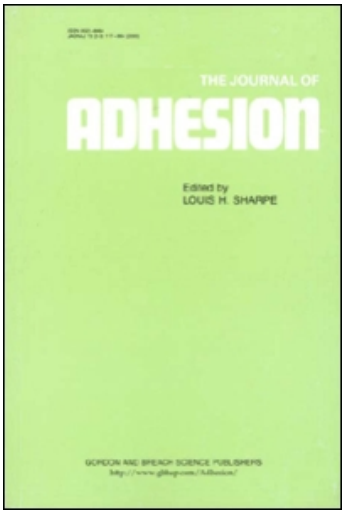

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Plasma Modified Polyaramid Fiber Surface and Fiber/Epoxy Interface*

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Kevlar-49® was surface-modified through cold air plasma treatment and plasma grafting of poly-acrylic-acid (PAA), polyethylacrylate (PEA) and their copolymer (PAA/EA). To evaluate the effect of modification, the single fiber pull out (SPFO) test was developed; at least three important physical quantities, G_i, F_{fr}/L and τ_o were obtained. For grafting with PAA/EA, G_i increased to 55 J/m^2 in comparision with 36 J/m^2 for Kevlar fibers with the sizing removed. The surface topography of fibers pulled from epoxy resin was studied by scanning electron microscopy (SEM).

KEY WORDS: Kevlar fiber; plasma treatment; surface grafting; poly(acrylic acid) (PAA); poly(ethyl acrylate) (PEA); poly(acrylic acid) -co-poly(ethyl acrylate) (PAA/EA); fiber/resin interface; SEM; XPS; single filament; surface morphology; failure mode.

INTRODUCTION

Poly(*p*-phenylene *tere*-phthalamide), PPTA, which is sold under the trade name Kevlar®by Du Pont, is a super performance fiber with high tensile strength, modulus and thermal resistance. Kevlar fiber is frequently used in composite materials as a reinforcing material. However, the high crystallinity of Kevlar-49 fiber leads to an inactive surface and poor adhesion between the fiber and the matrix. To overcome this problem, several modifications of aramid fiber have been attempted. Among these are surface roughening[1], the use of coating[2–4] and the introduction of reactive groups by either physical or chemical methods[5,6]. According to Eagles' results, the sized Kevlar fibers had the greater interfacial bond strength and frictional shear strength values for various matrix materials[7]. Wu[8] investigated polymer reactions, such as bromination followed by ammonolysis and nitration followed by reduction, on Kevlar-49 filament. In these reactions, significant concentration of primary amino groups (0.6 NH_2 per 100 Å^2) could be attained on filament surfaces without impairment of fiber tensile properties. Takayanagi[9] investigated the metalation of aramid fiber and Mercx used *N*-acrylation reaction to modify aramid fibers. Preliminary experiments had also shown that the presence of amino or epoxy

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groups on Kevlar fabric could provide remarkably improved peel strength and apparent interlaminar shear strength in epoxy laminates. Plasma treatment is another successful method. Wertheimer[10] investigated the effects of several types of microwave plasma, including non-polymer-forming plasma and polymer-forming plasma. Inagaki and coworker[11]combined plasma treatment and coupling agent treatment. They found that the combination process made the pull-out force of an aramid fiber/silicone rubber composite 2.5 times higher, compared with the plasma treatment or the coupling agent treatment alone. In this paper, Kevlar-49 was surface-modified through cold air plasma treatment and plasma grafting of polyacrylic acid (PAA), polyethylacrylate (PEA) and their copolymer (PAA/EA). Fiber surface properties were studied with XPS, while interface properties were studied with a developed single fiber pull-out (SFPO) test. The stated surface modifications evidently improved the interfacial adhesion and increased the interfacial fracture energy of the aramid/epoxy micro composite system.

EXPERIMENTAL

Materials

The fiber used was Kevlar-49 (from Du Pont Co.). For cleaning the fiber surfaces, the sizing was removed by extraction with ethanol and with water before plasma modification. Acrylic acid and ethyl acrylate (EA) of polymerization grade were distilled under reduced pressure before use.

