall goal of this project was to identify factors in surface preparation of a 177°C (350°F) curing graphite fiber/epoxy resin composite that result in reproducibly strong and durable adhesive bonds when using a room-temperature curing paste adhesive. Possible factors affecting adhesive bond performance include establishing mechanical interlocking through roughness, maximizing the thermodynamic work of adhesion, or forming specific primary chemical bonds across the interface.

Grit blasting roughens the surface and provides for mechanical interlocking. However, it also changes the surface chemistry significantly by removing contaminants such as mold release agents and introducing free radicals as a result of fracture processes.

Surface treatments that chemically alter the surface without introducing roughness can also be effective. For example, oxygen plasma treatment of epoxy composites results in excellent adhesive bonds but does not significantly roughen the surface (1).

The goal of the work described here was to determine the effect of surface engineering processes such as grit blasting and plasma etching on the surface properties of graphite/epoxy composites; we were specifically interested in determining if surface engineering provided for formation of specific chemical bonds between a composite and an adhesive that may contribute to adhesive bond performance. Thus, we have used X-ray photoelectron spectroscopy (XPS) to determine the surface composition of graphite/epoxy composites before and after surface engineering processes such as grit-blasting and plasma etching. We have also used XPS curve-fitting techniques to identify the functional groups present on the surfaces of the composites before and after pretreatment. However, since curve-fitting is not always unambiguous, we have also used derivatization techniques to facilitate identification of functional groups on the surface of as-tooled and surface engineered graphite/epoxy composites. Certain reagents are known to react only with specific functional groups on the surface of a material and to introduce elements, such as fluorine, for which the sensitivity of XPS is great. Thus, trifluoroacetic anhydride (TFAA) reacts with surface hydroxyl groups to give a fluorinated surface ester according to the following reaction (2):



while pentafluorobenzaldehyde (PFBA) reacts with amino groups to give a mono-substituted fluorobenzene through the following reaction (2).



2. EXPERIMENTAL

Graphite/epoxy composites were received from Boeing and were wrapped in aluminum foil and cut into 18 x 8 mm samples with a hacksaw. Dust from the cutting process was removed by blowing the sample surfaces with compressed N₂. Samples were stored overnight in a desiccator and then wiped with ethanol prior to analysis.

Etching in oxygen plasmas was carried out at the University of Cincinnati using an RF-powered (13.56 MHz), capacitively-coupled reactor; the power was 50 watts, pressure was 0.50 torr, and etching time was 30 sec. This comparatively gentle plasma etching removed contaminants and inserted new functional groups into the surfaces of the composites without creating weak boundary layers.

Fluorinated derivatizing agents were used to probe the surfaces for the presence of reactive functional groups. Composite samples were placed into 1 mL of either TFAA or PFBA in 15 mL of diethyl ether. Exposure of composites to TFAA was performed at 25°C for 1.5 hours but the limited solubility of PFBA in diethyl ether required slightly higher reaction temperatures (35°C). After removal from the derivatizing solutions, the samples were thoroughly rinsed with diethyl ether to remove any unreacted derivatizing agent.

Tetrabromobisphenol-A epoxy resin (Shell Epon Resin 1163) was purchased from Miller-Stephenson Chemical Company. A small amount of the resin was dissolved in toluene and as-tooled, grit-blasted (220-grit garnet), and plasma-etched composite samples were immersed in the solution for three days at room temperature. After three days, the samples were removed from the solution and thoroughly rinsed in toluene to remove any un-reacted epoxy from the surfaces. Samples were then immediately placed into the XPS system for analysis. Weight measurements of a composite panel soaked in toluene for 3 days at room temperature showed no increase in weight, indicating that the composite panel did not swell in the presence of toluene at room temperature.

All XPS investigations were carried out using a Perkin-Elmer model 5300 spectrometer; Mg K α X-rays ($h\nu = 1253.6$ eV, 300W) were used to excite the spectra. Survey spectra were acquired at pass energy of 89.45 eV while high-resolution spectra were obtained at pass energy of 35.75 eV. Spectra were corrected for charging by referring the C(1s) peak of saturated hydrocarbons to a binding energy of 284.6 eV. Curve fitting was performed using 90/10 Gaussian/Lorentzian peaks with Shirley background correction. Atomic concentrations were calculated using the sensitivity factors provided with the software (RBD Enterprises). All spectra reported here were collected using a take-off angle of 45°.

