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Effect of low-temperature-plasma surface treatment on the adhesion of ultra-high-molecular-weight-polyethylene fibres

Y. CHAOTING, S. GAO, Q. MU
Department of Basic Science, Chongqing Institute of Architecture and Engineering, Chongqing, People's Republic of China

The poor adhesion of ultra-high-molecular-weight polyethylene (UHMW-PE) fibres to epoxy resin (due to characteristics of their surface structure) makes it difficult to develop light composite materials with good mechanical properties. In our experiments a low-temperature plasma was applied to treat the surfaces of the fibres. The results showed that the surface energy of the treated fibres was increased greatly so that the fibres could be wetted very well by resin, which was an essential prerequisite in improving the adhesion of the fibre/epoxy resin systems; and the results also showed that the pull-out adhesion strength of the treated fibres to resin was increased significantly by about 10 times. This paper discusses the mechanism of the improvement of the adhesion. Two reasons for improvement are that: varieties of polar-oxygen-containing groups are produced in the non-polar surface layer, forming chemical bonds; and plasma-etched pits spread all over the surface of the fibres into which the resin penetrates to form a mechanical interlock between fibre and resin. A synthetic analysis and discussion of these two factors and of non-polar interactions influencing the adhesion is given, and a preliminary relationship between them is presented.

1. Introduction

It is possible to develop a new type of composite material with high specific strength and high specific modulus as well as low-price using ultra-high modulus polyethylene (UHMPE) fibres [1–3] and ultra-high molecular weight polyethylene (UHMW-PE) fibres [4–6] because of their fine mechanical performance, which can match that of some fibres with high performance. However, there are likely to be some reasons which make it difficult to achieve a satisfactory interface adhesion between the fibres and the polymeric matrix. First, polyethylene fibres have a low surface energy which makes it impossible for the resins to wet the fibres so that the factors which lead to adhesion play a role. Secondly, there is the chemical inertness and the complete absence of any polar groups on the fibres. Great efforts have been made to improve the adhesion of polyethylene fibres to resins by different surface treatments in some centres around the world [7–9]. The adhesion strength was increased to a great extent, and the mechanism of the improvement of the interface adhesion was discussed in these works. An examination [8] aiming to separate these effects was undertaken because, in fact, several factors influence adhesion. However, in general, the factors always act concurrently; it is very difficult to separate them. The magnitudes and the proportion of the contributions of these factors to the adhesion strength are different at different times during plasma treatment. In our experiments a low-temperature plasma was applied to treat the surfaces of the UHMW-PE fibres, and the effects of the treatment on adhesion and the chemical and physical mechanism of the improvement of adhesion have been studied in detail. A synthetic and quantitative analysis and discussion of the factors influencing adhesion has been undertaken to distinguish their influences on adhesion.

2. Experimental details

2.1. Materials

Two linear polyethylene fibres were used for this work: UHMW-PE fibres with different draw ratios, weight average molecular weight $\bar{M}_w = 3\,500\,000$ (made by Textile Academy, Ministry of Textile Industry, China), and conventional linear PE fibres (made by Shanghai Rope and Net Factory, China). A epoxy resin with the code name E-51 (made by Yueyang Chemical Plant, China) was used.

2.2. Plasma treatment

The plasma treatment was carried out using a PGT-II plasma-treatment equipment made by the Institute of Physics, Academia Sinica, China. It has a 200 W, 40 MHz radio-frequency power supply with a capacitively coupled electrode discharge. The plasma carrier gas was oxygen (if air a special statement will be given). The time, power and pressure of treatment could be adjusted.

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2.3. Measurement of adhesion strength

The fibre–resin interface adhesion strength was measured by the pull-out technique [7], adapted to our requirements. A monofilament was put through a box of resin and fixed vertically. The mixture of E-51 epoxy resin and hardener, with the code name 703, was poured into the box of resin after removing air bubbles. It was cured for 48 h at room temperature.

2.4. Determination of the surface energy of fibres

The surface energy of UHMW-PE fibres $\gamma_s = \gamma_s^d + \gamma_s^p$, where γ_s^d and γ_s^p are the dispersion component and the polar component of the surface energy, respectively. γ_s^d and γ_s^p were determined as in [10, 11]. The contact angles of liquid drops on the fibres must be determined while determining γ_s^d and γ_s^p. Two methods were used to determine the contact angles: the contact angles were measured by magnifying the drops directly, and the other method was to calculate the contact angles according to [12]. The results of the two methods were slightly different. But they were referred to each other to obtain better values for the contact angles.

2.5. Calculation and observation of the depth of etched pits of the treated fibres

The mechanical performance falls a little because of plasma etching. This can be considered to be a result of decreasing the area of the real cross-section of the treated fibre because of the formation of lots of etched pits on the surface. I. M. Ward and co-workers used the expression [8]

$$e = \frac{d}{2}\left(1 - \left(\frac{\sigma_p}{\sigma_0}\right)^{1/2}\right) \qquad (1)$$

to determine the depth, where d is the apparent diameter of the treated fibre, σ_p and σ_0 are the tensile strengths of the treated and untreated fibre, respectively. In order to avoid using a lot of fibres to undertake breaking examination, the expression

$$e = \frac{d}{2}\left(1 - \left(\frac{E_p}{E_0}\right)^{1/2}\right) \qquad (2)$$

was used to determine the depth, e, in addition to Equation 1. This expression is easy to obtain. E_0 and E_p are the moduli of UHMW-PE fibres before and after treatment, respectively.

