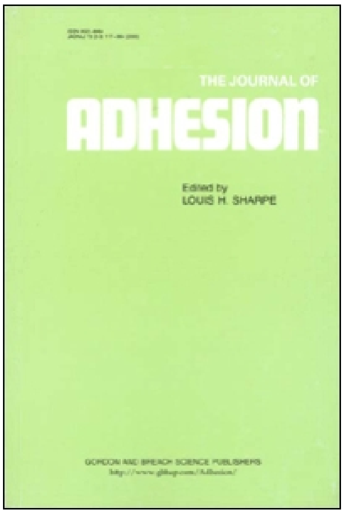

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Effects of Microwave Processing on Fiber-Matrix Adhesion. II. Enhanced Chemical Bonding of Epoxy to Carbon Fibers

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Effects of Microwave Processing on Fiber-Matrix Adhesion. II. Enhanced Chemical Bonding of Epoxy to Carbon Fibers

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The effect of microwave processing on the chemical interactions occurring between the carbon fiber surface and the epoxy matrix constituents was investigated using X-ray Photoelectron Spectroscopy (XPS). Monofunctional model compounds selected to duplicate the matrix constituents were exposed to the carbon fibers at temperatures similar to those encountered during composite processing. After solvent extraction, chemisorbed species were quantified by XPS. Differences were apparent in the C 1s and O 1s core electron regions of the microwave treated samples when referenced to the same elemental regions of thermally (convection) treated samples. Specifically, the atomic percentage of oxygen (in the form of carbon oxides) was increased to a greater degree when using the microwave treatment as opposed to the thermal treatments. The microwave treatment resulted in a substantial increase in the amount of chemical interaction between the fiber surface and the epoxy resin and amine components of the matrix. An epoxy resin/amine hardener adduct compound was also used to investigate the possible interaction of the adduct hydroxyl group with the carbon fiber surface. XPS results indicate a low to insignificant interaction of the hydroxyl with the carbon fiber surface under the conditions used in this study.

KEY WORDS carbon fibers; X-ray photoelectron spectroscopy; surface chemistry; microwave processing of composites; adhesion; epoxy.

1 INTRODUCTION

For most structural composite applications involving thermoset matrices, conventional thermal processing is the processing method selected. Electromagnetic processing involving the use of microwave frequency energy offers a new approach in which energy is coupled directly into the material without reliance on conduction and convection. Extensive work is being conducted to apply this approach to the processing of polymers as well as polymer composites. An earlier published result[1] reported that, in carbon reinforced epoxy composites, significant changes in fiber to matrix adhesion were measured. Under identical conditions, no change in adhesion to aramid or glass fibers was detected with the epoxy. The conductive nature of the carbon fiber has been shown to result in a preferential absorption of electromagnetic energy causing the fibers to attain a higher temperature than the surrounding epoxy matrix. This study was undertaken to determine if the increased temperature of the fiber resulted in a change in the chemical bonding between fiber and matrix.

2 APPROACH

It is not possible to determine the chemical bonding between a carbon fiber and epoxy matrix in the solid state with current analytical techniques. Therefore, a model system was established to simulate the composite. A single carbon fiber embedded in a large tensile dogbone-shaped coupon was selected as the experimental configuration. This duplicated conditions used in the earlier microwave processing studies and surface analysis methods can be applied to the fiber before and after exposure to the polymer to detect specific interactions.

In order to maintain the chemical interactions but without polymerizing the specimen, monofunctional compounds identical to the epoxy/amine oligomers were used in this study. In this manner, the samples could be processed with either thermal or microwave energy under identical conditions and without polymerization taking place. Specific chemical interactions between the functional groups on the model compounds and the carbon fiber surface could take place in the same manner as in the solid state. The unreacted species could then be removed with low temperature solvent extraction and the carbon fiber surface could be analyzed with X-ray Photoelectron Spectroscopy to quantitate chemical interaction between the amine or epoxy functionality and the carbon fiber surface.

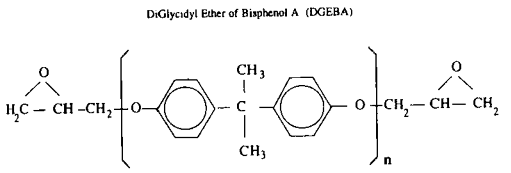
This approach allows interrogation of the actual fiber-matrix interface at the molecular level. At best, however, it represents the maximum degree of interaction since the chemical species are not hindered from interacting with all available sites on the surface as they might be in the melt during the processing cycle.