Plasma Treatment and Surface Grafting

Kevlar-49 was wound onto a glass support after Soxhlet extraction in ethyl alcohol and water. Then the fiber was treated by air plasma in a CGP-2 plasma generator. Pressure in the generator was reduced to 15–20 Pa by controlling the flow rate of air. Plasma was generated at given output power and for a predetermined period of time. The surface-activated fiber was immersed in a pre-degassed 10% monomer solution of acrylic acid (AA) or ethyl acrylate (EA), or both of them, for grafting onto the surface of Kevlar-49 fiber. Water was used as solvent for AA; *t*-butanol was used as solvent for EA and water/*t*-butanol (1:1 by weight) was used as solvent mixture for AA/EA (1:1 by weight). The graft polymerization was effected by heating at 50–60°C for 1 h under nitrogen. After the reaction, the grafted fiber was washed with the solvent to remove the unreacted monomers and homopolymers. The amount of grafted polymer and their thickness were determined by the weight gain.

Single Filament Pull-out (SFPO) Test

The interfacial properties of Kevlar-49/epoxy were estimated from a single filament pull-out test. Figure 1 is a schematic of the specimen, prepared by the same method reported in our previous paper[12]. The E-51 epoxy was mixed thoroughly in stoichiometric proportion with the curing agent (triethylene tetramine). The epoxy

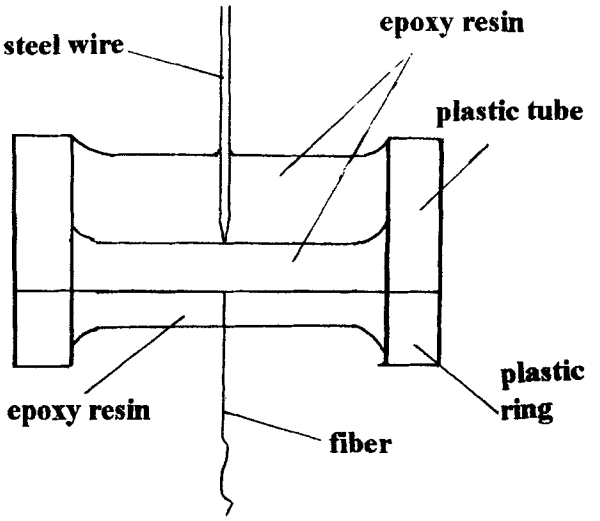

FIGURE 1 Schematic of a typical SFPO specimen.

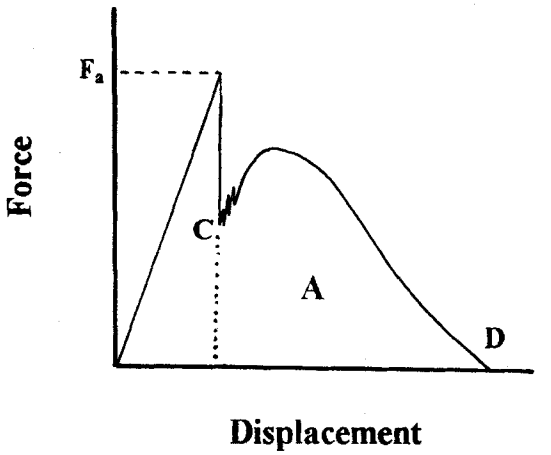

FIGURE 2 A typical load *vs.* displacement trace. (a) A cleaned Kevlar-49 fiber; (b) A plasma treated Kevlar-49 fiber (c) PAA grafted fiber; (d) P(AA/EA) grafted fiber.

resin was cured in the mold for 1 day at room temperature and was postcured for an additional 3 h at 50°C in an oven. A single fiber was pulled out from the embedding resin layer on a fiber strength testing machine, at a crosshead speed of 2 mm/min. A typical load *versus* displacement trace is shown in Figure 2. It may be shown that the force increases linearly with distance to a maximum value, F_a, at which the adhesion fails. The force falls, and subsequent pull out is controlled by the friction, which requires relatively little force. About 100 specimens were tested for each surface state.

Morphology

The morphology of the fiber surfaces was examined using a Hitachi S530 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The Surface Morphology of Kevlar-49 Fibers

Scanning electron micrographs are shown in Figure 3. It is seen that the surface of a cleaned Kevlar-49 filament is very smooth (Fig. 3a), and the plasma-treated fiber shows no features either (Fig. 3b). The rough surfaces of the grafted fiber indicate the existence of the modifier layer (Fig. 3c and d).

