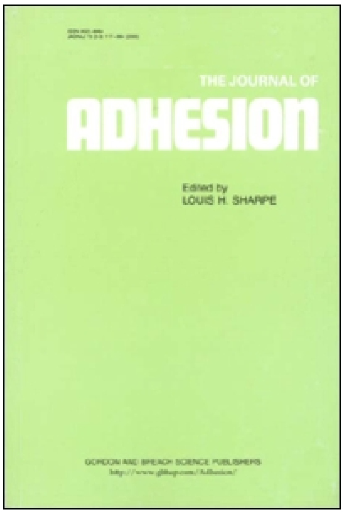

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P. Commerçon[a]; J. P. Wightman[a]
[a] Chemistry Department, Virginia Institute for Material Systems, National Science Foundation Science and Technology Center, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA

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Effect of Organic Gas Plasmas on the Adhesion of Matrix Resins to Carbon Fibers

P. COMMERÇON and J. P. WIGHTMAN*

Chemistry Department, Virginia Institute for Material Systems, National Science Foundation Science and Technology Center, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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IM7 carbon fibers were surface treated in methane, ethylene, trifluoromethane and tetrafluoromethane plasmas. The surface chemical composition of the fibers was determined by X-ray photoelectron spectroscopy (XPS). The adhesion between as-received and plasma-treated carbon fibers and polyethersulfone (PES) and an epoxy resin was measured by the microbond pull-out test. XPS showed that the methane and ethylene plasmas deposited a thin layer of hydrocarbon on the fiber surface. The trifluoromethane plasma deposited a layer of fluorocarbon on the surface of the fibers. The tetrafluoromethane plasma etched the fibers and introduced a significant amount of fluorine on the surface. The microbond pull-out test results indicated that an etching plasma, such as the tetrafluoromethane plasma, improved the adhesion between carbon fibers and PES. These results are consistent with earlier work performed with ammonia plasma. The adhesion is believed to be due primarily to the differential thermal shrinkage between the fiber and the matrix. It was shown that in the case of a reactive matrix such as an epoxy resin, the fiber chemical composition plays a role in the fiber-matrix adhesion. However, this chemical effect is secondary to the cleaning effect of the surface treatment.

KEY WORDS Carbon fibers; plasma treatment; organic gas plasma; fiber-matrix adhesion; microbond pull-out test; X-ray photoelectron spectroscopy; polyethersulfone; epoxy resin.

INTRODUCTION

Plasmas have been used effectively to modify the surface chemical composition and the surface energy of carbon fibers.[1–9] Oxidative plasmas were found to improve the adhesion between carbon fibers and epoxy,[7] bismaleimide[10,11] and thermoplastic[12–14] resins. The adhesion improvement has been attributed to the increased oxygen concentration on the fiber surface.[12,13] However, Drzal *et al.*[15] showed that removal of a "weak boundary layer" was the main cause for the adhesion improvement between AS4 carbon fibers and an epoxy resin. Yip and Lin[16] reached a similar conclusion and suggested that "the etching by fluorination of carbon fibers would promote the fiber resin adhesion similar to that of the oxidative treatments". Few studies have focussed

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* To whom correspondence should be addressed.

on the effect of organic gas plasma on carbon fiber-matrix adhesion.[13,14] To the authors' knowledge, no work has been reported on the effect of fluorinated gas plasma treatments of carbon fibers in relation to their adhesion to matrix resins.

In this study, intermediate modulus carbon fibers (IM7) were surface treated in hydrocarbon and fluorocarbon gas plasmas. The surface chemical composition of the fibers was determined by X-ray photoelectron spectroscopy (XPS). The adhesion between treated carbon fibers and polyethersulfone (PES) and an epoxy resin was measured using the microbond pull-out test. The results obtained with organic gas plasma treated fibers were compared to those obtained with fibers treated in air and in ammonia which were reported in a previous paper.[17]

EXPERIMENTAL

Unsized, PAN-based Hercules IM7 carbon fibers were treated in a radio frequency (13.56 MHz, 50 W) generated plasma of organic gases for 2 minutes. The gases used in this study were methane (CH_4), ethylene (C_2H_4), trifluoromethane (CHF_3), and tetrafluoromethane (CF_4). A constant pressure of 0.1 torr was maintained during the treatment by a combination of continuous evacuation and gas inlet through a microleak. The parameters used for the XPS analysis of the carbon fibers, the experimental conditions for the formation of the PES microdroplets, and the principle of the microbond pull-out test were described previously.[17]

