Plasma Surface Treatments on Carbon Fibers. II. Mechanical Property and Interfacial Shear Strength

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SYNOPSIS

Carbon fibers are surface treated by oxygen, argon, and styrene plasma to study the effects on fiber strength and interfacial shear strength with PPS resin. Interfacial shear strength between carbon fiber and high melting temperature thermoplastic resins is successfully measured with the microbond pull-out test with the help of scanning CO_2 laser beam which solved the difficulties in preparing PPS microspheres. Tensile tests show that etching by oxygen plasma and deposition with plasma–PS increase strength of the fibers in some cases. ESCA spectra deconvolutions demonstrate that the improved interfacial strength is strongly related to the hydroxyl, ether, or aromatic groups on the surface. On the other hand, hydrocarbon segments are detrimental to the interface. Surface area and roughness have little influences on the interfacial strength of carbon fiber/PPS composites.

INTRODUCTION

The properties of the fiber and matrix make critical contribution to the overall performance of fiber-reinforced composites. Hence, one approach to enhance composite performance is to improve the properties of the constituents of the composites. In addition to the material property requirements of the fiber and matrix, composite behavior is also governed by the chemical–physical interactions occurring at the fiber–matrix interface and encompassing interphase.[1]

Various surface treatments[2-8] were reported to improve the fiber/matrix adhesion, mechanical properties, interfacial shear strength, and toughness. However, they are mostly restricted to epoxy-based composites. Although some works are attributed the fiber/thermoplastic matrix adhesion to mechanical interlocking,[5,9] there is insufficient evidence to characterize it.

Interfacial shear strength (IFSS) is a reliable quantitative index of the adhesion between fiber and matrix. Although transverse compression, double

cantilever beam (DCB), and other flexural tests have been widely used to measure the interlaminar shear strength (ILSS) of the composites,[6] single filament composite (SFC)[1,8-13] and microbond pull-out test,[14-17] are more effective due to the direct measure of IFSS of the fibers and matrix. Up to now, most studies using the microbond pull-out technique are devoted to carbon fiber/epoxy composites. Some works studied glass fibers with low melting point thermoplastic materials (e.g., PP, PBT, PET, and nylon),[17] but the high performance thermoplastics (e.g., PEEK, PPS, PSF, PEI, etc.) have not been discussed yet. It is probably due to the difficulties in preparing the microspheres of the specimens.

In the present study, type I and type II carbon fibers were surface treated by oxygen, argon, and styrene gas plasma following the details described elsewhere.[18] The two-parameter Weibull distribution, with the help of maximum likelihood estimation,[19] analyzes the fiber tensile strength; student t-distribution facilitates the determination of the difference[20] (with 90% confidence) among individual sets of tensile measurements. Microbond pull-out tests measure the IFSS between carbon fiber and semicrystalline thermoplastic polymer, poly-(phenylene sulfide) (PPS). Carbon dioxide laser,

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because of its stability and even distribution of energy, is used successfully to melt PPS powders in specimen preparation. ESCA (electron spectrum for chemical analysis) probed chemical compositions of fiber surface and present some interesting relationships between IFSS and corresponding ESCA results.

EXPERIMENTAL

Materials

High modulus (M40) and high strength (T300) carbon fibers were purchased from Toray Co. PPS powders, grade P6, were supplied by Phillips Petroleum Co. Both materials were stored in electronic hygrometer below 45% RH.

Fiber Diameter Measurement

Single filaments are teased from the fiber tow, washed with trichloroethylene, and photographed by SEM. More than 60 filament diameters measured from SEM are averaged.

Mechanical Properties

Tensile tests of carbon fibers are performed from modified ASTM D3379-75 (1982) procedure. Single filament is glued to paper tabs on each end by cyanoacrylic adhesives. The tabs are connected with molten wax which melt with a soldering gun after being fixed in the grips of an Instron tester. The gauge length is held at 1 cm and the crosshead speed is 5 mm/min. The equipped microprocessor of the Instron tester automatically measured and displayed the load and strain data on the monitor.