3. RESULTS AND DISCUSSION

XPS survey spectra of the as-tooled composite showed peaks characteristic of C(1s), O(1s), N(1s), S(2p), and Si(2p) electrons (see [Figure 1](#)). Carbon, oxygen, and nitrogen were characteristic of both the epoxy and the curing agent while sulfur was characteristic only of the curing agent and silicon was probably related to a filler. Although the surfaces of similarly prepared composites are usually contaminated with fluorine characteristic of mold release agents, no fluorine was detected. The surface composition of this composite was about 73.1% C, 20.0% O, 4.7% N, 1.1% S, and 0.9% Si (see [Table 1](#)).

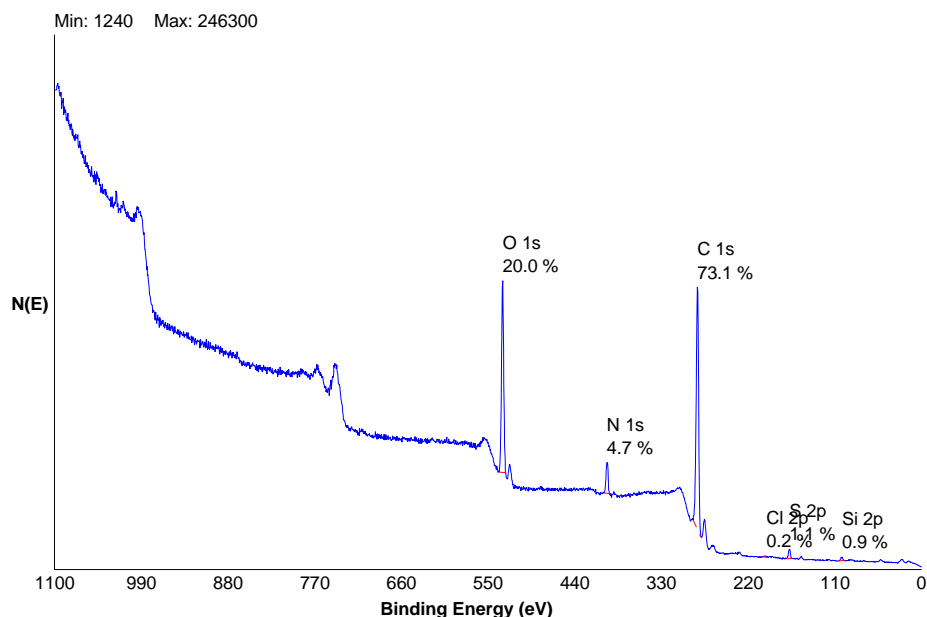


Figure 1. XPS survey spectrum of as-tooled composite.

Figure 2 shows the high-resolution C(1s) spectrum of the same as-tooled composite. The main component of the C(1s) spectrum was at 284.6 eV and was attributed to carbon that was bonded to other carbon or to hydrogen; an additional, medium intensity component was shifted toward higher binding energies by 1.5 eV and assigned to C-N and C-O bonds while a weak component shifted upward by 3.8 eV was attributed to O-C=O (ester) groups. C-N and C-O bonds were expected for the cured composite material but O-C=O groups were not. The ester groups may have resulted from an additive or from contaminants.

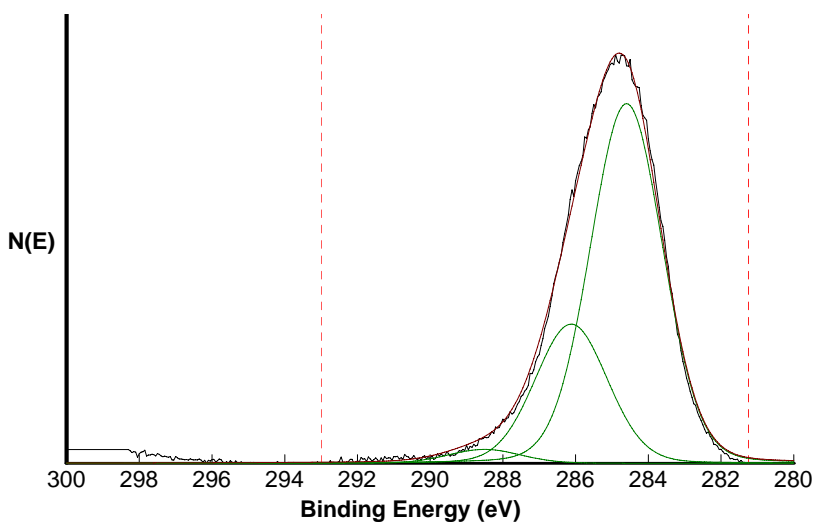


Figure 2. High resolution C(1s) spectrum of as-tooled composite surface.