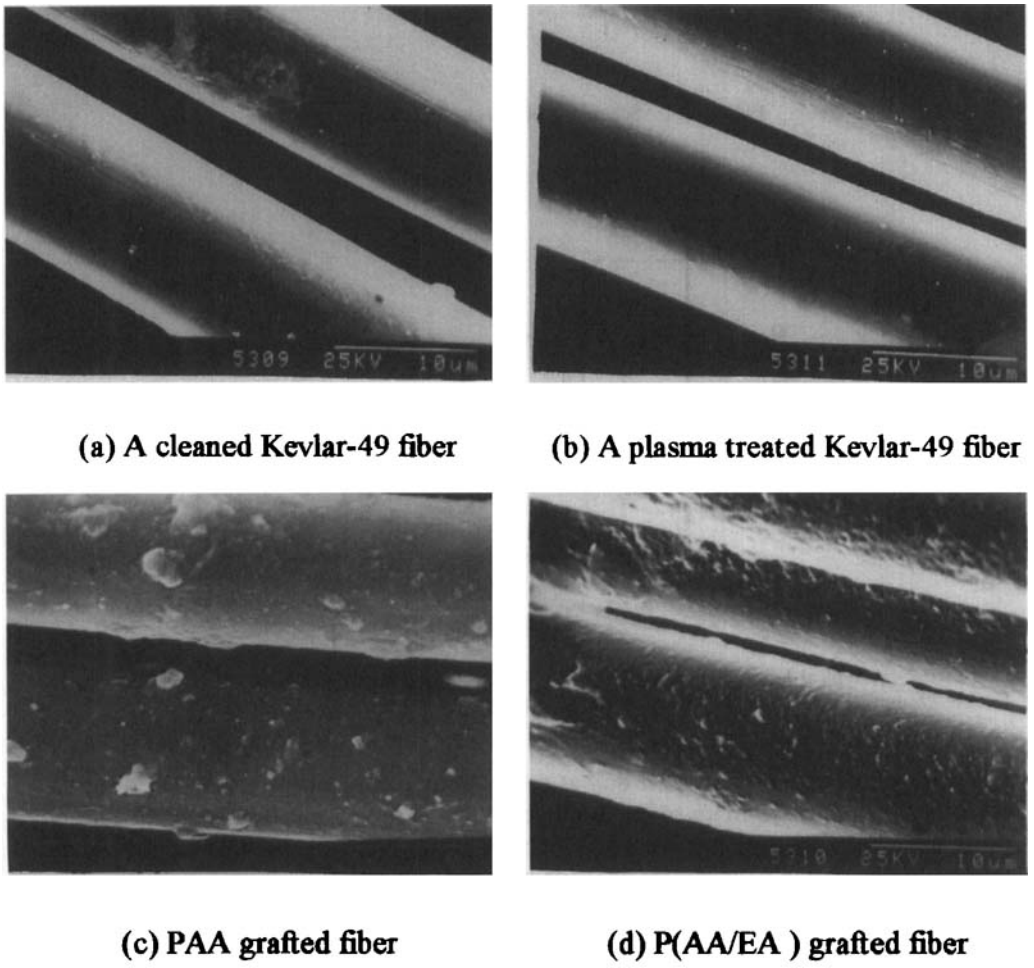

FIGURE 3 SEM photographs of Kevlar-49® fiber.

Chemical Structure of Modified Fiber Surface

Plasma treatment modifies fiber surface chemistry by reacting with fibers through abstraction of hydrogen in polymer chains, and by creating free radicals that later are oxidized into hydroxyl and carboxyl groups when exposed to air or initiate polymerization when exposed to monomer solution. An ESCA 750 of Shimadzu Co.Ltd. was employed to study the fiber surface. There are 5 peaks in the energy spectrum of photoelectrons generated from the initial fiber over 0 to 1000 eV binding energy, corresponding to O_{1s}, N_{1s}, C_{1s}, Si_{2s}, Si_{2p}, (Fig. 4). The unexpected appearance of Si_{2s} and Si_{2p} was attributed to organosilicon surfactant on the fiber surface. Both plasma treatment and plasma grafting change the surface chemistry of Kevlar-49 fiber. Energy spectra of plasma-treated and grafted fibers showed similar features to those of inital fiber except for decreases in the Si_{2s} and Si_{2p} peaks.