Interfacial Shear Strength Measurement

The microspheres in microbond pull-out tests were prepared by dipping very few PPS powders surrounding the filament. After transferring them through a CO_2 laser beam, near spherical- or elliptical-shaped microsphere, as shown in Figure 1, coagulated around the filament. All procedures were monitored under an optical microscope. The embedded fiber length is measured under 600× magnification of optical microscope. The microbond test specimens are tested at room temperature by the same Instron machine mentioned above, but the crosshead speed is set to 0.5 mm/min. At least 50
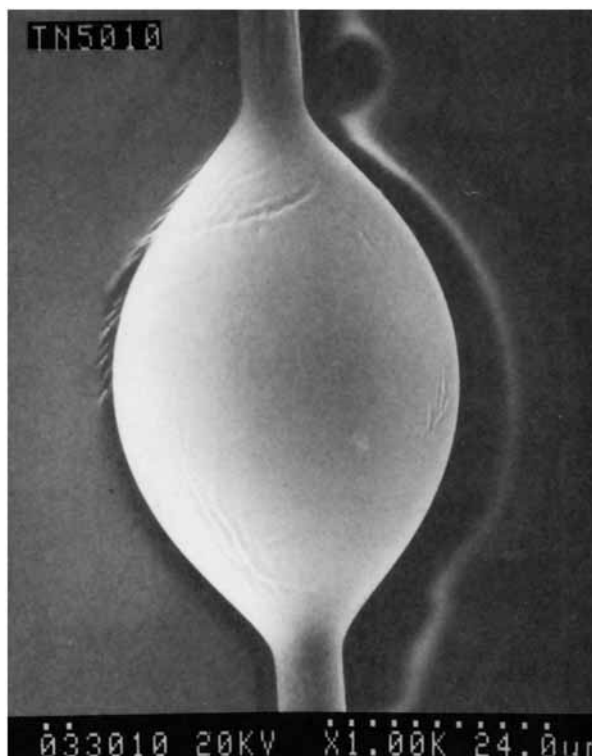

Figure 1 Microphotography of prepared microbond pull-out specimen.

successful data were averaged. Details of the microbond pull-out test can be found elsewhere.[14,15]

PPS Microspheres Preparation

In order to monitor the processing temperature of laser-irradiated PPS powders, 12.5 μm S-type thermocouple wires were jointed by acetylene–oxygen flame first, perforated into few PPS powders, and heated by scanner-attached CO_2 laser beam. An oscilloscope was used to record the thermocouple responses.

The PPS microspheres are characterized by differential scanning calometry (DSC), thermogravity analysis (TGA), mass spectrum (MS), and FTIR, respectively, to inspect the quality and structure of PPS before and after the CO_2 laser radiation.

ESCA Analysis

All procedures of the ESCA analysis are the same with the previous paper.[18] C_{1S} spectra deconvolutions were adopted to analyze chemical states of surface carbon atoms.

Table I Tensile Strength and Diameters of Untreated Carbon Fibers

	Tensile Strength (GPa)		Diameter (μm)	
	M40	T300	M40	T300
This study	2.79	3.34	6.80	7.15
Manufacture	2.75	3.53	6.50	7.00

RESULTS AND DISCUSSION

The measured average diameters are slightly larger than manufacturer's,[21] as Table I shows, but the differences are small. They are treated as cylindrical since the fibers have rather symmetric cross sections. No differences in diameters were observed for the plasma treatments.

Tensile Strength

The tensile strength of untreated fibers measured in this study are listed in Table I; the data from the manufacturer's are also included for comparison.

The differences are less than 5%, which is quite small considering the fact that both test methods and crosshead speed are different.[21] Typical load–displacement curves of tensile tests are shown in Figure 2.

Oxygen Plasma Treatments

M40 fibers treated with oxygen plasma resulted in strength reductions by most treatments but it recovered (as shown in Fig. 3a and Table II) with 50 W/20 min treatment. Some mechanisms are proposed to explain the strength reduction of carbon fiber.[5,22,23] The strength reductions are common,[24-27] although other studies had different results.[4,28]