Table 1. Surface composition of graphite/epoxy composites: TFAA - derivatized with trifluoroacetic anhydride; PFBA - derivatized with pentafluorobenzaldehyde.

| Sample ID | Surface Engineering Process | Derivatization Agent | Atomic Concentration (%) | | | | | | | |
|-----------|-------------------------------|----------------------|--------------------------|------|-----|-----|-----|-----|-----|-----|
| | | | C | O | N | F | S | Si | Cl | Al |
| R1 | None | None | 73.1 | 20.0 | 4.7 | - | 1.1 | 0.9 | 0.2 | - |
| R1 | None | TFAA | 63.8 | 20.9 | 4.1 | 8.1 | 1.2 | 1.9 | - | - |
| R1 | None | PFBA | 68.1 | 19.0 | 4.5 | 3.2 | 0.8 | 1.6 | - | - |
| R1* | O ₂ Plasma | None | 61.6 | 30.1 | 6.0 | - | 1.7 | 0.7 | - | - |
| R1* | O ₂ Plasma | TFAA | 63.7 | 21.5 | 4.3 | 8.5 | 1.1 | 0.9 | - | - |
| R1* | O ₂ Plasma | PFBA | 64.6 | 25.5 | 3.8 | 2.1 | 1.0 | 1.8 | - | - |
| R2 | Grit Blast (80 grit garnet) | None | 75.5 | 17.4 | 4.6 | - | 1.5 | 1.0 | - | - |
| R2 | Grit Blast (80 grit garnet) | TFAA | 68.0 | 18.2 | 3.2 | 8.4 | 1.4 | 0.9 | - | - |
| R2 | Grit Blast (80 grit garnet) | PFBA | 72.7 | 16.1 | 3.2 | 4.4 | 1.6 | - | - | - |
| R3 | Grit Blast (220 grit garnet) | None | 75.3 | 17.7 | 4.2 | - | 1.5 | 1.4 | - | - |
| R3 | Grit Blast (220 grit garnet) | TFAA | 66.8 | 19.5 | 4.0 | 7.4 | 1.4 | 0.9 | - | - |
| R3 | Grit Blast (220 grit garnet) | PFBA | 69.0 | 19.7 | 3.1 | 1.8 | 1.5 | 3.3 | - | - |
| R4 | Grit Blast (220 grit alumina) | None | 71.4 | 21.5 | 4.1 | - | 1.3 | 0.3 | - | 1.5 |
| R4 | Grit Blast (220 grit alumina) | TFAA | 64.3 | 19.9 | 3.6 | 9.7 | 1.4 | - | - | - |
| R4 | Grit Blast (220 grit alumina) | PFBA | 66.7 | 18.7 | 4.2 | 7.5 | 1.5 | - | - | - |

Grit-blasting with 80- or 220-grit garnet resulted in a small increase in the concentration of carbon on the surface of the composites and a small decrease in the concentration of oxygen (see [Table 1](#)). Thus, for example, the composite grit-blasted with 80 grit garnet had 75.5% C, 17.4 % O, and 4.6 % N on the surface while the composite grit-blasted with 220-grit garnet had 75.3%

C, 17.7% O, and 4.2% N on the surface. The effect of grit-blasting with 220-grit alumina seemed to be the opposite, resulting in a small decrease in carbon and increase in oxygen. Thus, the sample grit-blasted with 220-grit alumina had 71.4% C, 21.5% O, and 4.1% N on the surface.

Overall, grit-blasting did not have a great effect on the surface composition of the panels examined here. However, a peak characteristic of graphite fibers was observed at about 283.2 eV in the C(1s) spectra of grit-blasted samples, indicating that some graphite fibers were exposed after grit-blasting. An example is shown in **Figure 3** where the C(1s) spectrum of a composite that was grit-blasted using 220-grit garnet is presented; this spectrum consisted of components at 284.6 and 286.1 eV that were attributed to carbon that was bonded only to hydrogen or to other carbon as well as a component at 286.1 eV that was attributed to C–O and C–N bonds. However, a component was also observed at 283.2 eV and attributed to carbon in graphite fibers.