The epoxy resin was obtained by reacting stoichiometric amounts of EPON® 828 with JEFFAMINE® DU-700. The choice of this epoxy system was guided by the work of Rao *et al.*,[18] and Rao and Drzal,[19] who chose the JEFFAMINE® DU-700 as an epoxy curing agent because of its low volatility. EPON® 828 is a diglycidyl ether of bisphenol A (DGEBA) resin and was obtained from Shell. The JEFFAMINE® DU-700 is an amine-terminated urea condensate of amine-terminated polypropylene glycols and was obtained from Texaco Chemical Company.

Figure 1 illustrates the principle of the formation of the epoxy microdroplets for the microbond pull-out test. A short fiber attached to a copper wire was dipped into the liquid mixture of EPON® 828 and JEFFAMINE® DU-700. This resulted in the formation of a series of droplets. A single drop of liquid was then transferred from the short fiber to the one on the fixture simply by careful contact of the two fibers and slow withdrawal of the short fiber after contact. The epoxy droplets were then cured for 2 hours at 85 °C and post-cured for 3 hours at 125 °C.

RESULTS AND DISCUSSION

Surface Chemical Composition

The XPS analysis results are summarized in Table I. Both hydrocarbon plasmas increased the carbon surface atomic concentration while decreasing the oxygen and nitrogen concentrations. Nitrogen is assumed to come only from the carbon fibers. Its detection on the plasma-treated fibers indicates that the deposit resulting from plasma

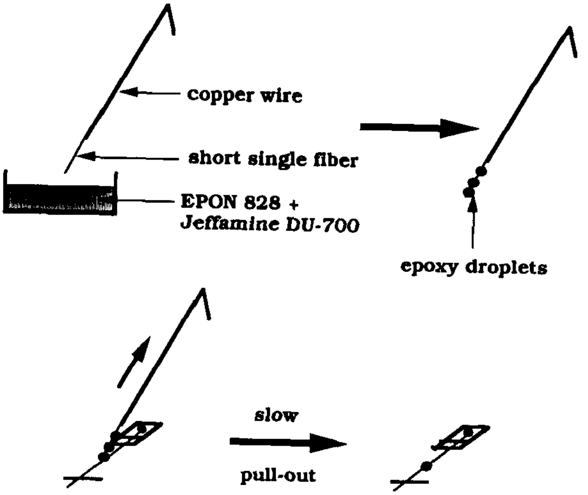

FIGURE 1 Procedure for the formation of the microdroplets of epoxy resin on single carbon fibers.

polymerization is either non-uniformly distributed on the fiber surface or very thin, with a thickness less than the depth of analysis of the XPS (≈ 6 nm). The lower nitrogen concentration observed in the case of the ethylene plasma, compared with the methane plasma, suggests that the polymeric coating is thicker or more uniformly applied in the former treatment. This suggestion is consistent with the higher deposition rate reported for an ethylene plasma compared with a methane plasma [Ref. 20, p. 302]. Curve fit carbon 1s spectra for methane and ethylene plasma-treated fibers are shown in Figure 2. The carbon 1s photopeak of the methane-plasma-treated fibers is curve fit with three peaks: C1, C2 and C3. The peak assignments are the same as for the as-received and inorganic gas plasma-treated fibers which were summarized in Table II of Ref. 17, where C1=C—C, C—H; C2=C—O, C—N, C=N and C3=C=O,

TABLE I
XPS surface composition (atomic %) of IM7 carbon fibers for various plasma treatments

	Carbon	Oxygen	Nitrogen	Fluorine
as-received	85.0 ± 1.3	9.9 ± 0.8	5.1 ± 0.6	—
CH_4 plasma (2 min.)	90.9 ± 0.8	5.8 ± 0.4	3.3 ± 0.4	—
C_2H_4 plasma (2 min.)	96.2 ± 0.9	3.2 ± 0.3	0.9 ± 0.5	—
CHF_3 plasma (2 min.)	36.5 ± 0.5	1.6 ± 0.1	0.7 ± 0.1	61.2 ± 0.5
CF_4 plasma (2 min.)	56.7 ± 0.6	3.3 ± 0.7	1.7 ± 0.2	38.4 ± 0.0
C_2H_4 (2 min.) + air (15 sec.)	85.9 ± 2.6	10.3 ± 2.4	3.8 ± 0.2	—
C_2H_4 (2 min.) + NH_3 (15 sec.)	88.3 ± 0.7	4.8 ± 0.7	6.9 ± 1.4	—