Because the two-parameter Weibull distribution effectively analyzes the fiber strength,[10,12,28-31] the shape parameter α and scale parameter β of it are listed in Table II for untreated and surface-treated fibers. The shape parameter α is an index of flaw frequency distribution[28] or strength data scattering[29] of the fibers; larger α indicates better fiber performance and quality. The scale parameter β will not be discussed here because this normalizing factor does not represent any physical quantity.[32]
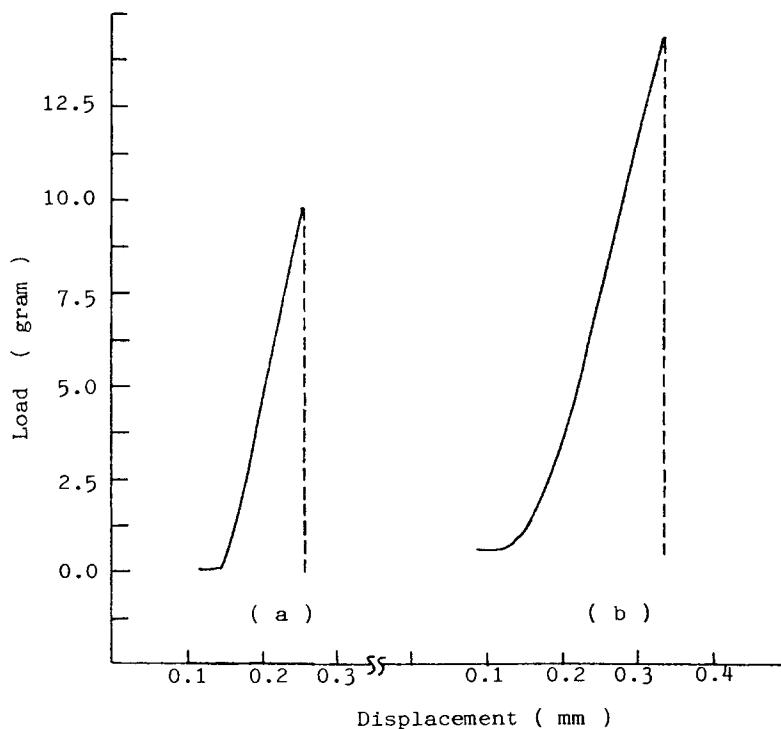

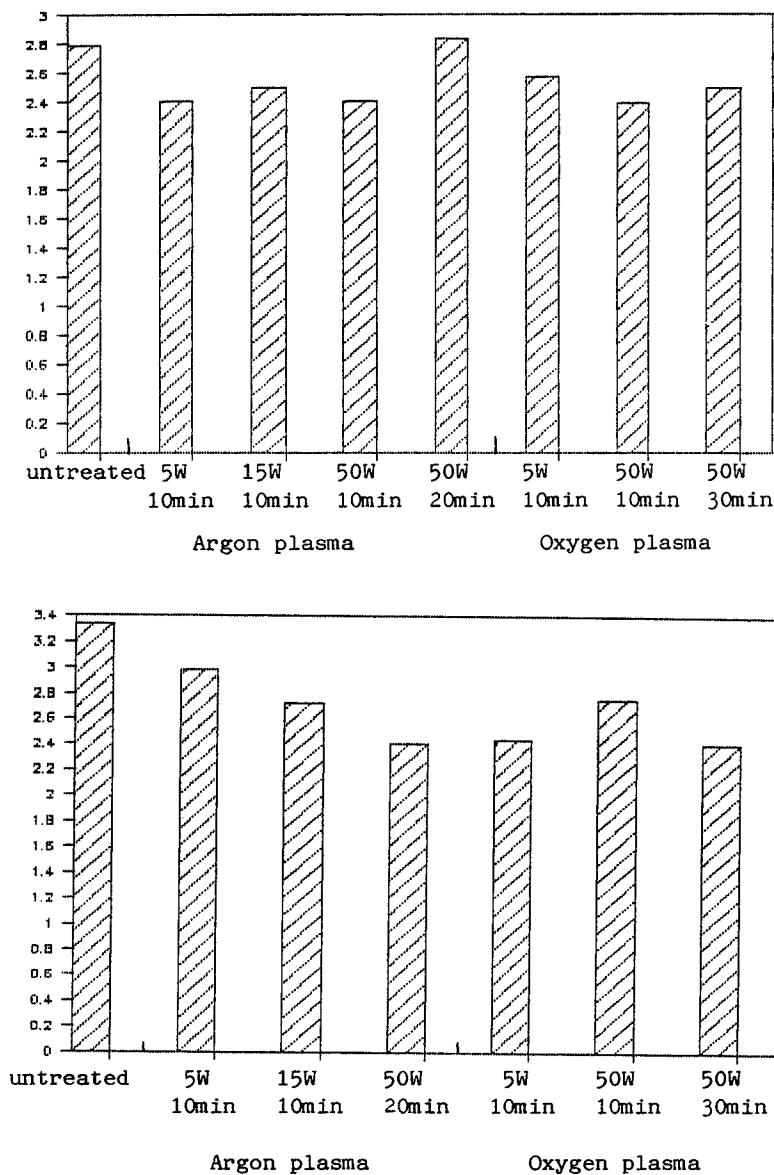**Figure 2** Typical load–displacement curves of single filament tensile strength tests: (a) M40; (b) T300.

Figure 3 Tensile strength histograms of carbon fibers treated with oxygen and argon plasma: (a) M40; (b) T300.

