Surface Modification of Ultrahigh Molecular Weight Polyethylene Fibers by Plasma Treatment. I. Improving Surface Adhesion

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SYNOPSIS

The fiber/epoxy resin adhesion increases after plasma treatment on ultrahigh molecular weight polyethylene (UHMW-PE) fibers. The surface modification of UHMW-PE monofilaments was studied using a combination of techniques: contact-angle measurements, SEM, and pullout tests. The results may be summarized as follows: Influenced by different plasma parameters and draw ratios of the monofilaments, the adhesion increases by at least four times by plasma treatment. Failure in the pullout tests involve rupture within a treated monofilament and the skin of it was peeled off; the degree of peeling-off is affected by different plasma treatment conditions and draw ratios of the monofilaments. There is only a slight decrease in the surface energy of the treated monofilaments with aging time. Ways of combining plasma etching with other chemical treatments to further improve the fiber/resin adhesion have also been studied. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The strength ($\sim$ 4 GPa) and tensile modulus ($\sim$ 120 GPa) of the ultrahigh molecular weight polyethylene (UHMW-PE) fibers match or even surpass that of the materials commonly thought to possess high stiffness and strength, such as Keviar fibers.[1] Moreover, the specific gravity of the UHMW-PE fibers is 1.0 g/cm^3 less, which makes it possible to produce composites that combine good mechanical properties with low specific mass. However, it is also realized that there are likely to be two aspects of the physical properties of these fibers that will make it difficult to achieve a satisfactory bond with a polymer resin.[2] First, there is the chemical inertness of linear polyethylene. Second, it is known that isotropic polyethylene has a low surface energy ($\simeq$ 33 mJ m^{-2}).

Ward and co-workers made remarkable achievements in the surface modification of ultrahigh modulus polyethylene (UHMPE) fibers by plasma treatment.[2-5] Their attention was concentrated on the effect of plasma treatment and mechanical properties of the composites. Using different gas-plasma treatments, other researchers devoted considerable effort to improving the adhesion and wettability properties of the polystyrene, polypropylene, polytetrafluoroethene, and isotropic films or fibers of comparatively low draw ratio polyethylene.[6-9]

Since interfacial studies on the high-performance polyethylene fiber composites are very limited, in this paper we first discuss the effects of plasma parameters on the fiber/resin adhesion for different draw ratio monofilaments, laying a foundation for finding the factors affecting interface adhesion and their quantitative relations. Then, we study the mechanism of the interface failure. We also discuss the effect of aging on the wettability of plasma-treated samples. Finally, we explore new ways of improving fiber/resin adhesion.

EXPERIMENTAL

Materials

UHMW-PE filaments $\sim$ 0.2 mm diameter, manufactured by the Chinese Academy of Textile Sci-

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ences, with draw ratio of 10.0 and 39.3, and average molecular weight $M_w \approx 350{,}000$ were prepared. Prior to treatment, the filaments were scoured in tribasic sodium phosphate to remove surface contaminants. The scouring procedure consisted of immersing the filaments in 200 mL of a 1% aqueous solution of tribasic sodium phosphate at 50°C for 20 min; the filaments were then rinsed in 200 mL of water for 30 min, then in 500 mL of acetone for 10 min, followed by two rinses in 500 mL of water for 10 min, using fresh water for each rinse. The filaments were dried overnight under vacuum at 25°C. A low-viscosity epoxy resin (E_{51}) provided by Yueyang Chemical Plant and curing agent (CS_{703}) provided by Chongqing Synthetic Chemical Plant were used throughout the experiment.

Plasma Treatment

The plasma treatments were carried out in a Plasma Discharge System PGT-II manufactured by China's Institute of Physics, Academia Sinca, and with oxygen as the carrier gas. This has an adjustable 200 W input power and an RF glow discharge of 13.56 MHz. Coils of monofilaments were first suspended in the reaction chamber. After evacuating the chamber, the plasma carrier gas was bled continuously through the chamber and the flow rate adjusted so as to maintain a constant pressure during treatment. The samples were then treated by glow discharge under a certain power, pressure, and time condition.