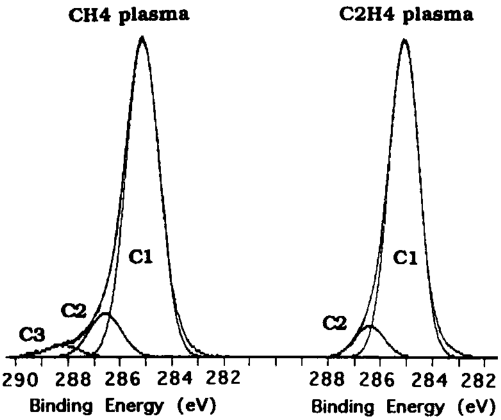

FIGURE 2 Curve-resolved carbon 1s photopeaks for methane and ethylene plasma-treated IM7 carbon fibers.

N—C=O. The C1 peak contributes to 85% of the total carbon 1s photopeak and the peaks C2 and C3 to 12% and 3%, respectively. The carbon 1s photopeak of ethylene-plasma-treated fibers is curve fitted with only two peaks. The C1 peak accounts for 91% of the total photopeak. It was not possible to distinguish between the carbon due to the fibers and that due to the plasma polymer.

The thicker coating formed in the ethylene plasma can serve as a "substrate" on which new oxygen or nitrogen functionalities can be grafted. IM7 carbon fibers were treated first in an ethylene plasma for 2 minutes and then in an air or an ammonia plasma for 15 seconds. There was no exposure to the atmosphere between the two

TABLE II
Contribution (%) of each functional group to the total carbon 1s spectrum of trifluoromethane and tetrafluoromethane plasma-treated IM7 carbon fibers

Functional group	binding energy shift (eV) (FC 1peak at 285.0 eV)		% total c 1s spectrum area (average of 2 samples)	
	CF_4 plasma	CHF_3 plasma	CF_4 plasma	CHF_3 plasma
FC 1: $\underline{C}$—C; $\underline{C}$—H	0.0	0.0	38	19
FC2: $\underline{C}H_2$—CF_2, $\underline{C}$—O CF—$\underline{C}$—CF	+ 1.4	+ 1.6	12	19
FC3: $\underline{C}HF$—CH_2	+ 2.6	+ 2.7	6	10
FC4: $\underline{C}HF$—CF_2	+ 4.1	+ 4.3	26	18
FC5: $\underline{C}F_2$—CHF, $\underline{C}F_2$—CH_2	+ 6.1	+ 6.3	13	20
FC6: $\underline{C}F_3$	+ 8.0	+ 8.5	5	14

treatments. The surface atomic compositions of the fibers after these combinations of plasma treatments are also reported in Table I. The ethylene/air combination introduced a majority of oxygen functionalities and the ethylene/ammonia combination created a surface richer in nitrogen functionalities. Almost 4% nitrogen was detected in the first combination of plasmas, where nitrogen would not be expected, and almost 5% oxygen was found in the second combination of plasmas where oxygen would not be expected.

Model studies on chrome plates showed that oxygen (up to 6%) was also found after an ethylene/ammonia combination. Similarly, nitrogen (1.4%) was detected on a chrome plate treated for 2 minutes in an ethylene plasma followed by a 15-second oxygen plasma, when no nitrogen was present before the oxygen plasma treatment. These experiments suggest that the oxygen and the nitrogen observed on the carbon fibers after the ethylene/ammonia and ethylene/oxygen plasmas combinations, respectively, do not come necessarily from the fiber but instead from post-plasmareactions.