Of the same strength, the α of 50 W/20 min treated M40 fibers are larger than untreated fibers. It means that treated fibers have better quality and less flaws distributed. Nonetheless, low α values are always accompanied with low strength. It is worth noting that fibers treated in 50 W/10 min plasma field have very high α value and the least strength scattering, as the standard deviation revealed. The weak surface layer of M40 fiber has been etched completely at this time[18]; the major defects are those flaws of inner structure.[31,33] As the basal planes and edges of the graphite crystallites are attacked by the plasma ions, the three-dimensional graphite structures, which are weaker in strength, are attacked first, and are peeled off layer by layer.[5] The remaining structures are more sound than the original sheath. Studies of Takahagi and Ishitani[34] and Ishida et al.[35] showed the graphite structures had somewhat changed by the plasma treatments. The structure beneath the surface is thus attacked by the plasma ions but the flaws are unobservable by the SEM. At the end of 50 W/20 min treatment, M40 fibers have sustained sufficient intensities of plasma ion bombardments to cause microcrevices.

Table II Tensile Strength and Weibull Parameters of Oxygen and Argon Plasma-Treated Carbon Fibers

	Mean (GPa)	Standard Deviation	α	β
M40 (untreated)	2.79	0.41	7.92	2.970
Oxygen				
5 W 10 min	2.41	0.33	6.50	2.612
15 W 10 min	2.50	0.26	7.75	2.605
50 W 10 min	2.41	0.11	16.2	2.406
50 W 20 min	2.83	0.28	8.64	2.895
Argon				
5 W 10 min	2.57	0.29	8.04	2.632
50 W 10 min	2.39	0.20	11.25	2.450
50 W 30 min	2.49	0.24	5.13	2.305
T300 (untreated)	3.34	0.287	13.58	3.465
Oxygen				
5 W 10 min	2.98	0.39	6.80	3.143
15 W 10 min	2.73	0.37	6.51	2.823
50 W 20 min	2.41	0.33	7.96	2.553
Argon				
5 W 10 min	2.44	0.24	6.99	2.585
50 W 10 min	2.75	0.42	6.31	2.860
50 W 30 min	2.41	0.21	6.43	2.613

These interior flaws and fiber core defects[33] are all responsible to the strength scattering in spite of the fact that the remaining fiber structures are stronger.

T300 fibers treated at the same conditions had dissimilar performances. Higher power of plasma environment results poorer fiber strength (Fig. 3b), although the α values increase. Plasma etching of the fiber surface has not scratched the outward weaker structures completely; thus the tensile strength is affected by the appearances of dual-type flaws.[21,22]

Higher plasma power produces more energetic ions which bombard the graphitic structure to cause sterner damages to the surface. The surface structure are hurt more as treating time increased, too. Therefore, more injured fibers result from higher plasma power or longer treating time, as seen in Table II.

The tensile strength of oxygen plasma-treated T300 fibers decreased 11–28% and the α values were also reduced. On the contrary, M40 fibers are less weakened and with smaller value variations with the same treatments. It is caused by the lower processing temperature of T300 fibers in manufacturing cycles and less perfect graphite crystallite structure in it so that energetic plasma ions remove T300 fiber surface structure more easily.

Argon Plasma Treatments

M40 fibers treated with Ar plasma have lower tensile strength, too. An interesting comparison revealed that the highest α value still occurs at the 50 W/10 min treatment. Both situations caused the same fiber strength, and they are the lowest within individual series. The indentions on the Ar plasma-etched surface[18] are suspected to limit the fiber strength since the indentions are of the same size which is necessary to have a high α value.

The strength of T300 fibers are also lowered with the argon plasma treatment. Unlike M40 fibers, T300 fibers with 50 W/10 min treatment have the least amount of strength reduction. Comparisons made between oxygen and argon plasma show the small strength variations and like appearances.[18] Hence, plasma gas source has little effect on the fiber quality with 50 W plasma-treated T300 fibers.

Styrene Plasma Treatments

The plasma-polymerized polystyrene (plasma–PS) film deposited on the fiber surface modifies the morphologies of them. The mechanical properties are shown in Figure 4 and the Weibull parameters are listed in Table III. Long treating time of low power plasma weaken M40 fibers, but it is beneficial to 25 W power plasma. With low powers of plasma treatment, plasma–PS formed small particles on the fiber surface[18]; they were not strong enough to mend the crevices of the fibers. Therefore, the stress transmission still failed, and low α values are plausible. The strength of T300 fibers are also reduced with lower plasma power treatments. The only difference is seen at the short treating time. In the beginning, plasma–PS adhered quite well on T300 fiber surface due to their high surface energies. These plasma–PS healed the microcrevices of the fibers[36] and caused the recovery of fiber strength. Further plasma–PS deposition is concentrated on the concave grooves, resulting in strength decrease, as the M40 fibers.