In the present paper, when the term "plasma treatment" appears without mentioning the plasma parameters, this refers to the treatment carried out with an input power 67 W, pressure 0.13 Torr, and time 300 s.

Chemical Treatments

The monofilaments were immersed in chromic acid or hot (70 ± 5°C) concentrated sulfuric acid for 300 s, after which they were immediately rinsed in five baths of deionized water followed by washing in running water for 1–2 h. The monofilaments were then given a further immersion in deionized water and dried overnight under vacuum at room temperature. For these treatments, the standard composition of chromic acid was $7K_2Cr_2O_7 — 12H_2O — 150H_2SO_4$ parts by weight. For the glycerol treatment, the monofilaments were dipped for 300 s in a 10% solution of glycerol in deionized water and then dried under vacuum at room temperature for 24 h.

Adhesion Measurements

The epoxy resin (E_{51}) and curing agent (CS_{703}) were first mixed with a ratio of 3.5 : 1; the mixture was then degassed in a vacuum desiccator for 3 min to remove air bubbles and poured into a polyethylene cylindrical mold of 3.5 cm i.d, so that it adhered to the monofilament that was vertically fixed in the mold. The adhesive was cured at room temperature for 48 h.

The fiber/resin adhesion was measured with the pullout technique,[10] adapted to our requirements. As shown in Figure 1, one end of a length of monofilament (~ 15 cm) was embedded in a disc of resin that rests on the horizontal platform of a loading device attached to an Instron base; the other end was wound around two capstan grips attached to the load cell of the Instron. The cross-head speed of the Instron is 100 mm/min. The thickness of the disc that determines the immersion length l of the monofilament in the resin disc was kept constant at 3.0 ± 0.3 mm. The lengths of the major and minor axes of the cross section of the monofilament were measured by a microscope, and, thus, the girth L was calculated. The fiber/resin adhesion τ was defined as

$$\tau = \frac{\text{failure load}}{\text{interface area}} = \frac{F}{L \cdot l} \qquad (1)$$

In this paper, the relative adhesion τ/τ_0, i.e., the adhesion for treated monofilaments (τ) divided by

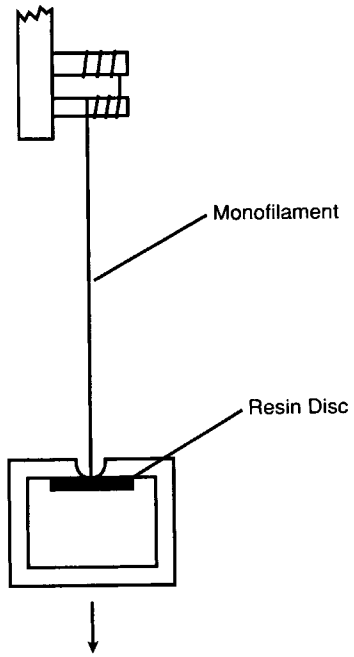

Figure 1 Pullout test.

that of the untreated ones (τ_0 = 0.9 MPa), is used to express the effect of plasma treatment on the fiber/resin adhesion.

Contact-angle Measurements and Surface Energy Calculation

To determine the surface free-energy components of UHMW-PE monofilaments, the contact angles were measured by determining the shape of liquid drops (glycerol and liquid epoxy resin) attached to the monofilaments following the work of Carroll.[11]

The surface free energy was determined by the following equations[12,13]

$$\text{Cos } \theta = 2[(\gamma_s^d \cdot \gamma_L^d)^{1/2}/\gamma_L + (\gamma_s^p \cdot \gamma_L^p)^{1/2}/\gamma_L] - 1 \quad (2)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (3)$$

where γ is the surface energy (the subscripts s and L refer to the solid and the liquid, respectively, and the letters d and p refer, respectively, to the dispersion component and the polar component of the surface energy). The surface energy γ_L, the dispersion component γ_L^d, and the polar component γ_L^p were, respectively, 63.4, 37.0, and 26.4 mJ m^{-2} for glycerol and 43.2, 40.2, and 3.0 mJ m^{-2} for liquid epoxy resin.