Both fluorocarbon gas plasmas introduced a significant amount of fluorine on the fiber surface: 61% for the CHF_3 plasma and 38% for CF_4 plasma (see Table I). Nitrogen and oxygen atomic concentrations decreased considerably upon fluorocarbon gas plasma treatment of the as-received fibers. Figure 3 shows the carbon 1s XPS curve fit spectra of IM7 carbon fibers after CF_4 (a) and CHF_3 (b) plasma treatments. Six

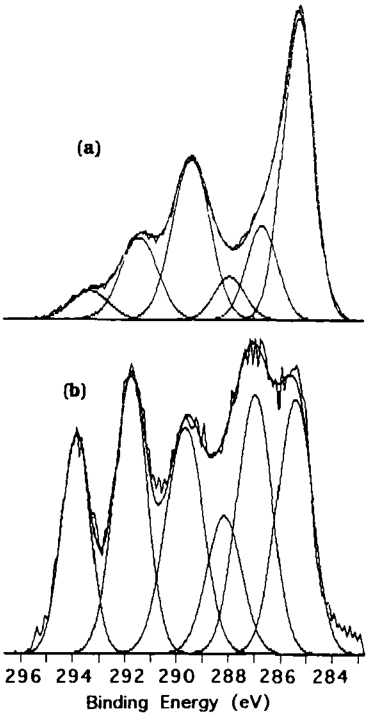

FIGURE 3 Curve-resolved carbon 1s photopeaks for tetrafluoreomethane (a) and trifluoromethane (b) plasma-treated IM7 carbon fibers.

peaks are fitted under the envelope curve of each spectrum. The binding energy shifts and the relative contributions of these peaks to the total carbon 1s spectrum are summarized in Table II. The assignment of the peaks to functional groups is based on the work of Clark *et al.*[21-23] The "graphitic" carbon peak (FC1) is the dominant peak in the case of CF_4-plasma-treated IM7 carbon fibers, and FC4 (due to $\underline{C}HF—CF_2$ groups) is the second most important peak, accounting for 26% of the total carbon 1s photopeak. The contribution of the FC6 peak, assigned to CF_3 groups, is small for CF_4-plasma-treated fibers: 5% compared with 14% for CHF_3-plasma-treated fibers. The carbon 1s spectrum of CHF_3-plasma-treated fibers is characterized by four remaining peaks of almost equal intensity: FC1, FC2, FC4 and FC5. Each peak corresponds to about 19% of the total spectrum.

The origin of the fluorine on the CF_4 and CHF_3 plasma-treated fibers is not the same for both plasmas. The CF_4 plasma is a strong etching plasma in which very little plasma polymer is formed.[24,25] The fluorine detected on the surface of the carbon fibers results from the direct fluorination of the fibers by fluorine atoms produced in the plasma. The CHF_3 plasma, by contrast, is characterized by a higher plasma polymer deposition rate and the fluorine detected in the fibers comes mainly from the fluorocarbon deposit. Support for the origin of the fluorine on the fibers is provided by a model study on chrome plates. XPS analysis at angles of 15° and 90° of chrome plates after a 2 min. CHF_3 plasma showed no trace of oxygen or chromium. The only elements detected were carbon and fluorine with atomic concentrations of about 33% and 67%, respectively, at both angles of analysis. These results indicate that a polymeric layer was deposited from the CHF_3 plasma onto the chrome plates. Chrome plates were also treated in a CF_4 plasma. The fluorine 1s spectrum obtained at a take-off angle of 15° was curve fit into two peaks at 685.5 eV and 688.8 eV corresponding to inorganic and organic fluorine, respectively. The organic fluorine comes from the formation of a plasma polymer, and the inorganic fluorine is due to the direct fluorination of the chromium oxide layer covering the surface of the chrome plates. The chromium $2p_{3/2}$ photopeak appears at a binding energy of 578.9 eV, indicative of partial fluorination of the oxide.

Fiber-Matrix Adhesion

Figures 4 and 5 show that the debonding load is independent of the droplet embedded length as previously observed.[17] Consequently, the average values of the debonding load are used as a measure of the fiber-matrix adhesion.

PES Matrix The average values (± 1 standard deviation) of the IM7 fiber-quenched PES debonding load are shown in Figure 6 for the various fiber surface treatments. Data pertaining to air and ammonia plasma treated fibers[17] are also reported in Figure 6 for comparative purposes. The strongest adhesion is obtained for ammonia and tetrafluoromethane plasma-treated fibers with debonding loads of 9.4 ± 0.8 g and 9.8 ± 1.0 g, respectively. An analysis of the variance at the 95% confidence level (ANOVA95)[26] shows that these values are statistically greater than that of as-received fibers (8.1 ± 0.8 g). The air plasma treatment improves the adhesion only moderately with a debonding load of 8.7 ± 1.0 g. The methane, ethylene and trifluoromethane