The values of e calculated from Equations 1 and 2 may be slightly different, but they may be referred to each other to achieve better values.

The above consideration does not take the effect of the defect and stress concentration into account. So the calculated values may be greater than the real values.

2.6. Scanning electron microscopy

First, the samples to be observed were coated with gold using a Ciko-IB-5 TOW COATER. Then their scanning electron micrographs were taken with a TEOL JSM-T300.

2.7. XPS analysis

Carbon, oxygen and nitrogen photoelectron peaks in the surface layer of fibres were scanned using an ESCALAB MKII photoelectron energy spectrometer (angle 45°, pressure 8×10^{-6} Pa and analysis energy 20 eV).

3. Results and discussion

3.1. Influence of the plasma surface treatment on the adhesion strength

Fig. 1 shows the relationship between the pull-out adhesion strength of polyethylene (PE) fibres and the treatment time. The influence of the treatment time on the pull-out adhesion strength (relative value) of UHMW-PE fibres is shown in Fig. 4. The pull-out adhesion strength of the treated fibres is increased greatly, in general, by 5–10 times, as shown in Figs 1 and 4. It can be seen from the two figures that the process of treatment is so fast that a good result is achieved in 30–90 s. Plots of the pull-out adhesion strength against the treatment power and the treatment pressure are shown in Figs 2 and 3, respectively.

The mechanism of the failure in pull-out tests is now discussed. The scanning electron microscopy (SEM) observations showed no evidence of a change in the surfaces of the untreated UHMW-PE fibres before and after the pull-out tests. Neither evidence of the remains of resin adhering to the surface of the fibres nor evidence of the appearance of peeling-off was observed. This suggests that failure during the pull-out test involves sliding of the fibres out of the resin along the fibre–resin interface. This is in agreement with the low pull-out adhesion strength from the pull-out test.

The appearance of the surface of the treated UHMW-PE fibre after pull-out (as shown in Fig. 5b) makes clear that the outside layer of the fibre is peeled off (compare with Fig. 5a). The appearance of the surface of groove of a hole on resin (see Fig. 6a) makes clear that the peeled-off layer of the treated fibre (see

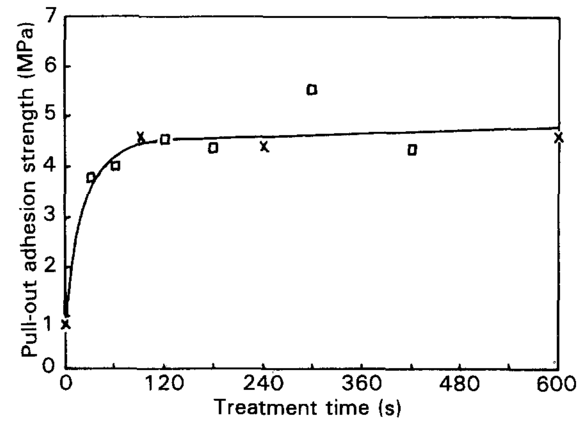

Figure 1 Relationship between the pull-out adhesion strength (to epoxy resin) and the treatment time of: (□) treated conventional PE fibres, and (×) treated UHMW-PE fibres (power 70 W, pressure 17 Pa (0.13 torr)).

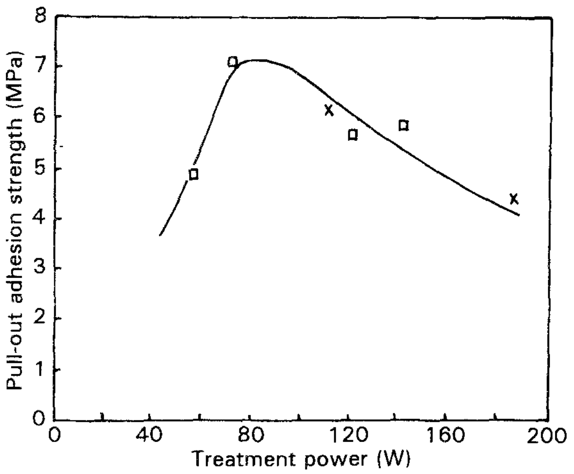

Figure 2 Relationship between the pull-out adhesion strength (to epoxy resin) and the treatment power of: (□) treated conventional PE fibres, and (×) treated UHMW-PE fibres (time 300 s, pressure 17 Pa (0.13 torr)).