3 EXPERIMENTAL

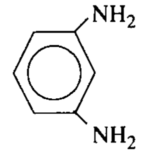
A Material

PAN-based AS-4 fibers with proprietary oxidative surface treatment, obtained from Hercules Inc., have been used in this study. The epoxy resin used in this investigation is a diglycidyl ether of bisphenol-A (Epon 828, Shell Chemical Co.) and the curing agent used is a meta-phenylene diamine (m-PDA, Aldrich

Chemical Co.). The chemical structures of these compounds are shown below:



DiGlycidyl Ether of Bisphenol A (DGEBA)

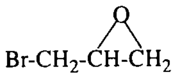


m-PDA

In order to investigate the various surface phenomena occurring during the processing of a carbon fiber reinforced composite, a series of related experiments have been completed involving various fiber surface treatments. The results of these experiments are reported on in this paper. Comparisons were made (for these treatments) between the effects of a thermal cure cycle and a microwave cure cycle, and the chemical reactions resulting in each of the respective procedures. All of the AS4 fiber surface chemical treatments used in this study are listed in Table I.

B Thermal "curing" environment

(a) The first set of experiments was designed to gather experimental evidence to investigate the possibility of reactions occurring between the carbon fiber surface chemical groups and the epoxide functionality. Epibromohydrin (Aldrich Chemical Co.), shown below, has both an epoxide group and a bromine "tag".



The bromine group is not likely to react with the fiber surface while the epoxide group is free to react. Carbon fibers, immersed in epibromohydrin, were heated for 20 minutes at 125°C in a convection oven. The fibers were then refluxed with acetone for 24 hours in a soxhlet extractor, followed by five rinses in

TABLE I
Description of XPS characterized samples and the various surface treatments used in the study

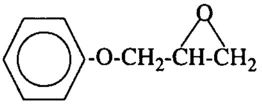
Sample	Type and surface reaction where applicable
a	DER 332 epoxy resin thick film
b	Hercules AS4 fiber "as received" from manufacturer
c	Thermal epoxy resin treatment (80°C) of AS4 fiber
d	Thermal epoxy resin treatment (150°C) of AS4 fiber
e	Microwave epoxy resin treatment of AS4 fiber
f	Thermal m-PDA treatment (130°C) of AS4 fiber
g	Microwave m-PDA treatment of AS4 fiber
h	Thermal epoxy resin/m-PDA adduct treatment (130°C) of AS4 fiber
i	Microwave epoxy resin/m-PDA adduct treatment of AS4 fiber
j	Thermal epibromohydrin treatment (125°C) of AS4 fiber

diethylether and then dried for 1 hour at 120°C. The yield of the reaction between the fiber surface and epibromohydrin was determined by analyzing the bromine content on the surface of the fiber using XPS.

(b) After establishing the reaction between the epoxide functionality and fiber surface groups, the second set of experiments was used to investigate the chemical interactions between the fiber surface and the epoxy resin. Carbon fibers immersed in epoxy resin were heated for 10 minutes at several preset temperatures. The fibers were then refluxed with acetone for 90 hours in a soxhlet extractor to remove the epoxy resin physisorbed to the surface, while leaving the chemisorbed epoxy on the surface. The fibers were dried one hour subsequent to extraction 120°C prior to XPS analysis.

(c) The third set of experiments was used to investigate the interactions of the amine hardener with the fiber surface chemical groups. A solution of m-PDA in phenylethyl ether (phenetole, Aldrich Chemical Co.) was prepared in which the amine content was greater than the equivalent amount necessary to condense a complete monolayer of amine on the carbon fiber surface. Phenylethyl ether has the same backbone structure as the epoxy resin and thus creates an "epoxy resin like" environment without any epoxide functionalities available for cross-linking. Carbon fibers dipped in this solution were heated for 10 minutes at 130°C and then refluxed with acetone in a soxhlet extractor for 48 hours to remove the unreacted m-PDA from the fiber surface. Both m-PDA and phenylethyl ether dissolve well in acetone. The treated fibers were dried for 1 hour at 120°C in a convection oven and analyzed by XPS.

(d) The fourth set of experiments was designed to study the interaction of the fiber surface with the hydroxyl-secondary amine complex formed when the epoxy group reacts with the primary amine of the hardener. In this case, the amine hardener was prereacted with a monofunctional epoxy to create a low molecular weight adduct with the epoxy resin prior to the fiber surface exposure. This compound simulates the interactions of the resin-hardener complex with the fiber surface during the processing of a carbon fiber reinforced composite. Phenylglycidyl ether (Aldrich Chemical Co.) was used in place of the epoxy resin (Epon 828). The structure of the phenylglycidyl ether is shown below:



Phenylglycidyl ether is a monofunctional epoxy which chemically resembles the Epon 828 structure. However, the phenylglycidyl ether reacts with m-PDA without resulting in any crosslinking. m-PDA was dissolved in acetone and a measured quantity (in 4:1 equivalents) of phenylglycidyl ether was added to the solution. The reaction between m-PDA and phenylglycidyl ether was monitored using an FTIR spectrometer (Perkin–Elmer, model 1800) where the disappearance of primary amine was followed to insure complete reaction. KBr windows were used in a heated cell, at 75°C, to monitor the *in-situ* reaction. Spectra were recorded at intervals of five minutes.

Acetone was evaporated from the m-PDA/phenylglycidyl ether solution under vacuum and the mixture was heated for 2 hours at 75°C in order to complete the reaction. Carbon fibers were then treated with the reacted mixture for 10 minutes at 130°C and refluxed with acetone in a soxhlet extractor for 72 hours. The fibers were subsequently analyzed using XPS.