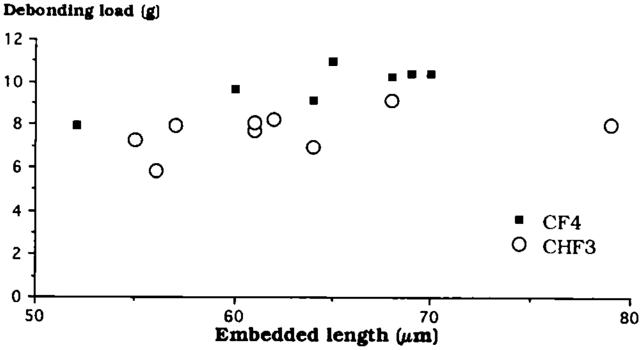

FIGURE 4 Debonding load *versus* embedded length for CF_4 and CHF_3 plasma-treated IM7 carbon fibers and quenched PES droplets.

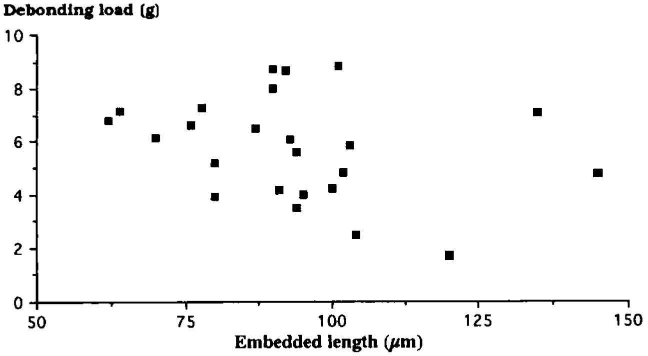

FIGURE 5 Debonding load *versus* embedded length for as-received IM7 carbon fibers and epoxy droplets.

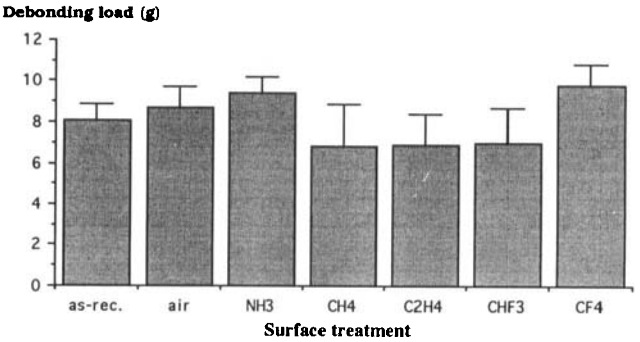

FIGURE 6 Debonding load of IM7 fiber-quenched PES samples for various fiber surface treatments.

plasma treatments gave the poorest adhesion with debonding loads of 6.8 ± 2.1 g, 6.9 ± 1.5 g and 7.0 ± 1.7 g, respectively. In addition, the values obtained with these three treatments are affected by a greater scatter than those of the other treatments.

There seems to be no obvious correlation between the surface chemical composition of the fiber and its adhesion to PES. However, the plasma treatments that have an etching effect (air, ammonia and tetrafluoromethane) do improve the fiber-matrix adhesion. This observation is in agreement with the interpretation of Drzal *et al.*[15] who proposed the following two-step mechanism for an oxidation surface treatment: step 1- removal of a "weak boundary" layer, followed by step 2- a surface oxidation. Our results seem to indicate that the improvement of the adhesion between IM7 carbon fibers and PES is due mainly to the removal of a contamination layer of adsorbed hydrocarbons from the surface of carbon fibers. These carbon fibers very likely have had the original weak boundary layer associated with the as-carbonized fibers removed by a standard proprietary surface treatment.

This interpretation can be extended to the decreased debonding load results of the methane, ethylene and trifluoromethane plasma-treated fibers in comparison with the as-received fibers. The standard explanation would be that the films which are deposited on the fibers decrease the non-dispersive component of the surface energy, thus decreasing the adhesion. However, it is also possible that these films act as a new "weak boundary layer," for lack of a better term. Further evidence supporting this explanation was found in experiments performed with epoxy/fiber samples presented later in the paper.

Following this approach, another interpretation is proposed to explain the adhesion improvement observed by Bascom and Chen[12] and by Yuan *et al.*[13] between carbon fibers and various thermoplastic matrices after plasma treatment. These authors argued that the adhesion improvement was due to the oxygen surface functionalities. The present results suggest that the etching effect of the plasma is the principal cause of the bond strength increase and the oxygen functional groups are merely a side effect. The apparent relationship between fiber surface oxidation and the bond strength reflects the greater ablative character of the oxygen plasma compared with the argon, nitrogen and ammonia plasmas.