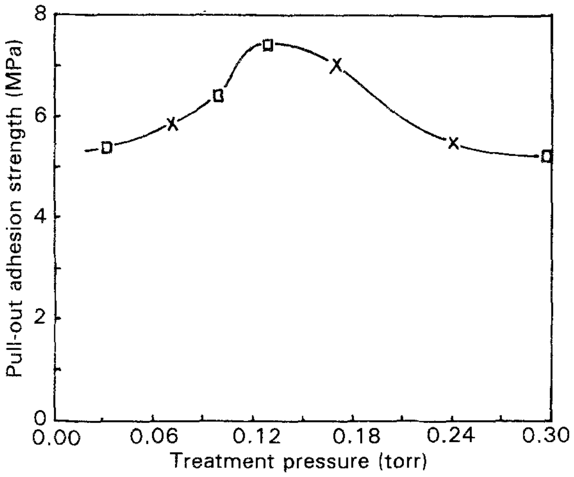

Figure 3 Relationship between the pull-out adhesion strength (to epoxy resin) and the treatment pressure of: (□) treated conventional PE fibres, and (×) treated UHMW-PE fibres (time 300 s, power 70 W).

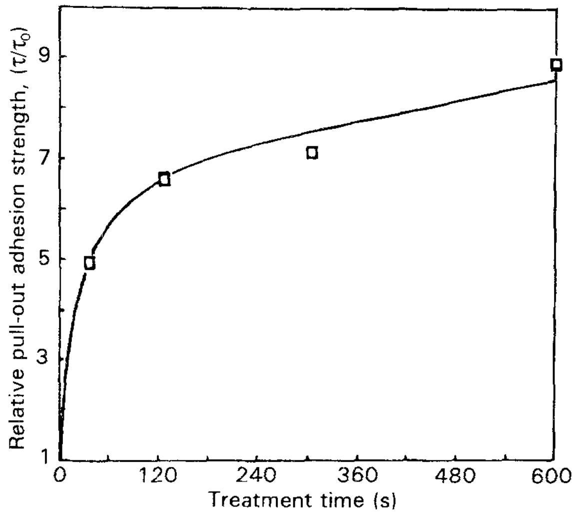

Figure 4 Relative value of the pull-out adhesion strength of treated UHMW-PE fibres with draw ratio 39.3 versus treatment time (power 67 W, pressure 4.0 Pa (0.03 torr)).

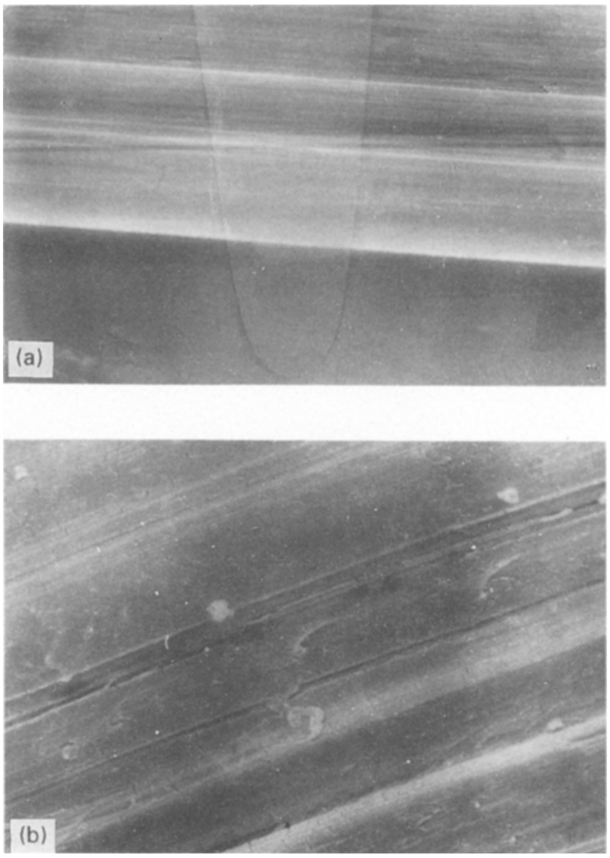

Figure 5 (a) Surface of the pull-out region of an untreated UHMW-PE fibre from the matrix, (b) surface of the pull-out region of a treated UHMW-PE fibre from the matrix.