For each of the separate experiments described above the same sample preparation and washing procedure was used. A tow of fibers, 10 cm. in length, was placed on a rectangular Teflon frame and the ends were securely fastened with Teflon clamps. This frame was then placed in a Teflon-walled bath containing appropriate chemicals for fiber treatment in accordance with the above mentioned set of experiments. The fixture was then heated in a convection oven at a preset temperature for a desired period. After the heating cycle, the Teflon frame with the carbon fiber tow was refluxed with acetone in a soxhlet extractor and then dried in a convection oven for 1 hour at 120°C.

C Microwave "curing" environment

All of the thermal cure experiments discussed above (except for the epibromohydrin reaction) were repeated in this section of the study with the substitution of a microwave curing procedure in place of the conventional thermal process. Subsequent to the microwave curing procedure the samples were all soxhlet extracted as was the case for the thermally cured samples. The methodology used for microwave curing of the fiber samples was the same as that used in the first paper of this series.[1] However, in this study a Teflon container which contained the appropriate chemicals and the carbon fiber tow was placed in the center of the bottom of the microwave cavity and in alignment with the excitation probe. In the previous study a silicone container was used. A fluoroptic temperature measuring system (Luxtron Model 750) equipped with four channels for measurement was used to monitor continuously the temperature of the reacting mixture.

Microwave power was coupled into the cavity through an adjustable excitation probe. A magnetron-based, fixed frequency (2.45 GHz) generator (Opthos MPG-4) with adjustable duty cycles from 5% to 85%, and power output from 0 to 120 watts, was used as the microwave source. For stability considerations, the power source was operated at higher power levels and the desired power was channelled through a 10 db directional coupler. A circulator was used to protect the source from the reflected power. 50-ohm impedance coaxial cables were used to transmit the power from the source to the cavity. Two 20 db directional couplers were used to decouple the incident and reflected signals. Both incident and reflected signals were attentuated and measured directly by power meters.

D Instrumental

Subsequent to the various surface treatments, samples of the treated carbon fibers were placed into a Perkin–Elmer PHI 5400 X-ray photoelectron spectrometer. The XPS spectra were obtained at a base pressure of approximately

10^{-9} Torr. The PHI 5400 XPS spectrometer was equipped with a Mg K_α standard source (PHI 04-548) and an Al K_α toroidal monochromatic source (PHI 10-410). The standard Mg source was used for all samples analysis and was operated at 300 W (15 kV, 20 mA). A continuously variable sample stage was used and was set to 45° (photoelectron take-off angle). The portion of the sample analyzed by the spectrometer is set through an initial lens system (PHI Omni-Focus). For all analyses, the lens was in the large area, small solid angle mode, and the size of the analysis area was set for a 3.3 mm diameter circle. Data were collected in the fixed analyzer transmission mode utilizing a position sensitive detector (PSD) and a 180° hemispherical analyzer. Pass energies were set at 89.45 eV for the survey scans (0–1000 eV) and at 8.95 eV for the high resolution narrow scans of the elemental regions. The instrument was calibrated using Mg K_α X-radiation with the initial lens system set for small area, large solid angle analysis. The Ag $3d_{5/2}$ peak of a sputter cleaned Ag foil had a binding energy of 368.2 ± 01. eV. The binding energy difference for the Cu $2p_{3/2}$ and the Cu $3p_{3/2}$ peaks was set to 857.5 eV ± 0.1 eV. Full width at half maximum (FWHM) for the Ag $3d_{5/2}$ peak was measured to be 0.80 eV at a count rate of 140,000 counts/s.

Instrument control, data collection and manipulation was performed with an Apollo 3500 workstation running PHI ESCA Version 3.0 software. The curve fitting was carried out using a modified Gauss-Newton non-linear least squares optimization procedure that is part of the instrumental software. The "graphitic" C 1s peaks (284.6 eV) were fit using an asymmetric Gaussian-Lorentzian function which is a combination of a regular Gaussian-Lorentzian function (used to fit the remaining peaks) and an exponential tail function. This exponential tail function is only applied to the higher binding energy side of the "graphitic" peak in order to include the effects of conduction band interaction (CBI).[2] The C 1s binding energy of the graphitic peak was set to 284.6 eV for calibration purposes.

4 RESULTS AND DISCUSSION

High resolution, narrow energy window scans are shown for the carbon and oxygen regions of each of the respective samples. The low resolution survey scans of the as-received and the treated samples are all essentially similar and have not been included in the figures.