The XPS spectra provide additional information about the composition of the fiber surface (see Tab. I). The N/C and O/C atomic ratios calculated from the

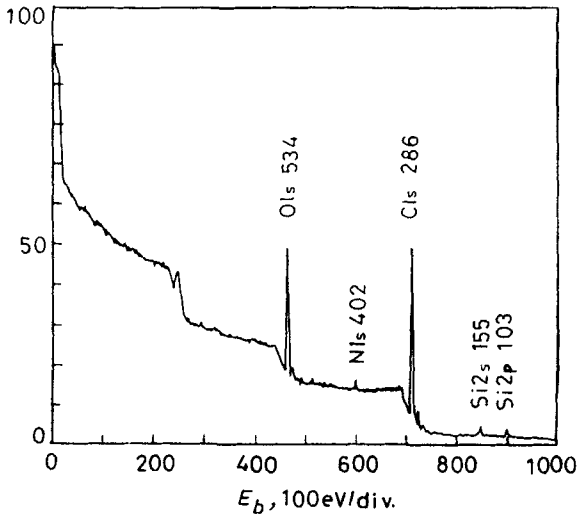

FIGURE 4 XPS spectrum of Kevlar-49 initial fiber.

TABLE I
Elemental composition of Kevlar-49® fiber surface

Kevlar-49	layer thickness	C	N	O	Si	N/C	O/C
calculated	initial	77.8	11.1	11.1	0	0.14	0.14
K-I	initial	73.6	1.83	20.5	4.12	0.03	0.28
K-P	plasma treated	75.4	5.23	16.4	2.97	0.07	0.22
K-C	cleaned	72.3	10.8	17.0	0	0.15	0.24
K-AA	PAA grafted 67 nm	69.1	10.8	20.1	0	0.16	0.29
K-EA	PEA grafted 65 nm	70.8	11.2	17.9	0	0.16	0.25
K-(AA/EA)	P(AA/EA) grafted 57 nm	71.3	10.4	18.3	0	0.15	0.26

chemical formula of PPTA are 0.143 and 0.143, respectively. The relative atomic composition as determined by the XPS measurement for Kevlar-49 original fiber is N/C = 0.03 and O/C = 0.28. The oxygen-rich layer at the surface arises from the organosilicon sizing. After cleaning to remove the sizing, the N/C of fiber surface is near to the calculated value, while the grafting of PEA, P(EA/AA) and PAA obviously increases the concentration of O. This can be understood from the much higher O/C ratio of 0.500 in PAA than that of 0.144 in Kevlar-49. Figure 5 shows the C_{1s} peak of the grafted fiber surface. The main peak is shifted and has a shoulder at 289 eV after plasma-grafting treatment, as compared with that of the initial fiber. The C_{1s} peak can be resolved into four component peaks: C—C and C=C at 285 eV, C—O at 287 eV, O=C—O at 289 eV and —(—C—C—)$_n$— at 283 eV. In the XPS spectra of plasma-grafted Kevlar fiber, the relative concentration of their four components assigned to carbonized carbon are summarized in Table II. All of these data verified that PAA, PEA or their copolymer did graft onto the fiber surface.

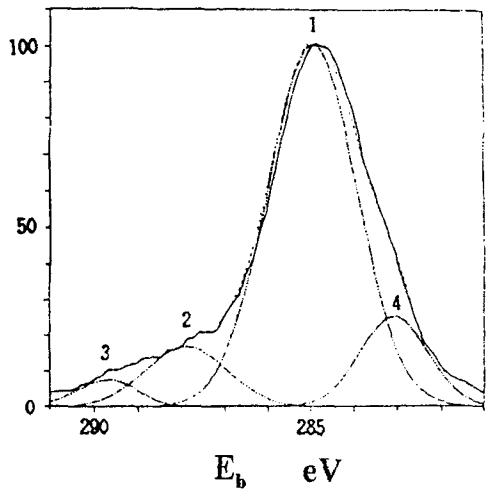

FIGURE 5 C_{1s} spectrum of PAA grafted fibers.

TABLE II
The relative concentrations of components in the C_{1s} peak

Kevlar-49	289	287.8	285	283
K-C	4.5	2.2	100	—
K-AA	6.2	15.2	100	15.8
K-EA/AA	7.1	12.1	100	15.3
K-EA	7.5	10	100	11.7

Development of SFPO Test

A micro-composite system was produced when a single filament was embedded in a E-51 epoxy resin disc, cured with triethylene tetramine. The pull-out test was carried out with different fiber embedded lengths in the epoxy resin. Generally, the shear strength of the interface, τ_a, is equal to $F_a/2\pi rL$ ($2r$, the diameter of fiber; L, the embedded length of fiber in epoxy matrix) and is taken as characterizing the adhesion strength of the interface without the fiber broken. However, it is not evaluated now as there was not a unique adhesion strength. A non-uniform shear stress distribution along the fiber embedded in a brittle epoxy matrix was found by theoretical analysis[13]. There is the shear stress concentration at the end of the embedded fiber under load. So, the maximum shear stress (or the stress of interface fracture), τ_o, is used as an important characterizing parameter. It can be obtained when $L=0$ by extrapolation of the plot of τ_a *vs.* L(see Fig. 6).