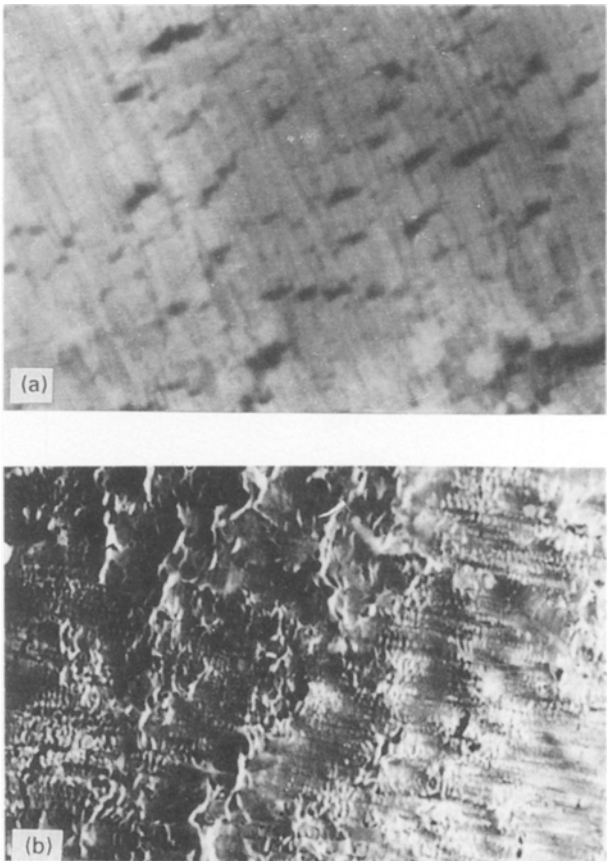

Figure 6 Surfaces of the groove after pull-out of a treated UHMW-PE fibre of: (a) a hole on resin, and (b) the groove of the same hole on resin dissolved by xylene at 130 °C.

Fig. 12) is attached to the surface of a groove so that the surface of the groove appears striated and cracked. Fig. 6b shows the protrusions, on the surface of a groove, which formed when resin penetrated into the pits on the surface of the treated UHMW-PE fibre after the peeled-off layer on the groove was dissolved with hot xylene.

Thus, the plasma treatment improves the adhesion of the UHMW-PE fibres to the resin greatly, so that during pull-out tests the samples fail within the fibre rather than along the interface between the fibre and resin.

3.2. Influence of the plasma surface treatment on the surface energy of the fibres

Fig. 7 shows the relationship between the surface energy of the treated UHMW-PE fibres and the treatment time. It can be seen that the surface energy is increased greatly from 3.4×10^{-2} N m^{-1} for untreated fibres to 6.0×10^{-2} N m^{-1}, which exceeds the surface energy of epoxy resin 4.3×10^{-2} N m^{-1}. This conduces to wettability of resins on fibres which is the essential prerequisite in improving the adhesion of fibres to resins. The surface energy, γ_s, increases with increasing treatment time, but the dispersion component, γ_s^d, of the surface energy decreases a little, and the polar component, γ_s^p, increases greatly. During plasma treatment, varieties of polar-oxygen-containing groups are produced on the surface of the fibres. This is why the polar component greatly increases. This will be discussed further in Sections 3.4 and 3.5.

The influence of the treatment power and pressure on the surface energy are shown in Figs 8 and 9, respectively. Figs 3 and 9 show that the treatment pressure has a small influence on the result.

It appears that Figs 1, 2 and 3 are very similar to Figs 7, 8 and 9, respectively. This suggests that the adhesion strength is correlative with the surface energy.

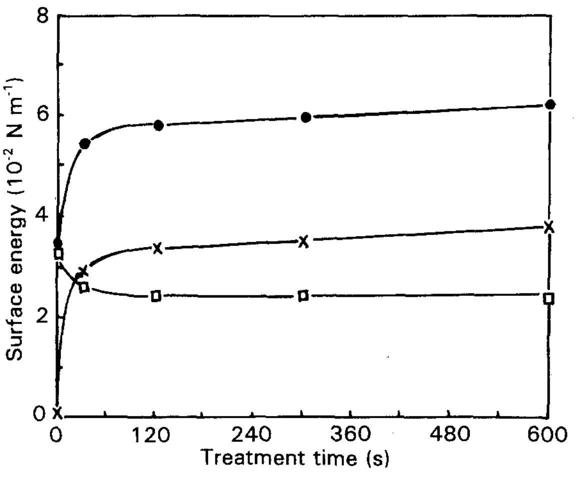

Figure 7 Relationship between (●) the surface energy, γ_s (×) its polar component, γ_s^p, and (□) its dispersion component γ_s^d (for treated UHMW-PE fibres) and the treatment time (power 67 W, pressure 4.0 Pa (0.03 torr), draw ratio 39.3).

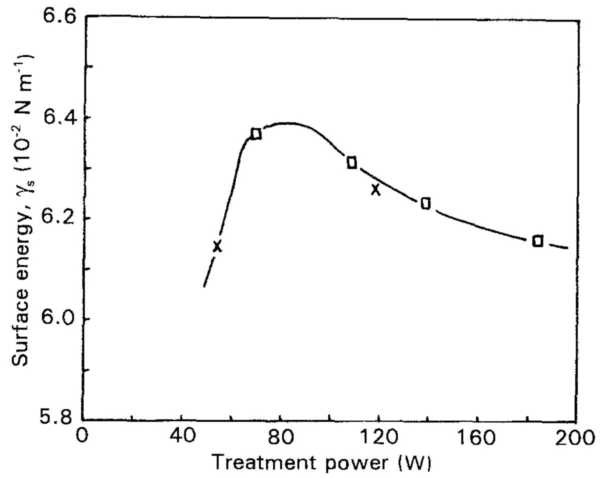

Figure 8 Relationship between the surface energy, γ_s, and treatment power for: (□) treated conventional PE fibres, and (×) treated UHMW-PE fibres (time 300 s, pressure 17 Pa (0.13 torr)).