Calculation of Fracture Energies

The fracture energy (Γ_s) is the energy required to create one unit of interfacial area of crack; its calculation allows one to predict bond stability in a given environment.[14] Kaelble and Moacanin suggested obtaining fracture energies starting from contact-angle data, via the calculation of the polar and dispersion components of the surface energy of the adhesive, the environment, and the adherend.[15,16] Γ_s is given by

$$\Gamma_s^2 = \mathrm{R}^2 - R_0^2 \quad (4)$$

where $R_0 = 0.25[(\alpha_1 - \alpha_3)^2 + (\beta_1 - \beta_3)^2]$, $R = (\alpha_2 - \mathrm{H})^2 + (\beta_2 - \mathrm{K})^2$, $\mathrm{H} = 0.5(\alpha_1 + \alpha_3)$, and $\mathrm{K} = 0.5(\beta_1 + \beta_3)$. In the above equations, Γ_s is the facture energy and α and β are the square root of the dispersion and the polar surface energy components of the adhesive (1), environment (2), and adherend (3).

Scanning Electron Microscopy (SEM)

The scanning electron micrographs were taken with a JEOL JSM-T300. Gold coating of the samples was carried out using a Ciko-IB-5 Vacuum Coating Unit, run at 1.0 kV and 10 mA for 5 min to obtain a 10 nm-thick layer without heating the specimen.

RESULTS AND DISCUSSION

Fiber/Resin Adhesion

The effect of plasma treatment on the fiber/resin adhesion, as measured by pullout tests, was dramatic. As shown in Figure 2, it can be seen that the adhesion increases with the increasing treatment time. Within 30 s, the adhesion increases from 0.9 to 3.8 MPa and within 90 s to 4.5 MPa. However, the speed apparently slows down after reaching this stage and the adhesion stops increasing after 300 s, reaching an extreme value of 5.3 MPa. This suggests that with a given condition, a corresponding maximum value of adhesion is achieved within a limited time. In fact, an endless increase of treatment time reduces adhesion; this is because more and more decomposed substances will form a weak boundary layer between the fiber and resin and long-time plasma etching causes a decrease of the mechanical strength of the fiber surface. As to the power and gas-pressure requirements for optimum adhesion results (Fig. 2), it is seen that power should be 70–100 W and gas pressure should be 0.1–0.2 Torr.

Figure 3 illustrates the relative adhesion vs. treatment time for monofilaments with different draw ratios of 10.0 and 39.3. It is seen that adhesion for higher draw ratio plasma-treated monofilament is greater. It is likely that several factors contribute to this result. First, the increase in the pit size with increasing draw ratio allows a more effective keying between resin and monofilament. Second, the initiation of the failure in the rough regions involves tensile failure of the fibrils as well as shear failure between the fibrils. Therefore, the increase in tensile strength of the fibrils with increasing draw ratio should be accompanied by a higher failure load for the pullout system.[4] Finally, the increase in the oxygen-containing groups on the fiber surfaces with increasing draw ratio leads to stronger chemical bonding between resin and monofilaments. In addition, consideration should be given to other factors such as surface energy, which will be further discussed in Part II of this article.

Mechanism of Interface Failure

As we have seen, the fiber/resin adhesion greatly increases after plasma treatment. In this section, first of all, we performed a morphological charac-