A Epoxy thick film

Figure 1*a* shows the curve-fitted C 1s region of a DER 332 (DOW epoxy resin) thick solid epoxy film which does not contain any curing agent. Because EPON 828 epoxy resin is a liquid in bulk form it was not possible to characterize the material using XPS. DER 332 was used because of the relative purity of the material (mostly composed of monomeric resin with a very low amount of higher molecular weight oligomers) and because it should give essentially the same XPS spectra as the EPON 828. Because of the purity of the DER 332 it is possible to

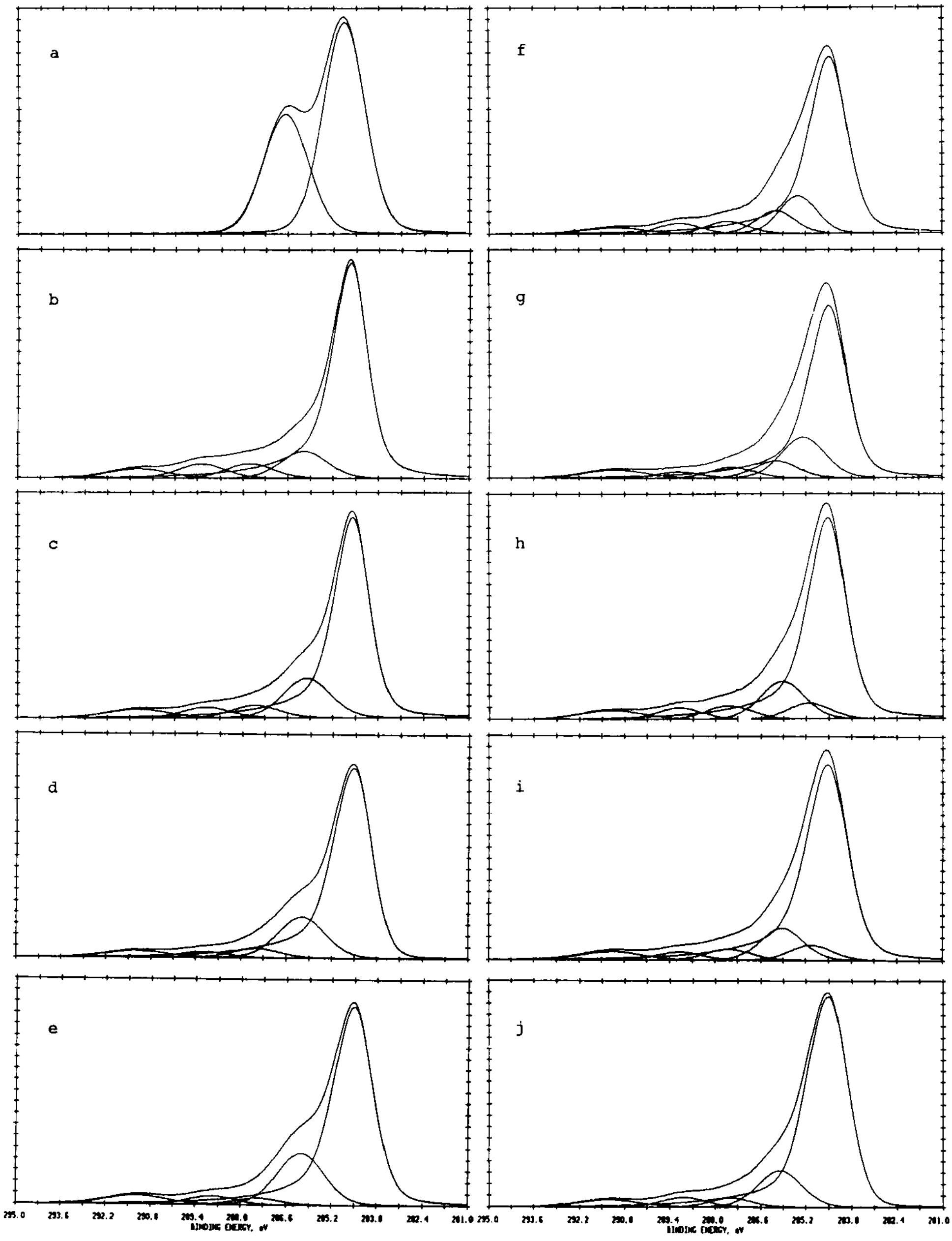


FIGURE 1 Curve fit C 1s spectra of a) DER 332 epoxy resin thick film b) Hercules AS4 fiber "as received" from manufacturer c) Thermal epoxy resin treatment (80°C) of AS4 fiber d) Thermal epoxy resin treatment (150°C) of AS4 fiber e) Microwave epoxy resin treatment of AS4 fiber f) Thermal m-PDA treatment (130°C) of AS4 fiber g) Microwave m-PDA treatment of AS4 fiber h) Thermal epoxy resin/m-PDA treatment (130°C) of AS4 fiber i) Microwave epoxy resin/m-PDA treatment of AS4 fiber j) Thermal epibromohydrin treatment (125°C) of AS4 fiber.