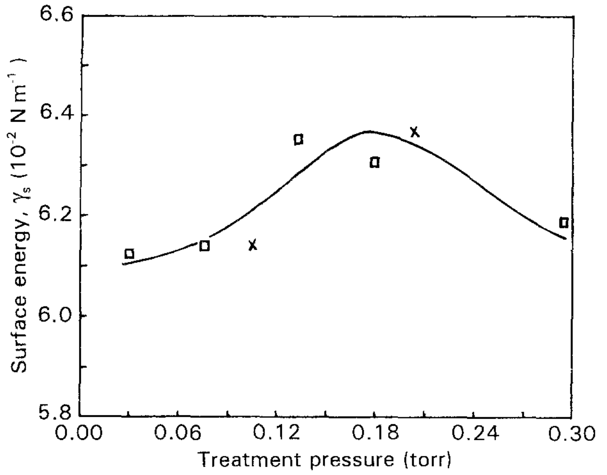

Figure 9 Relationship between surface energy, γ_s, and treatment pressure for: (□) treated conventional PE fibres, and (×) treated UHMW-PE fibres (time 300 s, power 70 W).

3.3. Influence of the plasma surface treatment on the appearance of the surface of the fibres

3.3.1. Plasma-treatment production of the etched pits over the surface of the fibres

Figs 11 and 12 show the appearances of the surfaces of the untreated and the treated UHMW-PE fibres, respectively. It can be seen that lots of etched pits, varying in diameter and depth in the range of several micrometres, spread all over the surface of the treated fibre. It is because of these etched pits that a mechanical interlocking structure between the fibre and resin forms when the resin penetrates into the pits. This is a major mechanism in the improvement of adhesion.

3.3.2. Depth of the etched pits

The depth can be calculated according to the theory in Section 2.5. Of course, the mean depth is used. The relationship between the calculated depth and the treatment power, time and pressure are shown in Fig. 10. First, the depth increases rapidly in the initial stage of treatment, then it increases more slowly. Secondly, the treatment power has a great influence

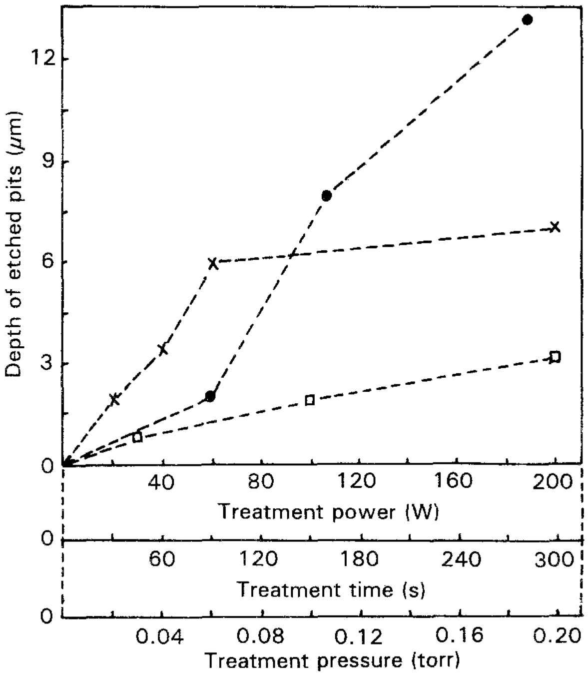

Figure 10 Depth of pits for treated UHMW-PE fibres versus: (●) power (W), (×) time (s), and (□) pressure (torr).

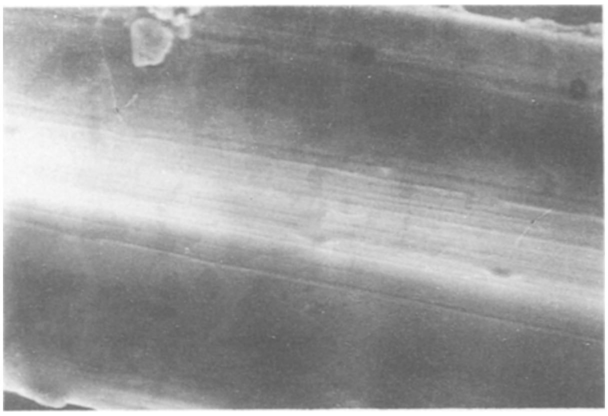

Figure 11 Appearance of the surface of the untreated UHMW-PE fibre with a draw ratio of 39.3.