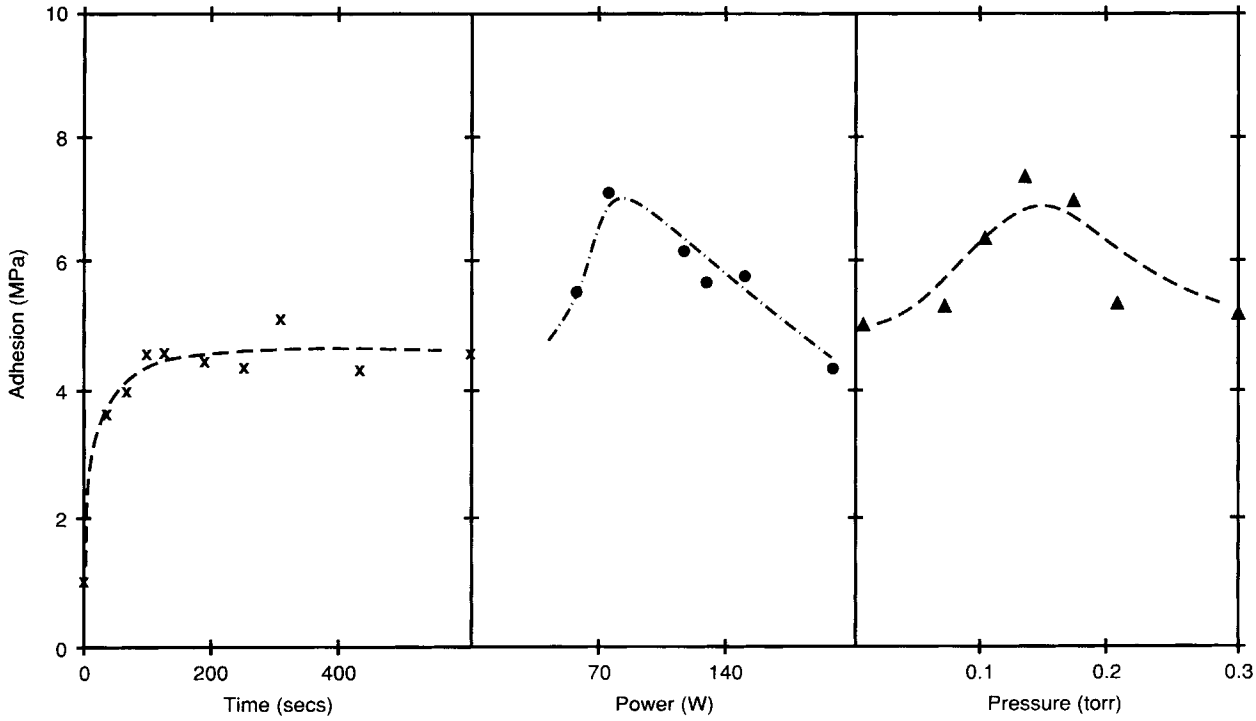

Figure 2 Time, power, and pressure of plasma treatment in relation to pullout adhesion.

terization of fracture surfaces, using SEM. As shown in Figure 4(a), the pullout test with untreated monofilament shows little change in the surface. No resin remains on the surface and no peeling-off layer of monofilament occurs; and no fiber skin or resin is left in the resin grooves [Fig. 4(b)], which are regular and smooth. This suggests that the interface failure involves sliding along the fiber/resin interface. This kind of interface structure cannot transfer stress effectively; hence, it causes poor adhesion.

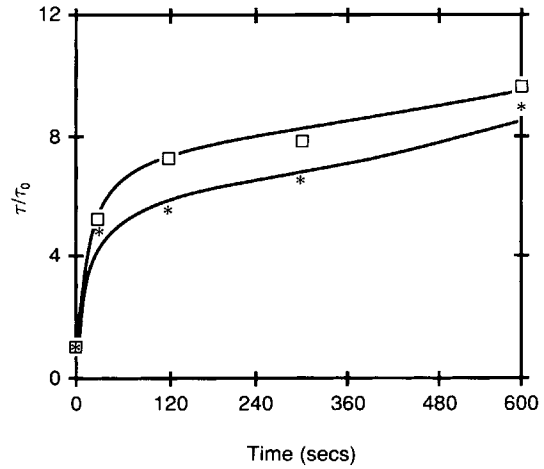

Figure 3 Relative adhesion for monofilaments of D.R. (*) 10.0 and (□) 39.3 vs. plasma treatment time (67 W, 0.03 Torr).