deposit the material from solution and form a glassy thick film. It was expected that this material would serve as an appropriate model for the EPON 828 epoxy resin. As expected, there are two main contributions to the overall line shape of the C 1s region for this sample. The most intense peak at 285.0 eV (charge corrected reference) corresponds to the C—C bonds which are found in the epoxy molecule. The higher binding energy component corresponds to the epoxide or oxirane functionality and the ether linkages that are found in the epoxy molecule (C—O type groups). This higher binding energy component is due to the chemical shift caused by a C—O single bond environment. The shift in the neat epoxy thick film is approximately 1.7 eV. No other chemical species are observed in the C 1s spectrum for this sample. The C 1s peak binding energies and relative peak areas for this sample are shown in Table II. Figure 2*a* shows the curve fitted O 1s region of the EPON 828 thick film. The O 1s region of the epoxy sample was curved fitted using 2 peaks. Peak 1 (for polymeric samples), the lower binding energy peak (≈532.0 eV), is the O 1s signal from C=O groups. However, the presence of this peak in the spectrum of the neat sample is most probably due to inorganic oxides originally present at the surface of the metal film used to support the epoxy film. Peak 2, the higher binding energy component (≈533.4 eV), corresponds to the presence of C—O—C linkages present as ether and epoxide groups in the epoxy molecule.[3] The binding energy and the relative areas of each peak in the total O 1s area are given in Table III. The influence of the epoxy stoichiometry on the curve fits and the relative atomic concentrations will be discussed for each of the sample treatments below.

B C 1s region of AS-4 carbon fibers

Figures 1*b*–*j* show the curve fitted C 1s region of the "as received" and reacted AS-4 carbon fibers. The AS-type carbon fiber receives a proprietary surface treatment during production which has been reported to promote adhesion to epoxy matrix materials through a two-step mechanism.[4] Firstly, the treatments remove a weak outer fiber layer initially present on the fiber. Secondly, surface

TABLE II

C 1s peak binding energies and relative peak areas of carbon chemical states

	Main Peak		Peak I		Peak II		Peak III		Peak IV		Peak V		Total oxide
Sample	B.E. (eV)	Area (%)	B.E. (eV)	Area (%)	B.E. (eV)	Area (%)	B.E. (eV)	Area (%)	B.E. (eV)	Area (%)	B.E. (eV)	Area (%)	II + III + IV (%)
a	285.0	63.0	—		286.8	37.0	—		—		—		37.0
b	284.6	76.6	—		286.1	10.1	287.7	5.1	289.2	4.2	291.2	4.0	19.4
c	284.6	76.3	—		286.0	12.5	287.6	3.8	289.1	3.4	291.2	3.9	19.7
d	284.6	76.0	—		286.1	15.7	287.5	3.3	289.2	1.8	291.2	3.3	20.8
e	284.6	71.8	—		286.2	19.0	287.6	2.4	288.9	3.0	291.0	3.9	24.4
f	284.6	68.0	285.4	12.5	286.2	8.6	287.7	4.1	289.2	3.5	291.2	3.2	16.2
g	284.6	67.3	285.4	16.0	286.2	6.0	287.6	4.1	289.2	2.3	291.1	4.3	12.4
h	284.6	71.5	285.2	4.2	286.1	11.8	287.7	4.6	289.2	3.5	291.3	4.5	19.9
i	284.6	74.5	285.1	4.5	286.0	10.7	287.6	3.8	289.1	2.4	291.2	4.0	16.9
j	284.6	77.4	—		286.1	12.9	287.6	3.0	289.1	3.3	291.4	3.3	19.2