It is instructive to plot F_a *versus* L(0.5–1.2 mm) as shown in Figure 7. One can observe the rising region at low L and the region of apparently constant value, F_p, for higher L, *i.e.*, the pull out load, F_a, is independent of L. Such a plateau region is implied in the early work of Outwater and Murphy[14] and has since been widely cited as an important contribution to the work of fracture of a composite[15]. The process that gives rise to the plateau is a continuing interface fracture, involving an energy absorption, G_i, per unit fracture area. G_i is given by[16]:

$$G_i = F_p{}^2/2\pi^2 r^3 E_f$$

where E_f is the modulus of the fiber.

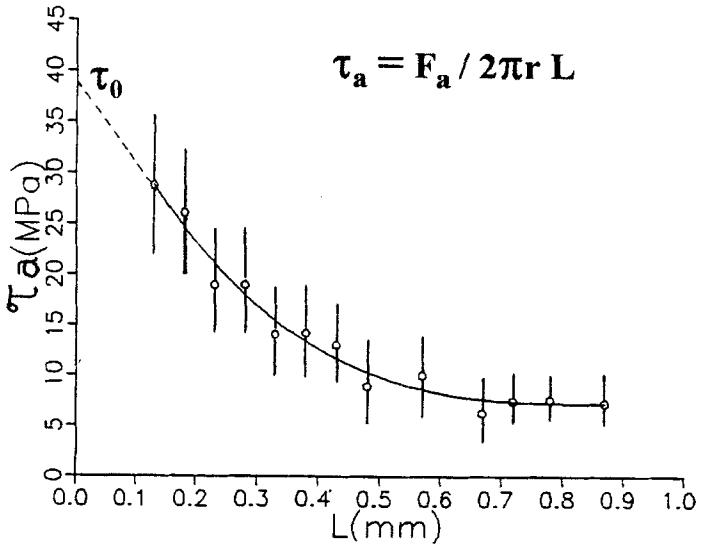

FIGURE 6 Plot of shear strength, τ_a, *vs.*embedded length, L.

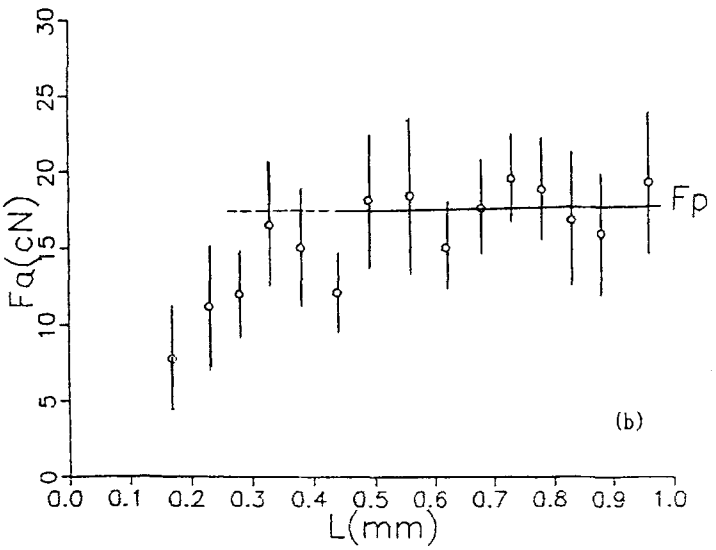

FIGURE 7 Plot of pull-out force *vs.* embedded length.