But the test with plasma-treated samples shows that the skin of the plasma-treated monofilaments [Fig. 4(c)] is partly or even completely peeled off [Fig. 4(d)]; the resin grooves are covered by what appears to be a layer of polymer [Fig. 4(e)], in which only rupture and the fiber structure can be seen. By treating the groove with hot xylene (130°C) to dissolve the adhered layer, the polymer layer apparent in Figure 4(e) disappears, but the resulting resin surface [Fig. 4(f)] is an accurate replica of the plasma-treated monofilament surface shown in Figure 4(c). Therefore, a remarkable change in the structure of the fiber/resin interface of plasma-treated fiber has occurred. In the pullout test, the surface layer of the monofilament is peeled off by the hard interface while the resin remains undamaged because the failure propagates within the polyethylene samples. This is likely to be associated with the high adhesion values obtained with these systems and it is possible that mechanical interlocking between fiber and resin plays an important role in bringing about this drastic increase of adhesion. In addition, the mechanical strength of the PE surface layer may be the determining factor.

With the aim of identifying the locus of failure, we then studied the surface energy of the fracture

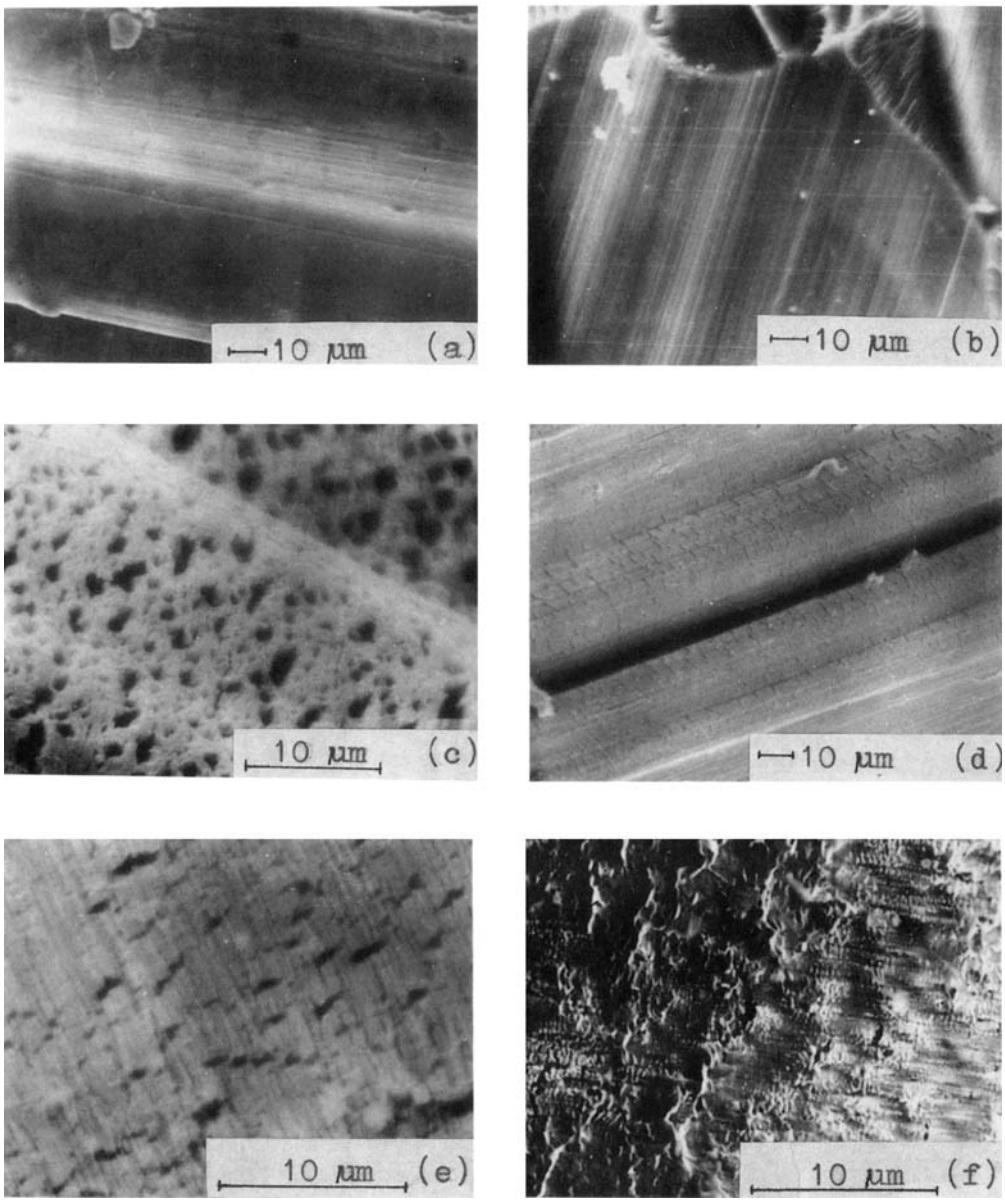

Figure 4 SEM micrographs of treated and untreated monofilaments and resin sockets: (a) untreated monofilament; (b) resin groove from untreated monofilament; (c) plasma-treated monofilament; (d) plasma-treated monofilament after pullout test; (e) surface of resin groove after pullout test of plasma-treated monofilament; (f) socket of resin dissolved by hot xylene.

surface. The treated PE/epoxy interface is three-layered: Bulk PE, modified PE, and epoxy layer are present. By taking as equal to zero the surface energy components of the environment (air atmosphere), we calculated the fracture energies of all the possible loci of failure of our system, i.e., PE–PE, PE-treated PE, treated PE–treated PE, treated PE-E_{51}, and E_{51}–E_{51}. Data are summarized in Table I and show that all the calculated values of fracture energy are positive, i.e., all interfaces require a mechanical stress for debonding. If mechanical stress is applied, the cohesive fracture in bulk PE is the most likely locus of failure; it is also possible to rupture in PE-treated PE, in agreement with the SEM findings.