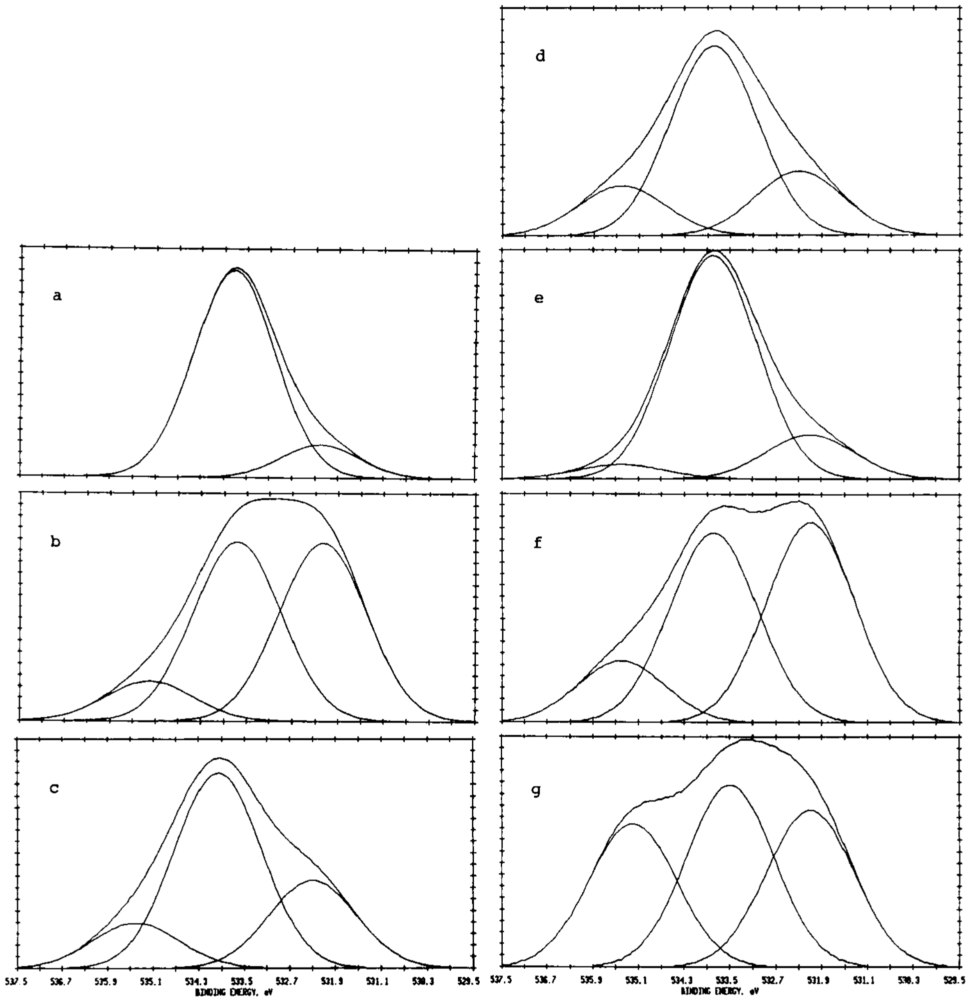


FIGURE 2 Curve fit O 1s spectra of a) DER 332 epoxy resin thick film b) Hercules AS4 fiber "as received" from manufacturer c) Thermal epoxy resin treatment (80°C) of AS4 fiber d) Thermal epoxy resin treatment (150°C) of AS4 fiber e) Microwave epoxy resin treatment of AS4 fiber f) Thermal m-PDA treatment (130°C) of AS4 fiber g) Microwave m-PDA treatment of AS4 fiber.

chemical groups are added which increase the interaction with the matrix. These functional groups give rise to binding energy shifted peaks in the XPS spectra of the various elements present on the fiber surface.[2] The XPS spectra of all samples studied ("as received" and all treatments) showed one main peak in the C 1s region at a binding energy of 284.6 eV, which corresponds to the "graphitic" structure present near the surface of these carbon fibers. Four types of functional groups were identified in this study (Peak I, II, III, IV). They were shifted approximately 0.7, 1.5, 2.9, and 4.5 eV from the main "graphitic" peak at 284.6 eV, respectively. Peak I corresponds to the signal from a C—N type of

TABLE III
O 1s peak binding energies and relative peak areas of oxygen chemical states

	Peak 1		Peak 2		Peak 3	
Sample	B.E. (eV)	Area (%)	B.E. (eV)	Area (%)	B.E. (eV)	Area (%)
a	532.2	13.0	533.7	87.0	—	
b	532.2	44.1	533.7	42.4	535.2	13.5
c	532.3	26.4	533.9	61.0	535.5	12.6
d	532.4	20.3	533.9	65.2	535.6	14.5
e	531.7	12.7	533.9	77.1	535.4	10.2
f	532.0	45.9	533.8	39.7	535.5	14.4
g	532.2	31.8	533.3	37.9	535.0	30.4
h	—		—		—	
i	—		—		—	
j	—		—		—	

chemical bond. Peak II corresponds to the C—OR type groups present at the fiber surface. These groups may be present as simple hydroxyl (C—OH) or as ether type (C—O—C) linkages. This area may also show an effect due to chemical bonding of the epoxy resin to the fiber surface. The oxirane functionality in the epoxy resin will contribute to this peak, as was discussed in the previous section. Peak III, shifted approximately 2.9 eV from the "graphitic" peak, corresponds to C=O (carbonyl) functional groups. Peak IV, shifted approximately 4.5 eV, is due to carboxyl (COOH) and/or ester (COOR) groups. A fifth peak (V), which was shifted approximately 6.8 eV from the main carbon peak was also identified and included in the curve fits for all of the samples. This fifth peak has been identified as arising from a plasmon excitation mechanism.[2]

The changes in the C 1s binding energy values and the relative area percentages for the "as received" fibers and all of the reacted fibers have been tabulated in Table II. The effects on the C 1s region of each of the chemical reactions and the processing environment used will be discussed in the following sections. The C 1s spectrum of the "as received" AS-4 carbon fiber is shown in Figure 1*b*. The most intense contribution to the spectrum is due to the "graphitic" peak at 284.6 eV. The main peak was fitted using a exponential tail function to take into account the effects of conduction band interaction (CBI). The shape of the tail used in this work was determined by comparison to the extent of asymmetry seen in the C 1s spectra of untreated HM and pitch-based fibers. The HM and pitch-based fibers are expected to have a more intact "graphite like" structure at the surface of the fiber in comparison with the AS-type fibers. The AS-type fiber surface treatments would be expected to "break up" the graphite structure at the surface of the fiber in order to introduce the chemical functional groups necessary for improved chemical adhesion to the epoxy resin. This degradation of the "graphite like" structure should decrease the CBI-induced asymmetry in the main carbon peak. After determination of the asymmetric tailing function used for the curve fit of the "as received" AS-4 fibers, this contribution was kept constant in the C 1s curve fitting of each of the reacted samples used in this study.