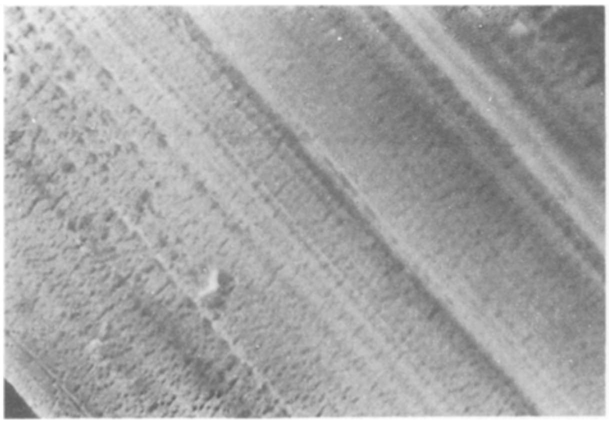

Figure 12 Appearance of the surface of the treated UHMW-PE fibre with a draw ratio of 39.3.

on the depth, so an accurate power value should be used for the treatment power. Thirdly, the treatment pressure has a small influence on the depth. This is in accord with the results for the treatment discussed previously. In addition, the calculated depths appear to be a little greater than those of the pits shown in Figs 12, 13 and 14. The reasons for this have been mentioned previously.

3.3.3. Effect of the draw ratio on etching

On comparing Fig. 13 with Fig. 14, it can be seen that the pit size of the fibre with a high draw ratio is greater than that with a low draw ratio. This may be because fibres with a high draw ratio have a greater surface stress. Because the etched pit size of the fibre with a high draw ratio is greater than that of the fibre with a low draw ratio, the adhesion from mechanical interlocking should be greater for the fibre with a high draw ratio. This was found to be true in our examination. This result is in accordance with the findings of others.

3.4. Influence of the plasma surface treatment on the chemical properties of surface of the fibres

It is shown by Fig. 15 that the C_{1s} peaks from the treated UHMW-PE fibres are shifted to high binding

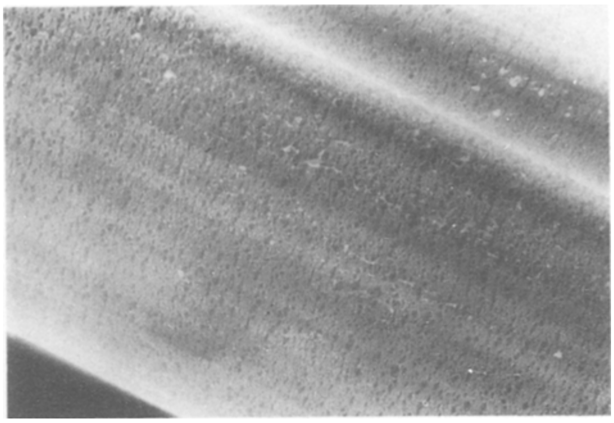

Figure 13 Appearance of the surface of the treated UHMW-PE fibre with a draw ratio of 10.0 for 5 min.

Figure 14 Appearance of the surface of the treated UHMW-PE fibre with a draw ratio of 35.8 for 5 min.

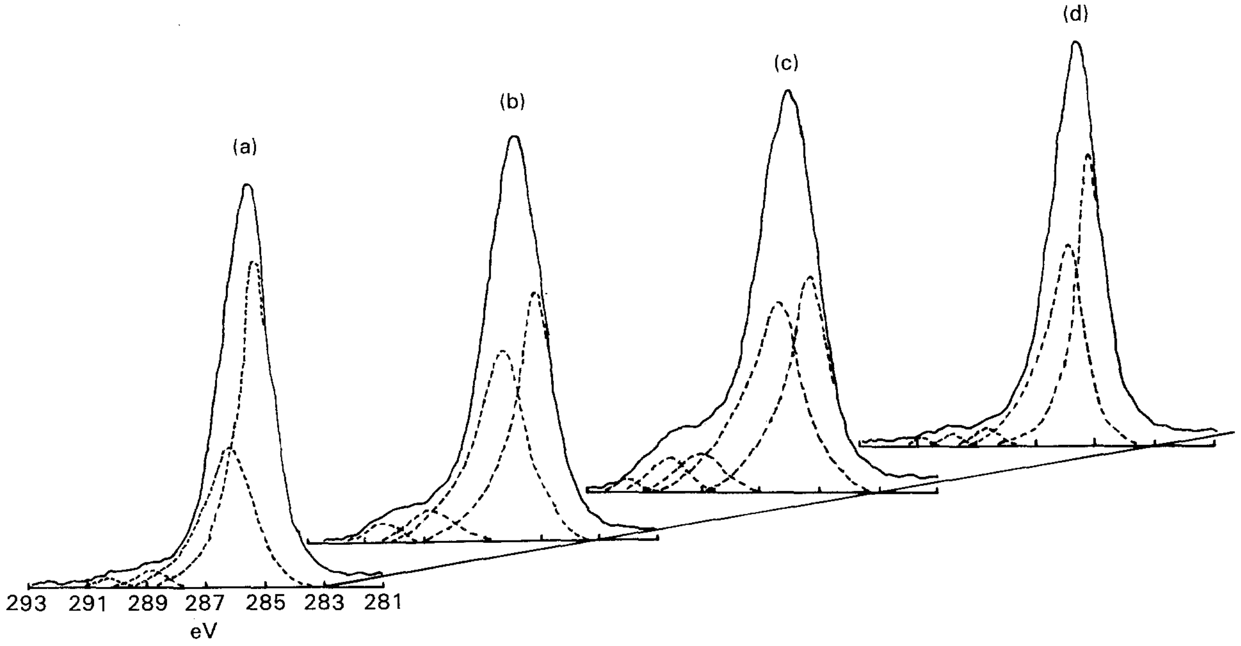

Figure 15 Contrast of C_{1s} XPS peaks of untreated and treated UHMW-PE fibres. (a) Untreated, (b) oxygen plasma treated for 2 min, (c) oxygen plasma treated for 10 min, and (d) air plasma treated for 10 min.

energies and that shoulder peaks appear. This suggests that the carbon atoms are in a quite different chemical state from the carbon atoms in the surface layer of the untreated UHMW-PE fibres.