In Figure 2, from C to D is a fiber pull-out process after interfacial debonding. The force decreases with the distance pulled out in our test. So the curve from C to D reflects the external force required against pull-out friction and the area A under the CD curve is the work against friction, W_f. The pull-out friction has been discussed in detail by Piggott[17]. The calculation of friction work, W_f, is a very complex problem; many parameters such as the normal pressure, P, Poisson's ratio of fiber and matrix as well as the friction coefficient, μ,(combination of static friction and sliding friction) are important parameters that affect friction in the pull-out process. Based on some assumptions, the calculation of friction force, F_{fr}, is simplified as follows:

$$A = W_f = \int_0^L F_{fr} dL = \pi r P \mu L^2$$

$$F_{fr} = 2\pi r P \mu L$$

If W_f is plotted *versus* L^2, a straight line is obtained with a slope of $\pi r P \mu$ (see Fig. 8). As a characterizing quantity for the interphase, the apparent friction force per unit embedded length, F_{fr}/L, can be calculated from the slope. By using our developed SFPO test, at least three useful physical quantities to characteristic fiber/matrix interphase properties could be obtained: G_i, the fracture energy of the interface (per unit area), τ_o, the maximum interfacial failure stress and F_{fr}/L, the apparent pull-out friction per unit embedded length.

Interfacial Properties of Aramid/Epoxy

A micro-composite system was produced when the initial filament and plasma-modified and plasma-grafted filaments were embedded in epoxy the matrix. Their

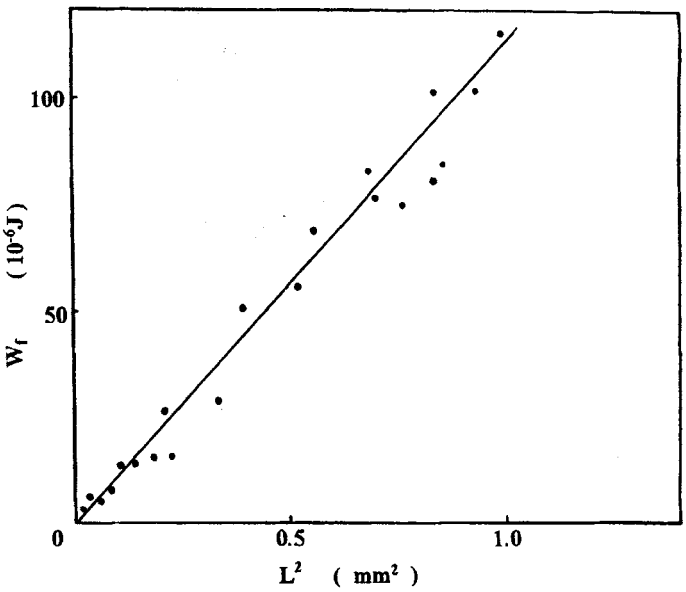

FIGURE 8 Plot of friction work, W_f, vs. embedded length, L^2.

TABLE III
Interfacial properties for different Kevlar-49/epoxy systems

Fiber	τ_0 (MPa)	G_i (J/m^2)	F_{fr}/L (cN/mm)
K-I	21	45	15
K-P	39	36	26
K-C	24	28	27
K-AA	47	48	27
K-EA	37	43	20
K-AA-EA	45	55	29

interfacial properties, τ_o, G_i and F_{fr}/L were determined by the SFPO test. Table III summarizes a comparison of the interfacial properties of the studies aramid/epoxy systems. Increase of τ_o and G_i were observed after the fiber was treated with plasma or grafted polymer. The reactive group, COOH, and the energy absorbing layer introduced on Kevlar-49 were responsible for the improvement in Kevlar/epoxy interphase properties, because of the chemical bond formed between the carboxylic groups and the epoxy resin and the molecular interaction between the polymer chain grafted on the fiber surface and the epoxy matrix. The polyacrylic acid-co-ethyl acrylate grafting layer seems optimum for the aramid fibers according to these results.

The Failure Mode of Kevlar-49/Epoxy Resin Microcomposites

Fibers pulled out from the epoxy resin matrix were examined in the SEM to study the failure mode. Interface failure prevailed for the cleaned or original Kevlar-49

fibers. The surface of a fiber pulled out of the matrix is shown in Figure 9; it can be seen that the surface is smooth. For grafted fibers, interface failure still prevailed; a typical micrograph is given in Figure 10. It is shown that the surface has several concave scratches along the fiber axis after the SFPO test. For the fibers modified