It should be noted that grit-blasting did not have a significant effect on the surface composition of the composites investigated here because the surfaces were not highly contaminated during fabrication and handling. However, when the surfaces of composites are contaminated, significant changes in surface composition due to removal of material from the surface during grit-blasting can be anticipated.

There was a significant change in the surface composition of the composites after etching in O₂ plasmas. The concentration of carbon on the surface decreased to 61.6 % while that of oxygen increased to about 30.1%. Reference to **Figure 4** indicates that the C(1s) spectra of a composite that was etched in an O₂ plasma for 30 sec consisted mostly of three components at 284.6, 286.1, and 288.6 eV; these components were attributed to carbon that was bonded only to hydrogen or to other carbon, carbon in C–O and C–N groups, and carbon in O–C=O groups, respectively.

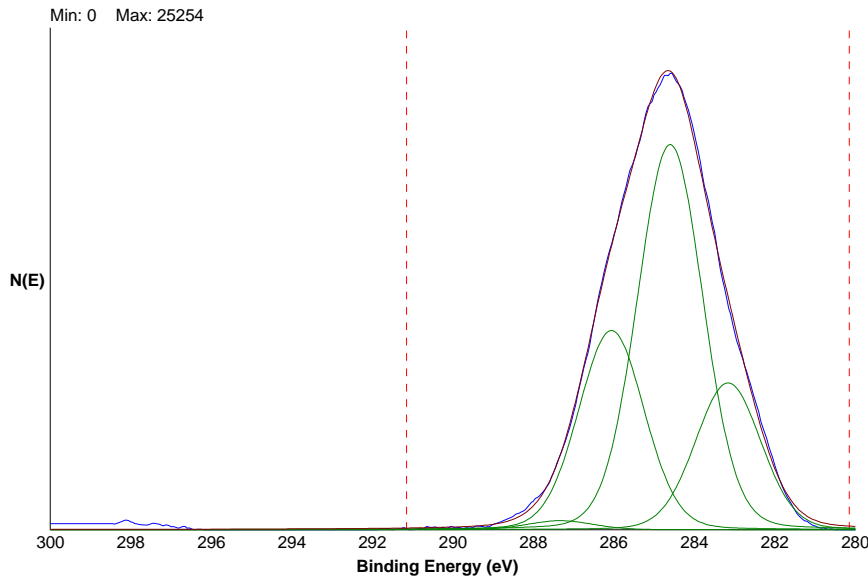


Figure 3. High resolution C(1s) spectrum of graphite/epoxy composite that was grit-blasted with 220 grit garnet.

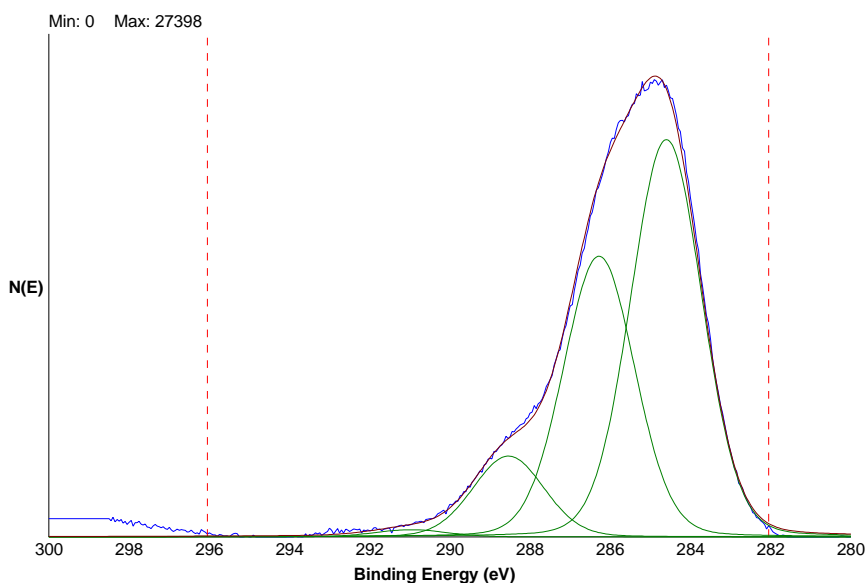


Figure 4. High resolution C(1s) spectrum of graphite/epoxy composite that was etched in an O₂ plasma for 30 sec.