In Table I it can be seen that the relative contents of O_{1s} in the surface layer of the treated UHMW-PE fibres increases. This suggests that the plasma treatment produces a great quantity of oxygen in the surface layer of the fibres. It can be seen that there are more than four types of polar-oxygen-containing groups $=\overset{|}{C}-OH$, $O=\overset{|}{C}-$, –COOH, and $O=\overset{|}{C}-O-$, in the surface layer of the treated UHMW-PE fibres when the C_{1s} peaks are divided with fitting.

Table I also shows that there is a small amount of nitrogen (0.9%) in the surface layer of the air-plasma-treated fibres. The nitrogen content is so small that it plays little role in adhesion. Comparing the contents of the oxygen-containing groups of the oxygen-plasma-treated fibre (10 min) with those of the air-plasma-treated fibre (10 min), the difference in the contents of –OH is very small whereas the contents of the oxygen-containing groups with high activity =C=O, –COOH and $O=\overset{|}{C}-O-$ are evidently different in these two cases. This is why the result of the air-plasma treatment is less good than that of the oxygen-plasma treatment.

When the treatment time is increased the contents of the oxygen-containing groups increases whereas the content of –H decreases; then all the contents reach a stable value (see Fig. 16). Thus, the chemical structure and the chemical components in the surface layer change a great deal after the plasma treatment.

The content of –OH for the untreated fibres is about 25% which is high, but the adhesion strength is still very low. The contents of the groups =C=O, –COOH and $O=\overset{|}{C}-O-$ have a large relative increase after the plasma treatment. So the groups which have a great influence on the adhesion are =C=O, –COOH and $O=\overset{|}{C}-O-$ rather than –OH.

The interface adhesion decreases linearly when the carbon/oxygen ratio increases (see Fig. 17). This suggests that the polar-oxygen-containing groups have a very great influence on the adhesion. Taken together, the chemical bonding formed through the groups is another main mechanism in the improvement of the adhesion.

3.5. A synthetic analysis of the factors which influence the adhesion

The improvement of adhesion of the plasma treated UHMW-PE fibres to epoxy resin was discussed above as were the following factors: the mechanical interlocking produced by etched pits, the chemical bonding by polar-oxygen-containing groups and the non-polar interaction produced by the dispersion force.

Apparently, it is necessary to discuss further how much influence each factor has on the adhesion and how much contribution each makes to the adhesion strength. This will be analysed and discussed in detail from different angles according to the experimental results, and a preliminary quantitative relationship between the results is presented.

For convenience, the results which will be related in the discussion are now mentioned. Fig. 18 shows the relationship between the mean depth of etched pits and the treatment time; the curve in Fig. 18 will be explained below in point 6. Fig. 19 shows the relationship between the polar component of the surface energy and the carbon/oxygen ratio. It can be seen that the polar component decreases linearly when the carbon/oxygen ratio increases. In addition, Figs 4 and 7 will be used in the analysis.

In order to find out the contributions of the factors to the adhesion strength, some assumptions and

TABLE I XPS analysis data for UHMW-PE fibres (draw ratio 39.3)

Treatment gas	Treatment time (s)	C_{1s} (eV)										O_{1s}		N_{1s}		N content (%)	C content (%)	O content (%)	C/O
		–C–H		–C–OH		–C=O		–COOH		O=C–O–									
		E_b (eV)	Content (%)	E_b (eV)	Content (%)	E_b (eV)	Content (%)	E_b (eV)	Content (%)	E_b (eV)	Content (%)	E_b (eV)	CPS relative content	E_b (eV)	CPS relative content				
	0	285.0	71.1	285.9	26.1	288.1	2.0	288.5	0.8			532.8	2800				91.7	8.3	11.0
Oxygen	120	285.0	58.6	286.2	32.1	288.2	5.2	289.5	2.8	290.5	1.2	534.3	7100				83.5	16.5	5.1
Oxygen	600	285.2	46.2	286.3	37.6	288.2	8.6	289.4	5.4	290.6	2.3	534.3	8200				75.2	24.3	3.0
Air	600	285.0	62.2	286.2	30.3	288.1	4.6	289.4	2.4	290.5	0.6	534.2	5500	402.0	410	0.9	83.0	16.0	5.2