The tetrafluoromethane plasma treatment gave a low sample testing success rate. More than 60% of the specimens that were tested would break instead of debond. This observation highlights an obvious but important limitation to the microbond pull-out test. The test cannot measure the adhesion between a fiber and a matrix when the load required to debond the droplet exceeds the strength of the single filament.

Fibers treated for 15 sec. in both air and ammonia plasmas from the previous study[17] and for 2 min. in a tetrafluoromethane plasma were aged for one week at 50°C and 80–90% relative humidity. Figure 7 shows that the debonding load of humid-aged, quenched PES samples prepared with plasma-treated fibers was approximately equal to 7.5 g. This value is not statistically different from that of quenched samples made with as-received fibers, regardless of aging conditions. During the humid-aging water is assumed to have diffused through the small PES droplet to the interface. If bond weakening resulting from moisture ingression was due essentially to an interface effect, it would be expected that the adhesion loss would have been greater for the samples made with air and ammonia plasma-treated fibers than those made with

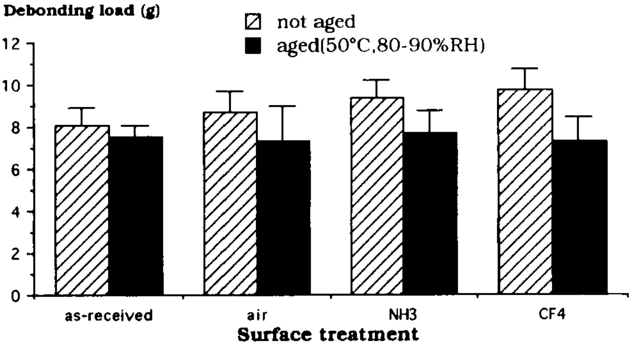

FIGURE 7 Comparison of the debonding loads between humid-aged and unaged quenched PES samples for IM7 carbon fiber surface treatments.

tetrafluoromethane plasma-treated fibers. The tetrafluoromethane plasma-treated fibers should be less hydrophilic than the air and ammonia plasma-treated fibers that have a large non-dispersion term. The results reported in Figure 7 indicate an equally low debonding load for all humid-aged samples, regardless of the surface treatment. This result strongly suggests that the adhesion of PES to carbon fibers for humid-aged samples is controlled by the matrix. The water absorption of PES, when immersed in water for 24 hours at 23°C, is 1.8%.[27] The producer of PES also indicates a volumetric expansion of 0.15–0.3% due to water absorption. This dimensional change explains, at least qualitatively, the lower debonding loads observed for humid-aged samples and suggests that mechanical clamping plays a significant role.

Following Di Landro and Pegoraro,[28] the adhesion between IM7 carbon fibers and PES is attributed to the differential thermal shrinkage of fiber and matrix. A concentric cylinder model was used to calculate the clamping stress due to thermal contraction of PES on IM7 carbon fibers. In this case, $\Delta T = -200°C$ and the matrix radius is set at 20 µm. The calculation leads to a compressive radial stress (P) of about 20 MPa. The coefficient of friction (μ) can be calculated from the relation

$$\tau = \mu P$$

where τ is the shear stress at the interface. A coefficient of friction of 3.7 was calculated for quenched PES on as-received IM7 carbon fibers. This value is greater than the value of 1.55 obtained by Di Landro and Pegoraro for a high-strength carbon fiber/PES system. The difference between these two values of coefficient of friction is due to the value chosen for the interfacial shear strength (τ). A τ value of 74.3 MPa was calculated for quenched PES on as-received IM7 carbon fibers that gave an average debonding load of 8.1 g for an embedded length of 63 µm. Di Landro and Pegoraro[28] obtained a τ value of 23.5 MPa from the fragmentation test. In any case, the large value of the coefficient of friction suggests again that the clamping stress plays a significant role in the bond strength.

Epoxy Matrix The bar graph in Figure 8 compares the debonding load of IM7 carbon fiber-epoxy samples with that of IM7 carbon fiber-PES quenched samples.