There was no evidence of components related to graphite fibers in the C(1s) spectra of composites etched in O₂ plasmas. These results showed that grit-blasting and plasma etching had considerably different effects on the surface properties of the composites. Grit-blasting had a significant effect on the surface morphology whereas plasma etching did not. However, plasma etching had a stronger effect on surface composition than grit-blasting.

Derivatization of the composites was carried out to identify the surface functional groups more completely. After derivatization of an as-tooled composite with TFAA, a new peak indicative of F(1s) electrons appeared near 690 eV in the survey spectrum (see [Figure 5](#)). A new peak

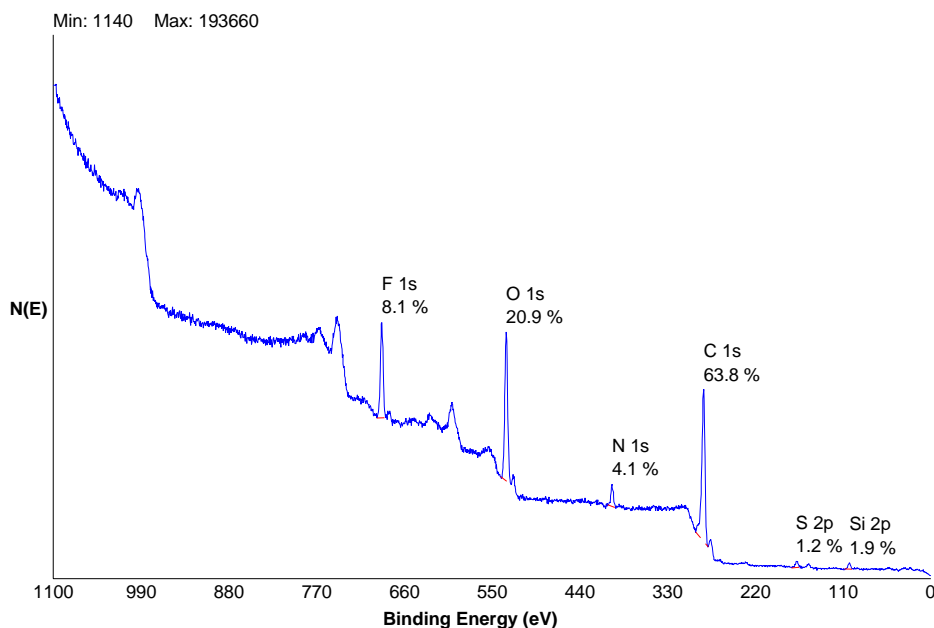


Figure 5. XPS survey spectrum of as-tooled graphite/epoxy composite after reaction with TFAA.

characteristic of the CF_3 groups in fluorinated ester groups appeared near 292.5 eV in the C(1s) high-resolution spectra (see [Figure 6](#)). Atomic compositions calculated from the high-resolution XPS spectra showed that there was approximately 8.1% fluorine on the TFAA-derivatized surface and about 3.2% fluorine on the PFBA-derivatized surface (see [Table 1](#)). Considering that each reaction of a hydroxyl group with TFAA introduced three fluorine atoms into the surface while each reaction of an amino group with PFBA introduced five fluorine atoms, it was concluded that almost five reactions with TFAA occurred for each reaction that occurred with PFBA. Thus, it was concluded that hydroxyl groups tended to dominate the surface properties of the as-tooled composite.

Mostly similar results were obtained when the other composites were derivatized with TFAA and PFBA. The smallest number of reactions with TFAA relative to reactions with PFBA was for the sample that was grit-blasted with 220-grit alumina. In that case, 9.7% and 7.5% fluorine were detected after the surfaces were derivatized with TFAA and PFBA, respectively, indicating that there were approximately two reactions of hydroxyl groups with TFAA for every reaction of an amino group with PFBA. Thus, hydroxyl groups and amino groups were both important in the surface properties of composites that were grit-blasted with 220-grit alumina. However, when plasma-etched composites were reacted with TFAA and PFBA, 8.5% and 2.1% fluorine, respectively, was detected on the surfaces. This result indicated that there were approximately eight times as many reactions between hydroxyl groups and TFAA as between amino groups and PFBA. It was concluded that etching in O_2 plasmas tended to add hydroxyl groups to the surface of the graphite/epoxy composites and that hydroxyl dominated the surface properties of composites etched in O_2 plasmas.