Functional group contributions to the C 1s region of the "as received" AS-4 fibers were also apparent. Peaks II, III, IV as well as the plasmon feature are seen for this fiber. The greatest functional group contribution to the C 1s line shape of the "as received" fibers is from the C—O type of chemical bond.

C O 1s region of AS-4 carbon fibers

Figures 2*b*–*j* show the curve fitted O 1s region of the "as received" and reacted AS-4 carbon fibers. Three types of oxygen bonding environments were identified on the surface of the carbon fibers. Peaks 1 and 2 were discussed previously in the XPS characterization of the epoxy resin thick film. Peak 1, at approximately 532.0 eV, is a contribution from C═O chemical bonding. Peak 2, at approximately 533.4 eV, is a contribution from oxygen/carbon single bonds. Hydroxyl type (C—OH) functional groups as well as ether chemical bonds may fall into this category.[3] Peak 3 in the O 1s curve fits, at approximately 536.0 eV, is probably due to adsorbed water and trace adsorbed O_2 on the fiber surface.[2] The changes in the O 1s binding energy values and the relative area percentages for the "as received" fibers and all of the reacted fibers are tabulated in Table III. The effects on the O 1s region, subsequent to each of the chemical reactions and processing treatments used, will be discussed in the following sections.

D Thermal and microwave epoxy resin treatments

Figures 1*c*–*e* and *j*, show the C 1s curve fitted regions of the various epoxy treatments used in this study. Figures 1*c*, *d*, and *j*, correspond to the use of a thermal processing cycle to simulate the curing process of a composite. As a result of the thermal epoxy treatments, there is a significant increase in the C 1s peak II intensity of both sample *c* (12.5% of area) and sample *d* (15.7% of area). Peak II corresponds to the C—O type chemical bond. There is also a small decrease in peak III, C═O type bond, for both of the samples. The overall change in the oxide contribution to the C 1s peak shape for these two thermal treatments is shown in the final column of Table II. Figure 1*j*, shows the C 1s curve fit of the epibromohydrin treated AS-4 fibers. The overall curve fit is very similar to the results for sample *d*, the 150 degree thermal epoxy treatment. The epibromohydrin molecule has one oxirane functionality which is available for reaction with the surface of the fiber. The bromine "tag" can then be used as an indicator of the degree of chemical bonding that is occurring at the fiber surface. It should be noted that the contribution of the bromine signal to the overall relative atomic percentage (0.6%) is not as great as one would expect from the corresponding increase in the oxygen atomic percentage (2.2% relative atomic amount). This may be an indication of instability of the bromine atom with respect to heat and light. However, the low Br 3d signal intensity (0.6% relative atomic amount) does indicate that the overall degree of chemical bonding occurring at the fiber surface is quite small. Figure 1*e* shows the effects of a microwave curing procedure on the chemical bonding that occurs between the epoxy resin and the fiber surface. The C 1s signal shows a strong shoulder at 286.2 eV B.E., which indicates a large increase in the surface C—O concentration (19.0% of area). The increase in this peak intensity is significantly greater than in the case of either of the thermal treatments. This would seem to indicate an increase in the chemical interaction occurring between the fiber surface and the epoxy resin. This is marked by a large increase in the C—O type of functional group which would correspond to a greater concentration of epoxy resin molecules being chemically bound to the surface than in the case of the thermal samples. A drop in the C=O peak at 287.6 eV, similar to that seen for the thermally treated samples, is also apparent. However, in this case the drop is more pronounced than in the previous two cases ($\approx$2.5% decrease). There appears to be little variation in the peak IV and V intensities for all of the samples discussed up to this point.

Figures 2*c*–*e* show the O 1s curve fits for the thermal and microwave epoxy resin treatments. The sharp increase in the peak 2 intensity for all of the treatments, in comparison with the "as received" fiber, is very noticeable. All of the epoxy resin treated samples reflect an increase in peak 2 with the microwave treated fibers (Figure 2*e*) showing the largest increase in the O 1s peak 2 intensity (Table III). This corresponds well with the results from the C 1s region which showed a general increase in the C—O bonds at the surface from the lowest temperature thermal treatment to the microwave treatment. Again, this reflects an increase in the chemical bonding that is occurring between the epoxy resin and the fiber surface as a result of these treatments, with the microwave treatment appearing to have the largest effect on the degree of chemical bonding that occurs.

E Thermal and microwave m-PDA hardener treatments

1*f* and *g* show the C 1s curve fits for the thermal and microwave m-PDA hardener treatments. The most noticeable change in these treatments from those previously discussed is the appearance of C–N intensity in the C 1s peak shape. This suggests the occurrence of a chemical reaction between the fiber surface and the amine hardener molecule. As shown in Table II, the most pronounced degree of chemical bonding is seen in the case of the microwave m-PDA treatment. There is also a decrease in the C–O intensity for both of these treatments.