Furthermore, to characterize the degree of peeling-off as a function of plasma-treatment time, the surface energies of the treated monofilaments before and after the pullout test were measured, as shown

Table I Fracture Energies (mJ/m^2) Assuming Different Loci of Failure (Treatment Time 300 s, Draw Ratio 39.3)

Locus of Failure	Fracture Energy
PE–PE	34.4
PE–treated PE	40.4
Treated PE–treated PE	60.0
Treated PE–E51	46.4
E51–E51	43.2

in Figure 5. It can be seen that the greater the surface energy decreases after pullout, the thicker the peeling-off layer is, for monofilaments with the same draw ratio. With 300 s plasma treatment, the surface energy of the monofilament of draw ratio 39.3 showed the greatest decrease in pullout, which was the same as that of the untreated monofilaments, i.e., 34 mJ m^{-2}; hence, the fracture is in bulk PE and the peel-off proceeds the deepest inside the monofilament. This is consistent with the adhesion result obtained with this system (see Fig. 2). With 30 s treatment, the modified PE layer of the samples was partly peeled-off. The peeling-off layer of the samples with 600 s treatment may be very thin owing to the weak boundary layer formed by overetching as discussed above.

In addition, the surface energy of the monofilament of draw ratio 10.0 decreased below 45 mJ m^{-2} after pullout (Fig. 5, also), which is lower than that of monofilament of draw ratio 39.3. This indicates that the peel-off proceeds easily inside the monofilament of a lower draw ratio, which is in agreement with the adhesion result obtained for this system (Fig. 3), the reason for which is that tensile strength of the fibrils decreases with decreasing draw ratio. Therefore, the degree of the peeling-off is also determined by the draw ratio—high draw ratio produces the thick peeling-off layer.

Chemical and Plasma Treatments

The plasma treatment causes great chemical and physical changes to the surface of monofilaments and the fiber/resin interface. Observed through SEM, not all the plasma-etched pits are filled up with resin. There are still some air bubbles in the pits. Therefore, it is necessary to combine plasma treatment with other chemical techniques to improve the fiber/resin adhesion.