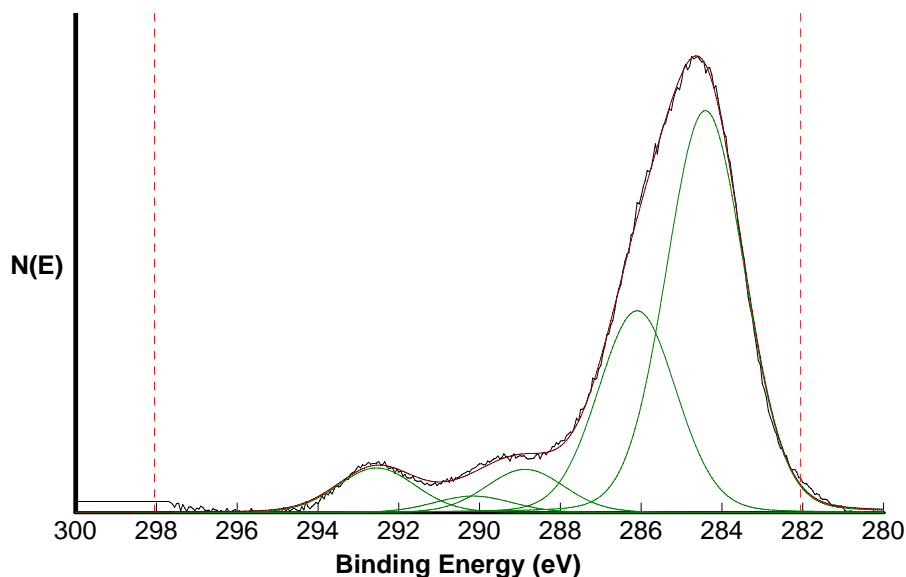


Figure 6. High resolution C(1s) spectrum of as-tooled composite after derivatization with TFAA.

The results described above indicated that hydroxyl and amino groups were both present on the surfaces of the composites investigated in this study and that both types of functional groups were accessible for reaction with reagents such as TFAA and PFBA. In order to determine if any chemical reaction would occur between functional groups in a cured composite and an epoxy resin at ambient temperatures, an as-tooled panel was immersed in a solution of brominated epoxy resin for several days. Since bromine is readily detected by XPS, this technique was suitable for differentiating between the substrate epoxy and any grafted epoxy molecules. The composite surfaces were then rinsed with toluene to remove unreacted brominated epoxy from the surface. XPS showed no residual bromine on the surface of the as-tooled composite. However, a weak peak characteristic of Br(3d) electrons was observed by XPS after exposure of the surfaces that were grit-blasted with 220-grit garnet or etched in an O₂ plasma, implying that a reaction occurred to chemically bind the brominated epoxy to the surface of the composite and providing evidence that such reactions may be important when bonding graphite/epoxy composites with room-temperature curing epoxy adhesives. The intensity of the Br(3d) peak increased intensity when the electron take-off angle was decreased from 45° to 15°, indicating that the bromine was, as expected, confined to the composite surfaces.

We have previously reported the surface energy of these composites (3) expressed as the sum of dispersive (γ_s^d) and polar (γ_s^p) components; the results are presented in Table 2. Comparing Tables 1 and 2 indicates that there was a strong correlation between surface composition and surface energy for as-tooled and plasma-etched samples. Thus, the as-tooled sample (R1) had relatively low oxygen content (20%) and a low value of γ_s^p (2.6 mJ/m²) while the plasma-etched sample (R1*) had relatively high oxygen content (30.1%) and relatively high γ_s^p (27.6 mJ/m²).

The composite that was grit-blasted with 220-grit alumina also seemed to follow that trend, having intermediate values of oxygen content (21.6%) and γ_s^p (9.6 mJ/m²). However, samples that were grit-blasted with 80- and 220-grit garnet did not follow this trend. Both of those samples

had low oxygen content (17.4 and 17.7%, respectively) and relatively high values of γ_s^d (20 and 22 mJ/m², respectively).