Figures 2*f* and *g* show the O 1s curve fits for the thermal and microwave m-PDA treatments. The relative peak areas for the O 1s region are quite similar to those for the "as received" fibers. Of interest in the case of the microwave treatment is the large increase in the peak 3 intensity, which is probably due to adsorbed water and trace amounts of O_2 at the fiber surface. This may indicate a sensitivity to the atmosphere which was not carefully controlled for this study. Table IV shows the N 1s/C 1s and O 1s/C 1s ratioed atomic amounts for these samples. Both of the m-PDA treatments indicate an increase in the N concentration at the surface of the fiber. This type of increase was not seen in the case of the epoxy resin treatments, which had N 1s/C 1s ratios similar to the "as received" fibers.

TABLE IV
O 1s, N 1s, and Br 3d atomic amounts expressed as a ratio of the total C 1s atomic amount

				O 1s/C 1s (total) (%)				Br 3d/C 1s total (%)	N 1s/C 1s (total) (%)
Sample	C 1s	O 1s	N 1s	Peak 1	Peak 2	Peak 3	Total		
a	82.1	17.9	—	2.8	19.0	—	21.8	—	—
b	87.4	9.1	3.5	4.6	4.4	1.4	10.4	—	4.0
c	85.9	10.1	3.9	3.1	7.2	1.5	11.8	—	4.5
d	85.3	11.8	3.0	2.8	9.0	2.0	13.8	—	3.5
e	82.9	13.7	3.4	2.1	12.7	1.7	16.5	—	4.1
f	85.1	8.4	6.5	4.6	3.9	1.4	9.9	—	7.6
g	86.6	6.3	7.1	2.3	2.8	2.2	7.3	—	8.2
h	87.2	8.7	4.2	—	—	—	9.9	—	4.8
i	86.5	8.7	4.8	—	—	—	10.1	—	5.6
j	84.0	11.3	4.1	—	—	—	13.5	0.7	4.9

F Thermal and microwave adduct treatments

Figures 1*h* and *i* show the C 1s curve fits for the thermal and microwave epoxy (phenylglycidyl ether)/m-PDA hardener treatments. This treatment was designed to investigate the reactivity of the hydroxyl functional group on the epoxy molecule that has been initially reacted with the amine hardener. This reaction results in a ring opening of the oxirane functional group and the formation of a hydroxyl. This treatment should also give some indication of the reactivity of the secondary amine form of the m-PDA hardener. There appears to be a small degree of chemical interaction between the adduct molecule and the fiber surface as reflected in the C 1s peak I intensity (Table II). Table IV also shows a small increase in the N 1s/C 1s atomic amount for both the thermal and the microwave adduct treatments in comparison with the "as received" fiber ratio. It would, therefore, be expected that the reactivity of the secondary amine with the surface of the fiber is not very significant in relation to the reactivity of the primary amine form (unreacted) of the m-PDA hardener. There is no significant difference between the oxide intensities (peaks II, III, and IV) of the adduct treatments and the "as received" fiber. This would seem to indicate that the reactivity of the hydroxyl group on the adduct molecule with the fiber surface is very low. In light of the small increase seen in the N 1s intensities of the adduct treatments, this combined information may indicate that the C—N formation occurring in these treatments is only occurring between primary or unreacted amine in the adduct mixture and the fiber surface.

5 CONCLUSIONS

The use of a microwave heating environment can result in a substantial increase in the amount of chemical interaction between the fiber surface and the epoxy resin and amine components of the matrix. Changes in the chemical bonding present at the surface of the carbon fibers were seen in the case of both the thermal and microwave procedures used in this study. The use of the epibromohydrin reaction indicates that the overall amount of chemical interaction occurring at the fiber surface is small. However, the use of the microwave curing procedure effectively doubled the degree of chemical interaction occurring between the fiber and the epoxy resin in comparison with the most effective thermal treatment (*i.e.* 150°C).

Chemical interaction of primary amine with the carbon fiber surface was the same in either the thermal or microwave environment when the amine was not competing with the epoxy group for the carbon fiber surface.

The use of an adduct compound to study possible interaction between the fiber surface and the adduct hydroxyl group indicates a low to insignificant interaction under these conditions. A smaller degree of C–N bonding in this portion of the study may be the result of the chemical interaction between the fiber surface and any unreacted primary amine hardener in the adduct mixture.

A larger than expected increase in the O 1s peak 3 intensity for the microwave m-PDA treatment may be indicative of either sample contamination from the reaction materials or a process sensitivity to atmospheric conditions (which were not carefully controlled or monitored in this study).

Overall, the extent of chemical bonding of an epoxy-amine polymer with the AS-4 carbon fiber surface is less than 5% when processed thermally. Microwave processing appears to increase substantially the probability of chemical bonding in the solid state. The combined results suggest that the change in composite performance resulting from the use of a microwave curing procedure, instead of the more typical thermally cured process, may be partly due to an increase in the chemical interactions between the fiber surface and the matrix material.

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