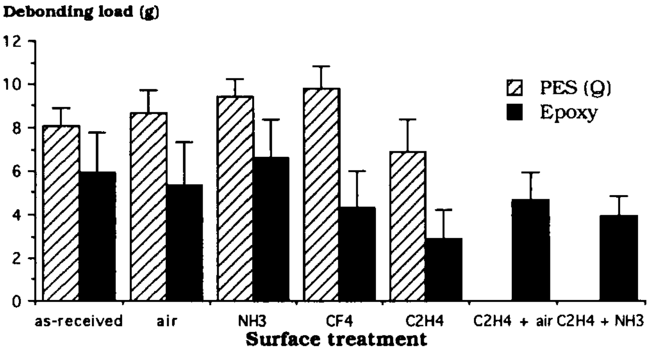

FIGURE 8 Debonding load of IM7 carbon fiber-epoxy samples compared with IM7 carbon fiber-quenched PES samples.

Results for 15 sec. air and ammonia plasma-treated fibers are indicated for comparative purposes. The epoxy samples are characterized by a larger scatter in the data, compared with the corresponding PES samples. The debonding loads of the epoxy droplets are lower than those of the PES droplets and the difference is particularly dramatic in the case of tetrafluoromethane plasma-treated fibers. The 15 sec. air and ammonia plasma treatments had no effect on the fiber-epoxy adhesion when compared with as-received fibers. The lowest debonding load was obtained for ethylene-plasma-treated fibers: 2.9 ± 1.3 g. This low value is not too surprising since ethylene-plasma-treated fibers are coated with a hydrocarbon layer that has little affinity for chemical interactions with the epoxy matrix.

A subsequent 15 sec. air or ammonia plasma treatment on the ethylene-plasma-treated fibers improved the adhesion with debonding loads increasing to 4.7 ± 1.2 g and 3.9 ± 0.9 g, respectively. The subsequent air plasma treatment tripled the surface oxygen atomic concentration and quadrupled the nitrogen concentration, when compared with the ethylene plasma treatment alone. Similarly, the complementary ammonia plasma treatment increased the oxygen concentration by 50% and the nitrogen concentration almost eight times. There seems to be a relationship between these large changes in surface composition and the adhesion improvement resulting from the secondary plasma treatment of ethylene-plasma-treated fibers. These results suggest that the surface chemical composition resulting from plasma treatments does play a role in the adhesion between IM7 carbon fibers and an epoxy matrix. However, surface chemical composition alone cannot explain the adhesion results. The tetrafluoromethane plasma treatment and the combination ethylene/air plasmas give similar debonding loads (4.3 ± 1.7 g in the former case), even though the fiber surface chemical compositions are very different.

The comparison of ammonia and tetrafluoromethane-plasma-treated fibers shows clearly that a chemical effect is involved in the case of an epoxy matrix. Both the ammonia and the tetrafluoromethane plasmas were etching plasmas but only the ammonia plasma introduced chemical groups, namely, nitrogen containing moieties, susceptible to react chemically with the epoxy resin. The ethylene/ammonia plasma combination did not give better results than the ammonia plasma alone because, in the former case, the subsequent ammonia plasma did not remove completely the hydrocarbon layer that could act as a "weak boundary layer". In spite of the large nitrogen surface atomic concentration introduced by the ethylene/ammonia plasma combination compared with the ammonia plasma alone, the latter treatment gave the strongest adhesion. These results emphasize the importance of the removal of a "weak boundary layer", in this case the deposited hydrocarbon layer, as the dominant effect in the fiber-epoxy adhesion.

SUMMARY

The adhesion of polyethersulfone to carbon fibers was measured by the microbond pull-out test and compared with the adhesion of an epoxy resin to the same fibers. No significant relationship was found between the fiber surface chemical composition and adhesion to PES. However, plasmas with a strong ablative character, such as the tetrafluoromethane and the ammonia plasmas, did improve fiber-PES adhesion. Plasmas which deposited layers of hydrocarbon or fluorocarbon gave the poorest adhesion. The study of the fiber-epoxy adhesion was useful in showing that, in the case of a reactive matrix, the surface chemical composition of the fibers did affect the adhesion. This chemical effect could be detected by the microbond pull-out test. However, the chemical effect was secondary to the "cleaning" effect of the surface treatment. These results support the two-part mechanism proposed by Drzal *et al.*[15] Current results showed that, in the case of a thermoplastic matrix, the chemical effect is minimal and that the adhesion improvement resulting from a fiber surface treatment is essentially due to the cleaning effect of the treatment.

Acknowledgements

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