Table 2. Dispersive and polar components of the total surface energy of graphite/epoxy composites as a function of surface engineering processes.

| Sample ID | Surface Engineering Process | Surface Energy | | |
|-----------|-------------------------------|-----------------------------------|-----------------------------------|---------------------------------|
| | | γ_s^d (mJ/m ²) | γ_s^p (mJ/m ²) | γ_s (mJ/m ²) |
| R1 | none | 34.1 | 2.6 | 36.7 |
| R1* | O ₂ Plasma etch | 31.8 | 27.6 | 59.4 |
| R2 | Grit-blast (80 grit garnet) | 28.7 | 20.0 | 48.7 |
| R3 | Grit-blast (220 grit garnet) | 29.2 | 22.0 | 51.2 |
| R4 | Grit-blast (220 grit alumina) | 41.0 | 9.6 | 50.6 |

These results can be compared with those of Pocius and Wenz (4) who considered the effect of several surface engineering processes, including peel ply, grit-blasting with 100-grit alumina, sanding with 150-grit SiC abrasive paper mounted on an orbital sander, and abrasive treatment with a Scotchbrite® pad, on the surface composition and properties of graphite/epoxy composites. XPS showed that the untreated composites had about 14.8% fluorine on their surfaces from residual mold release agents but that the fluorine concentration was decreased to 2.6% by grit-blasting, 0.4% by sanding, and to 1.2% after abrasion of the surface with a Scotchbrite 7446 pad. The dispersive and polar components of the surface energy of the untreated composites were 32 and 4 mJ/m², respectively. After grit-blasting, the dispersive and polar components of the surface energy were 33 and 11 mJ/m², respectively; grit-blasting thus primarily affected the polar component of surface energy. Sanding and abrasion with the Scotchbrite pad had somewhat smaller effects on the surface energies of the composites. Thus, after sanding, the dispersive and polar components of surface energy were 37 and 4 mJ/m², respectively. After abrasion with the Scotchbrite pad, the dispersive and polar components of surface energy were 35 and 6 mJ/m², respectively.

The results obtained here can also be compared to those of Chin and Wightman (5), who investigated the effect of surface engineering processes such as grit-blasting, O₂ plasma etching, and peel ply removal on the surface properties of bismaleimide/graphite composites. They found that the as-received composites had a low surface energy due largely to fluorine on the surface. Surfaces that were grit-blasted, plasma etched, or prepared by removing a peel ply had no fluorine and had considerably higher surface energies. Thus, the surface that was grit-blasted had $\gamma_{total} = 39.1$ mJ/m² while the surface that was plasma etched had $\gamma_{total} = 78.7$ mJ/m².

Chin and Wightman observed a good correlation when they plotted total surface energy as a function of the sum of the oxygen and nitrogen concentrations. We made a similar plot for our results (see Figure 7) and included the data of Chin and Wightman for comparison. The data of Chin and Wightman for graphite/bismaleimide composites are represented by squares while the triangles represent the data obtained here for graphite/epoxy composites. The solid line in the plot represents a least-squares fit to the data of Chin and Wightman. All of the data fit the linear plot reasonably well despite the fact that the data was obtained for two different composite systems.

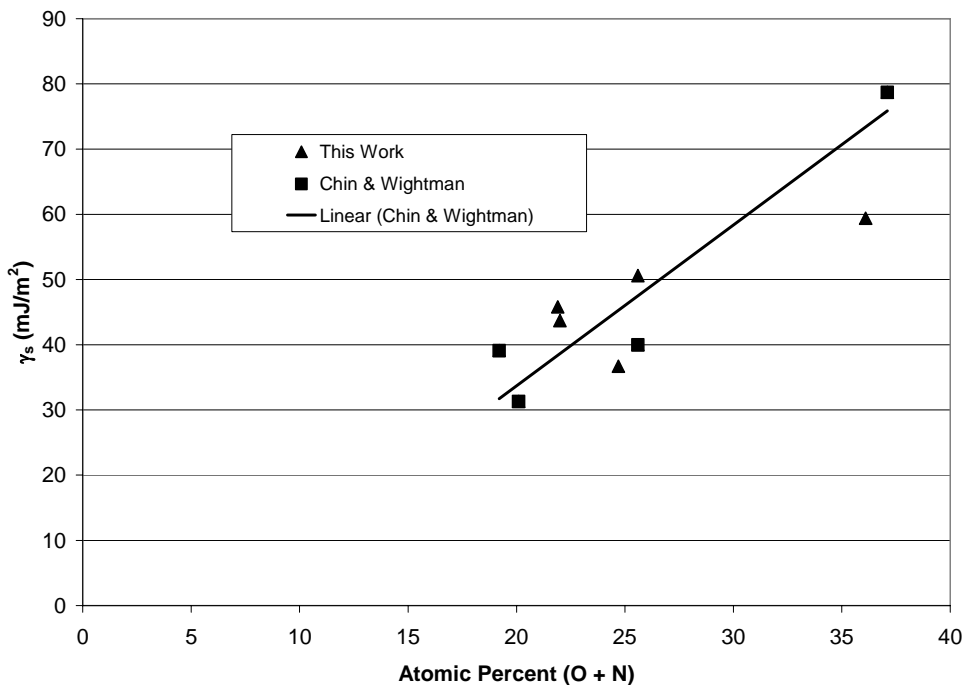


Figure 7. Plot of total surface energy versus the sum of the oxygen and nitrogen concentrations for surface engineered graphite/epoxy composites. Data points obtained in this work are represented by triangles; points obtained by Chin and Wightman (5) are represented by squares.