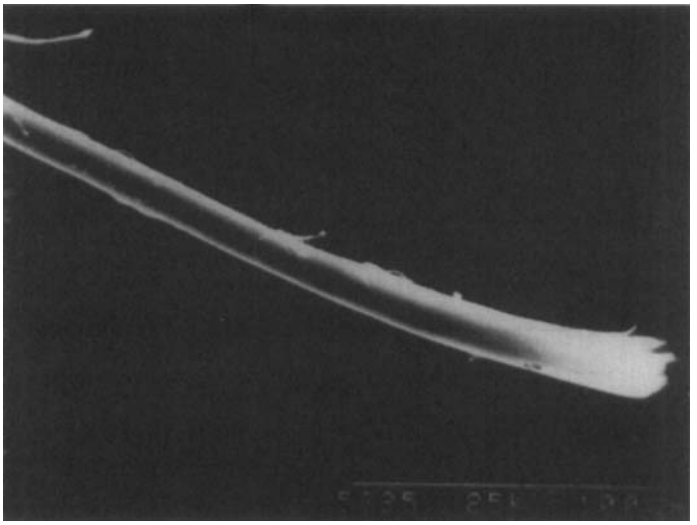

FIGURE 9 SEM photograph of pulled out fiber with smooth surface.

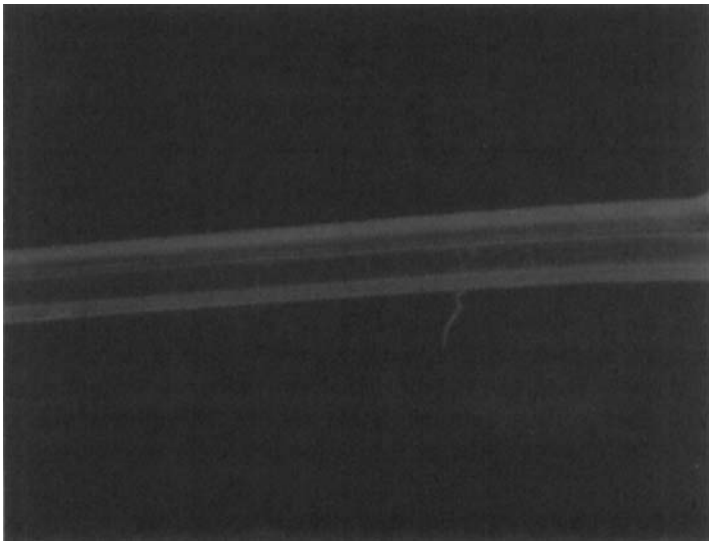

FIGURE 10 SEM photograph of pulled out K-EA fiber. The surface has several concave scratches along the axis.

by plasma treatment or by grafting with PAA, both adhesion failure and fiber cohesion failure were obtained. In Figure 11, it can be seen that the skin of the filament has been stripped away, and the fiber core is pulled out. These results confirm Morgan's model[17] as well as that aramid fibers consists of a more complete fibrillar skin and a looser crystalline core. The special skin-core structure of aramid fibers results in the unique mechanical characteristics that include high longitudinal strength, low transverse strength, easy separation of skin from core, and axial splitting. However, with respect to this, plasma treatment and PAA grafting are the better ways to modify the surface for improving adhesion. After plasma treating or grafting PAA on the fiber surface, the enhanced adhesion strength at the interface between modified fiber and epoxy resin, in some cases may exceed interfibrillar strength and cause the cohesion failure of Kevlar-49 fibers. The probability of fiber cohesion failure is summarized in Table IV. These results perhaps indicate that the

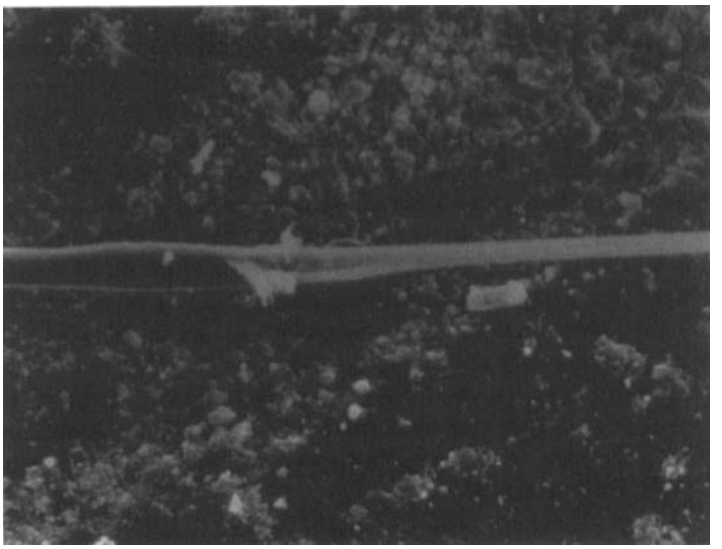

FIGURE 11 Photograph of split filament in the SFPO test.