It is seen that, in the 25 W plasma field, both M40 and T300 fibers get stronger when the treatment proceeded for 30 min. Ions generated by the higher power possess more kinetic energy to attack the polymer film. Though the propagation rate may be equal, these films are packed denser by the attacks and behave stronger. These highly crosslinked plasma–PS films not only initially healed the surface flaws but also transmit the stress.[10] Drzal et al.[37]
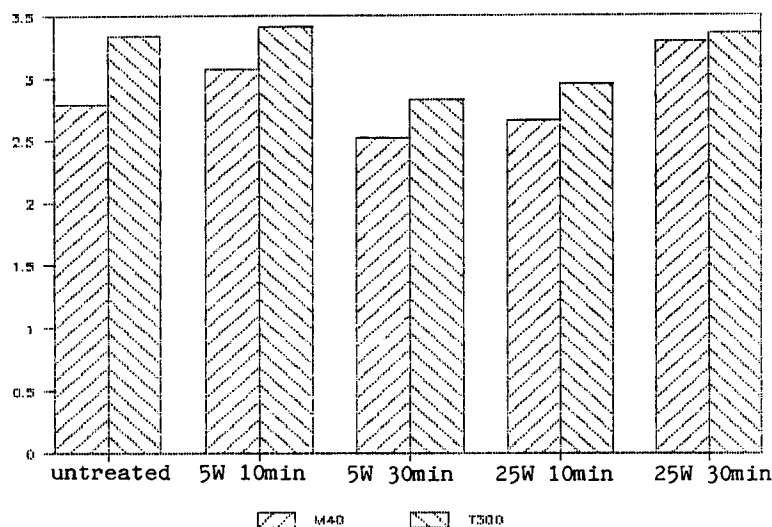
Figure 4 Tensile strength histogram of plasma–PS deposited carbon fibers.

noted the same effects in epoxy-based sizings of carbon fibers.

An interesting fact can be pointed out that the strength of 25 W/10 min treated M40 and T300 fibers happens to be between those of 5 W/30 min and 25 W/30 min treated fibers. From the viewpoint of degree of crosslinking, it is natural to have films of intermediate properties with 25 W/10 min treatment. A further increase in plasma power lowered the strength again since there were vital larger particles adhered on the surface.[18]

Interfacial Shear Strength

S-type thermocouple response curve of CO_2 laser radiation (Fig. 5) showed that PPS is far from decomposition; thermogravity analysis (TGA) confirmed it, too. On the other hand, PPS microspheres analyzed by mass spectroscopy (MS) and FTIR displayed the same structure after the irradiation except that DSC thermograms (Fig. 6) indicate the amorphous structure of the microspheres because they were quenched instantaneously when the laser beam turned down.

If the fiber embedded length is large enough such that the shear stress transferred through the interface surpassed the strength of fibers, fibers will break before they are pull out from microspheres. Therefore, microspheres of 50–90 μm in size are carefully prepared to avoid the failure. However, some other sizes were reported elsewhere.[14,15,17] The representative curves of pull-out tests are shown in Figure 7 and the results are tabulated in Table IV. M40 fibers

have better IFSS when etched by oxygen and argon plasma. Fibers deposited by plasma–PS film are worse in IFSS than the untreated fibers. There are no advantages of longer treating time or higher power with the IFSS values although the surface become smoothed. It is seen, from the table, that those fibers treated with 5 W/30 min, 25 W/20 min, and 25 W/30 min styrene plasma had different shear strength, even though they all have smooth surface. The surface area of fibers can be varied with surface roughness, but this variation is of little importance[6,38,39] to the fiber/matrix interfacial strength. Examinations of IFSS values and morphologies show that no relationships exist between them, which is true for plasma-treated carbon fibers.