The results shown in Figure 7 indicated that there might be a general correlation between surface composition and surface energy. Kinloch, Kodokian, and Watts made a similar suggestion some time ago (6,7). According to Kinloch et al, the weighted dipole moment (WDM) for a surface can be calculated by determining the percentages of the various functional groups present on the surface of a polymer and then multiplying by the dipole moment for each functional group. They showed a linear correlation between the WDM and the polar component of the surface energy for several thermoplastic composites that were exposed to a corona discharge for various times.

We have applied the methods of Kinloch et al to the data obtained here and plotted WDM as a function of the polar component of the surface energy. However, the data did not fall on a straight line. Although there could be several explanations for this behavior, perhaps the most important was concerned with the surface roughness of the grit-blasted samples.

Finally, we have determined the effect of surface engineering processes on the fracture energy of double cantilever beam specimens prepared from composite substrates (see Table 3). Specimens prepared from as-tooled substrates failed at the interface between the adhesive and the composite at relatively low values of G_{IC} . This behavior was related to the low surface energy of the substrates and to poor wetting of the substrates by the adhesive. Specimens prepared from grit-blasted substrates failed at much higher values of the fracture energy. Initial failure of these specimens was within the first ply of the composite but quickly became inter-laminar. Similar results were obtained from specimens prepared from substrates that were etched in O_2 plasmas except that the initial failure of those samples was cohesive within the adhesive. The improved performance of DCB specimens prepared from grit-blasted and plasma-etched substrates was related to the greater surface energy of the substrates and to improved wetting of the substrates by the adhesive.

Table 3. Effect of surface engineering processes on the mode-I fracture energy for double cantilever beam specimens.

| Sample | Surface Process | Initiation | | Propagation | |
|------------|------------------------------|---------------------|------------------------------|--------------|------------------------------|
| | | Mode | G_{IC} (J/m ²) | Mode | G_{IC} (J/m ²) |
| CN-1A (1) | None | Interfacial | 385 | Interfacial | 193 |
| CN-15A (2) | None | Interfacial | 210 | Interfacial | 385 |
| L1 (2) | Grit-blast (80 grit garnet) | Cohesive, first ply | 1,314 | Interlaminar | 1,664 |
| L2 (2) | Grit-blast (80 grit garnet) | Cohesive, first ply | 1,436 | Interlaminar | 1,699 |
| O8 (2) | Grit-blast (220 grit garnet) | Cohesive, first ply | 2,067 | Interlaminar | 1,699 |
| M1, M2 (2) | O_2 Plasma | Cohesive, adhesive | 1,997 | Interlaminar | 1,646 |

5. CONCLUSIONS

Grit-blasting and plasma etching are both effective processes for surface engineering of composites prior to adhesive bonding. However, grit-blasting and plasma etching are very different processes and result in substrates with significantly different surface properties. Thus, plasma etching results in relatively large changes in the surface composition of composites, primarily by removing contamination from the surface and introducing new, oxygen-containing functional

groups into the surface. Plasma etching has relatively little effect of the surface roughness of a composite. Grit-blasting results in removal of material from the surface of a composite and in roughening of the surface. If the surface is initially contaminated, significant changes in surface composition can occur. However, grit-blasting may not introduce new functional groups into the surface unless free-radicals are introduced that react with oxygen or water vapor in the environment. There is a correlation between the surface energy and surface composition of a composite. Thus, increasing the concentration of oxygen and nitrogen atoms on the surface leads to an increase in the surface energy. Moreover, there is evidence to indicate that the surface energy of a composite can be calculated from the dipole moments associated with the functional groups found on the surface of the composite. When oxygen is present in the form of hydroxyl groups, as is the case for epoxy resins cured with amines or for plasma-etched surfaces, the hydroxyl groups may dominate the surface chemical properties of the composite and may form covalent bonds with an epoxy adhesive.

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