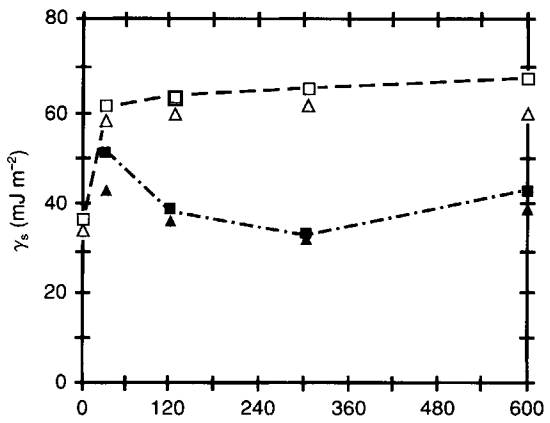

Figure 5 Surface energy before and after pullout test vs. plasma treatment time for monofilaments with D.R. 10.0 [(△) before; (▲) after)] and 39.3 [(□) before; (■) after].

As listed in Table II, the surface energy is generally further increased after combining chemical treatment with plasma treatments. However, in some cases, the surface energy is a little lower, but still the fiber/resin adhesion is better, e.g., the adhesion after AI + D treatments (4.8 MPa) is 1.1 times as much as that after AI treatment only (4.3 MPa). Although there is no change in surface texture of the chromic acid-treated monofilament, a great increase in the adhesion is noted, which suggested the chemical changes in the fiber surface.[5] It therefore can be concluded that the adhesion can be increased through plasma etching alone and can be further improved if the appropriate chemical treatments are also employed. The techniques of combining the two treatments are worth developing.

The Effect of Aging on the Surface Wettability

To assess the effect of aging in air atmosphere at 298 K, the surface energies of plasma-treated mono-

Table II Influence of Chemical and Plasma Treatments on Surface Energy

	Treatment										
	AI	AII	B	C	D	B + AI	D + AI	AI + D	AI + B	AII + D + AII	AI + B + AI
γ_s (mJ/m^{-2})	61	58	55	55	41	62	62	59	59	63	63

AI: plasma oxygen treatment for 300 s; AII: plasma oxygen treatment for 150 s; B: chromic acid treatment; C: sulfuric acid treatment; D: glycerol treatment.

Table III Surface Free Energy for Oxygen Plasma-Treated Samples as a Function of Aging Time

Time (h)	γ_s^d (mJ m^{-2})	γ_s^p (mJ m^{-2})	γ_s (mJ m^{-2})
0.08	24.1	36.3	60.4
24	24.5	33.1	57.6
52	23.8	33.2	57.0
72	24.1	31.5	55.6
144	24.5	30.3	54.8
240	24.3	29.2	53.5

filaments were measured and a function with aging time was obtained (Table III). It can be seen that the surface energy dropped by about 7 mJ m^{-2} and reached the plateau values within 2–3 days. The decrease was mainly in the polar surface energy component rather than in the dispersion component.

After plasma treatment, for UHMW-PE fibers, the top layer underwent rearrangement within itself by thermally activated macromolecular motions.[17] However, the decrease of the surface energy was not a dramatic one, due to cross-linking during plasma treatment, which is likely to reduce macromolecular mobility within the surface layer.

CONCLUSIONS

The UHMW-PE fiber/epoxy adhesion increases by at least four times after plasma treatment. The optimum results of adhesion are obtained when the plasma parameters were the following: treatment time 90–300 s, power 70–100 W, and gas pressure 0.1–0.2 Torr. Monofilaments of higher draw ratios produce better adhesion after the treatment.

The failure for plasma-treated samples involves rupture within the monofilaments, rather than at the interface between resin and monofilaments, in agreement with fracture energy calculations, so that a skin of monofilament is peeled-off. The thickness of the peeled-off layer is determined by plasma-treatment time and draw ratios of the monofilaments.

The surface of plasma-treated UHMW-PE fiber is insensitive to aging. After a slight decrease within the first 2–3 days following the treatment, the surface energy reaches its plateau value.

Combining plasma etching with other chemical treatments can further improve the fiber/resin adhesion. This technique is worth developing.

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