TABLE IV
The probability of fiber cohesion failure occurrence in SFPO test

	embedded length (mm)			
Kevlar fiber	0.2–0.4	0.41–0.60	0.61–0.80	0.81–1.00
cleaned	nil	nil	nil	nil
plasma treated	29/100	28/100	29/100	15/100
PAA-grafted	20/100	25/100	7/100	15/100
PEA-grafted	nil	nil	nil	nil
P(AA/EA)-grafted	nil	nil	nil	nil

interfaces between epoxy matrix and fiber that were modified by air plasma treatment or by plasma grafting with PAA were very rigid, whereas improvement was achieved by grafting with PEA or with P(AA/EA) copolymer. The fibers grafted with PAA or P(AA/EA) were comparable with the fibers treated by air plasma or grafted with PAA in limit shear strength and fracture energy of the micro-composite; however, adhesive failure was observed exclusively

CONCLUSIONS

A single filament pull out (SFPO) test method has been developed which is a successful method to characterize fiber/matrix interface properties. At least three important physical quantities can be obtained from the SFPO test. They are the maximum shear stress at interface, τ_o, the energy of interface fracture, G_i, and the apparent friction force per unit embedded length, F_{fr}/L. They correspond to the strength of the interfacial bond and are the key parameters in adjusting the fiber/matrix interface. The fracture of composite material is dependent on these physical quantities.

The surface of Kevlar-49 fiber was modified by air plasma treatment and plasma grafting in monomer solution. The surfaces grafted with PAA, PEA and P(AA/EA) were rougher than those of the original fibers. Their layer thickness was about 60 nm according to the weight gain. Their chemical components were verified by XPS. The mechanical properties of the interface of Kevlar-49 fiber/epoxy matrix were effectively improved by the plasma grafting modification. In the case of epoxy micro-composites, the interface fracture energy, G_i, was increased to 55 J/cm^2 by grafting P(AA/EA) copolymer in comparison with 45 J/cm^2 for original Kevlar-49 fiber which was modified with the sizing and was only 36 J/cm^2 for the cleaned fiber from which the sizing was removed. The P(AA/EA) grafted on the Kevlar-49 fiber surface is the best one of three polymers grafted; it offers the possibility of increasing the fiber-matrix adhesion by diffusion into the matrix and by chemical reaction between —COOH and epoxy groups.

Acknowledgment

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References

1. M. Breznick, J. Banbaji, H. Guttmann and G. Marom, *Polym. Comm.*, **28**, 55 (1987).
2. R. Martin, W. Gotz and B. Vollment, *Angew. Makromol. Chem.*, **133**, 141 (1985).
3. EP 0347540.
4. L. S. Penn, F. A. Bystry and H. J. Marchinonni, *Polym. Comm.*, **4**(1), 26 (1983).
5. F. P. M. Mercx and P. J. Lemstra, *Polym. Comm.*, **31**, 252 (1990).
6. L. S. Penn and B. Jutis, *J.Adhesion*, **30**, 67 (1989).
7. D. B. Eagles, B. F. Blumentritt and S. L. Cooper, *J. Appl. Polym. Sci.*, **20**, 435 (1976).
8. Y. Wu and G. C. Tesoro, *J. Appl. Polym. Sci.*, **31**, 1041 (1986).
9. M. Takayanagi, S. Ueta, W.-Y. Lei and K. Koga, *Polym. J.*, **19**(5), 467 (1987).
10. M R. Wertheimer and H. P. Schreiber, *J. Appl. Sci.*, **26**, 2087 (1981).

11. N. Inagaki, S. Tasaka and H. Kawai, *J. Adh. Sci. Tech.*, **6**(2), 279 (1992).
12. C. Zhang, S. Jin and Y. Yu, *J. Mater. Sci. Technol.*, **9**, 423 (1993).
13. R. J. Gray, *J. Mater. Sci.*, **19**, 861 (1984).
14. J. C. Outwater and M. C. Murphy, *24th Ann. Conf. SPI, Section II* -2.
15. B. Harris, J. Morley andD. C. Phillips, *J. Mater. Sci.*, **10**, 358 (1975).
16. P. S. Chau and M. R. Piggott, *Comp. Sci. Tech.*, **22**, 33 (1985).
17. R. J. Morgan *et al. J. Polym. Phys. Ed.*, **21**, 1757 (1983).