Table III Tensile Strength and Weibull Parameters of Plasma–PS-Deposited Carbon Fibers

	Mean (GPa)	Standard Deviation	α	β
M40 (untreated)	2.79	0.41	7.92	2.970
5 W 10 min	3.07	0.29	11.78	3.200
5 W 30 min	2.52	0.20	5.00	2.580
25 W 10 min	2.65	0.31	7.81	2.679
25 W 30 min	3.29	0.30	8.80	3.306
T300 (untreated)	3.34	0.287	13.58	3.465
5 W 10 min	3.41	0.43	9.67	3.590
5 W 30 min	2.83	0.42	7.01	2.966
25 W 10 min	2.95	0.34	6.47	2.938
25 W 30 min	3.36	0.32	9.68	3.450

y-axis label: volts
x-axis top label: .10000E 0
y-axis bottom labels: .00000E 0, .00000E 01

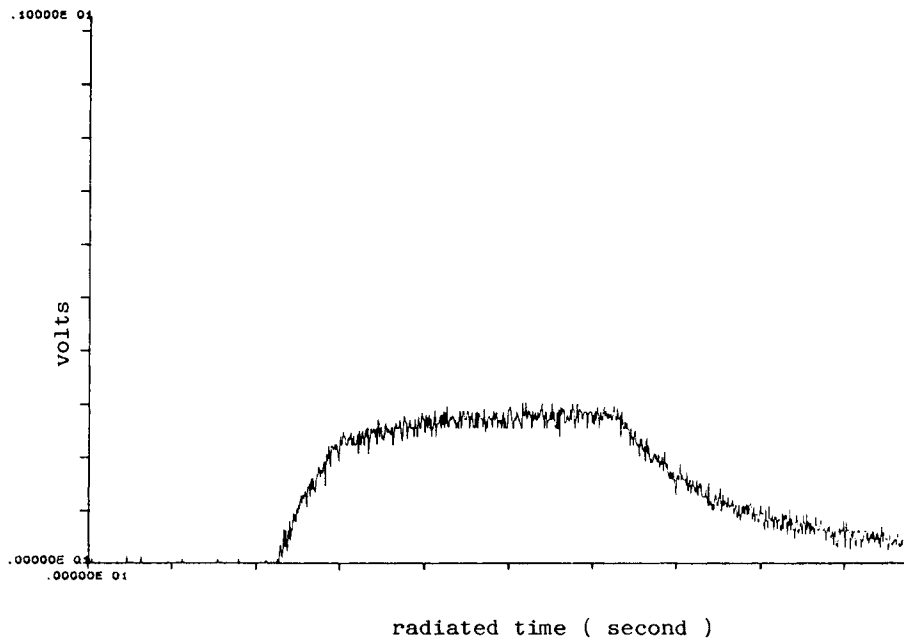radiated time (second)

Figure 5   S-type thermocouple response curve of PPS powders irradiated by carbon dioxide
laser.

T300 fibers have the same trends of decreasing IFSS with 25 W treated fibers. Again, morphology has no effect on IFSS in this case. The IFSS values show that the T300/PPS interfacial adhesion is stronger than M40/PPS whether they are plasma surface treated or not. Five watts for 10 min film deposited fibers have the most enhancement of IFSS. The higher IFSS of T300/PPS is attributed
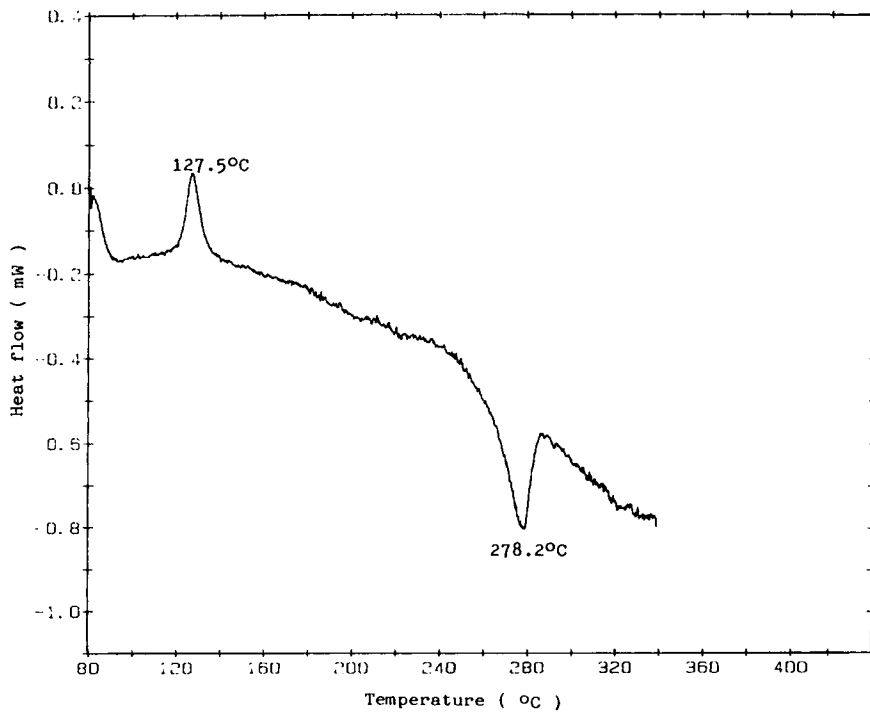

y-axis label: Heat flow (mW)
Peak label: 127.5°C
Peak label: 278.2°C
x-axis label: Temperature (°C)

Figure 6   DSC thermogram of PPS microspheres. Heating rate: 10°C/min.
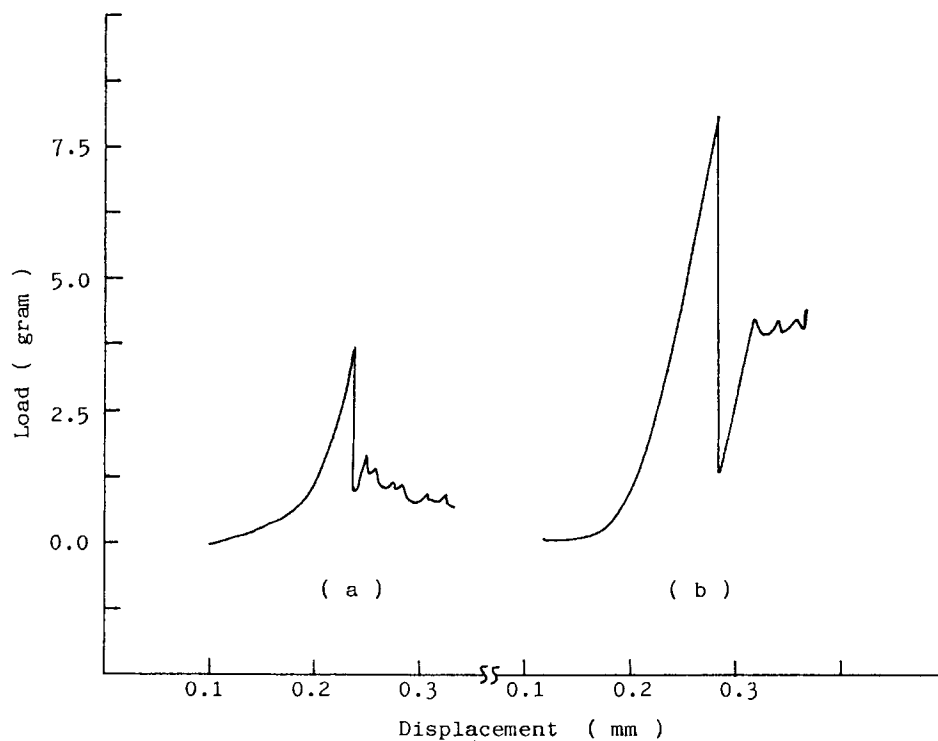
Figure 7 Typical load–displacement curves of microbond pull-out tests: (a) M40/PPS; (b) T300/PPS.

to the high surface energy[23] and the lower level of shear loading of perfect graphitized M40 fibers.[38] Photographs of the specimens elucidated better wetting of T300/PPS microspheres. Drzal et al.[37] showed IFSS differences between type I and type II carbon fibers with epoxy resins.

The interfacial adhesion between type II carbon

fiber/epoxy resin were measured, by microbond pull-out technique, within 50–70 MPa[14,15]; 25–35 MPa IFSS of glass fiber/PP, PET, and nylon resins[17] are published. No IFSS values were reported, to the authors' knowledge, with carbon fiber/PPS except the data of bulk carbon fiber/PPS composites that the interlaminar shear strength are around 70 MPa.[40,41]

Table IV Interfacial Shear Strength of Carbon Fiber/PPS Microbond Pull-Out Tests

	M40		T300	
	Mean (MPa)	Standard Deviation	Mean (MPa)	Standard Deviation
Untreated	18.27	4.20	33.1	7.73
Oxygen plasma				
50 W 30 min	24.40	6.62	—	—
Argon plasma				
50 W 30 min	30.60	9.26	—	—
Styrene plasma				
5 W 10 min	14.56	2.61	43.45	6.48
5 W 30 min	14.95	2.69	31.28	6.62
25 W 10 min	13.29	4.14	36.01	5.63
25 W 20 min	12.50	2.60	33.14	5.75
25 W 30 min	12.35	2.66	29.50	11.00

However, we should keep in mind that it is dissimilar in meaning to the IFSS of microbond tests.

Surface Chemistry

The results of ESCA surface chemistry are listed in Table V. The aromatic carbon atoms of plasma–PS film are assigned to those having 283.3–283.7 eV binding energies, which is the C_{1S} spectrum of PPS resin. Carbon atoms of hydrocarbon states are also found on the film surface.

Plasma-treated M40 fibers were more oxidized (higher O/C ratio) in surface than the untreated. Considering both the IFSS values and O/C ratios of fibers, it can be found that high IFSS is not solely determined by high O/C ratio, as evident from the comparisons between argon plasma-treated and plasma–PS film-deposited fibers.

C_{1S} spectra deconvolutions show the chemical composition variations on the film surface. Longer treating time of 5 W power had small differences in O/C ratios; 25 W power treated fibers varied in O/C ratios, hydroxyl groups, and hydrocarbon groups with varying treating time. Other differences, such as disappearance of aromatic groups and increased hydroxyl groups, are also observed since these variations have strong relationships with IFSS value changes.

All fibers etched by argon and oxygen plasma have better interfacial adhesion than the untreated fibers. The plentiful hydroxyl and ether groups on the sur-

face may be the main reason. A little lower IFSS of oxygen plasma-treated fibers, compared with argon-treated fibers, is caused by ether and hydrocarbon groups replacing the hydroxyl groups of argon plasma-etched fibers. All these descriptions seem to recommend that more hydroxyl groups, less hydrocarbon groups are necessary to raise the interfacial adhesion; aromatic groups are also necessary on film surface due to the compatibility between plasma–PS and PPS matrix.

With 25 W styrene plasma-treated T300 fibers, IFSS decreases are observed as the ether and hydrocarbon groups formed on the surface. Examinations of 5 W plasma-treated and untreated fibers also display the effects of hydroxyl and aromatic groups on the surface. The superiority of hydroxyl group within generated functionalities is also supported by the IFSS difference between 5 W/10 min and 25 W/20 min treated fibers since both have a similar O/C ratio and aromatic group contents.

Surface chemistry analysis may also partly resolve the causes of IFSS difference between T300 and M40 fibers since T300 fiber has more oxygen-containing functionalities on it.

It is agreed that crosslinking is one of the possible reactions in the curing of PPS.[42] The hydroxyl groups on surface are probably attracted by the sulfur atoms of PPS molecules or oxygen atoms of crosslinked PPS structures[43] through the hydrogen bonding so that enhancement of the interfacial strength between fiber and PPS matrix are achieved.

Table V   Surface Analysis Results of Carbon Fibers

	Aromatics	Hydrocarbon	Hydroxyl	Ether	O/C	
Untreated	0.00	0.661	0.226	0.113	0.334	M40 fiber
Oxygen plasma						
50 W 30 min	0.00	0.240	0.760	0.000	0.474	
Argon plasma						
50 W 30 min[a]	0.00	0.000	0.900	0.000	0.826	
Styrene plasma						
5 W 10 min	0.04	0.159	0.714	0.000	0.725	
5 W 30 min	0.20	0.000	0.800	0.000	0.693	
25 W 10 min	0.10	0.140	0.760	0.000	0.896	
25 W 20 min	0.00	0.286	0.714	0.000	0.714	
25 W 30 min	0.00	0.310	0.690	0.000	0.710	
Untreated	0.00	0.452	0.333	0.215	0.421	T300 fiber
Styrene plasma						
5 W 10 min	0.24	0.000	0.76	0.000	0.535	
5 W 30 min	0.34	0.000	0.66	0.000	0.421	
25 W 10 min	0.08	0.000	0.92	0.000	1.043	
25 W 20 min	0.17	0.000	0.00	0.830	0.525	
25 W 30 min	0.06	0.196	0.00	0.745	0.657	

[a] 10% carbon atoms in graphite state.

CONCLUSION

The microbon pull-out technique is successfully utilized in measuring the interfacial shear strength of carbon fiber and PPS matrix. Scanned CO_2 laser beam provides the processing feasibility of PPS microspheres. Plasma surface treatments cause fiber strength changes as well as interfacial strength variations. Although most tensile strength are decreased by the plasma treatments, some of them recovered or increased by oxygen plasma etching and plasma–PS film depositions. Interfacial strength measurements show that plasma–PS film deposition has some advantages to T300 fibers whereas M40 fibers prefer oxygen and argon plasma etching only. Surface analysis reveals the necessity of hydroxyl or ether groups and the superfluities of hydrocarbon segments on the fiber surface to improve interfacial strength. The data also illustrate the independency of morphological roughness with interfacial strength for plasma treated carbon fibers.

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