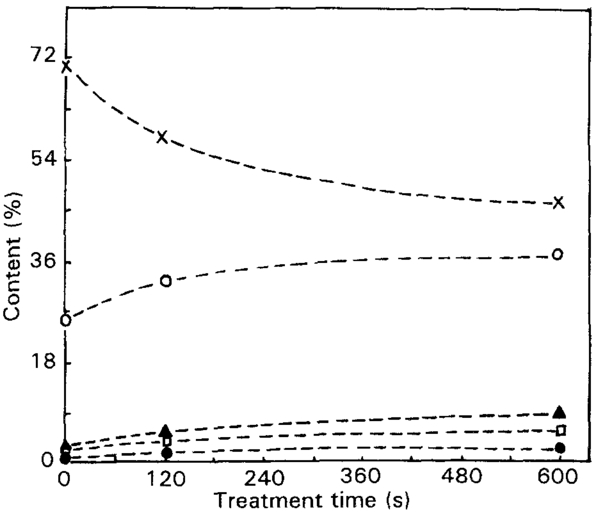

Figure 16 Relationship between contents of the different oxygen-containing groups in the surface layer of treated UHMW-PE fibres and treatment time (draw ratio 39.3): (×) =C–H, (○) =C–OH, (▲) –C=O, (□) O=C–OH, (●) O=C–O–.

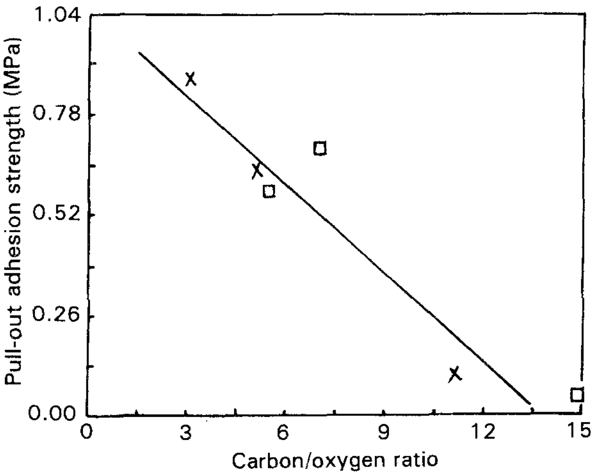

Figure 17 Relationship between the pull-out adhesion strength and the C/O ratio in the surface layer of the treated UHMW-PE fibre: (×) a draw ratio of 39.3, and (□) a draw ratio of 29.0.

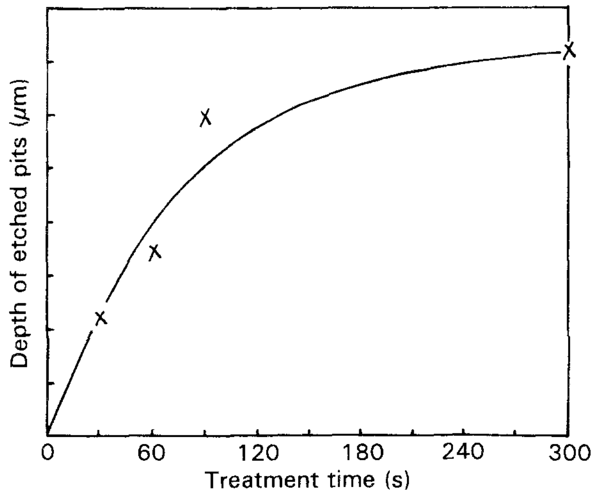

Figure 18 Relationship between depth of etched pits of treated UHMW-PE fibres and the treatment time: (×) calculated values. The curve is obtained according to the consideration put forward in the paper. Power 67 W, pressure 4.0 Pa (0.03 torr), draw ratio 39.3.

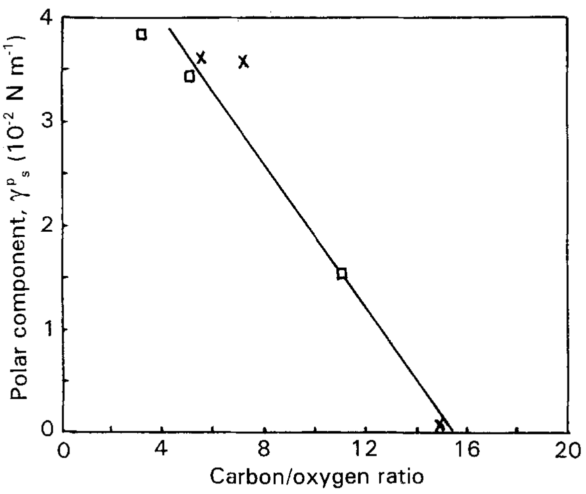

Figure 19 Polar component of surface energy of the treated UHMW-PE fibre versus C/O ratio: (×) draw ratio 29.0, and (□) draw ratio 39.3.

expressions indicating the roles of the factors will be made; then the assumptions and the expressions will be justified using the discussion of the experimental results.

1. Let $\tau(t)$ express the pull-out adhesion strength. Let $\tau_m(t)$, $\tau_c(t)$ and $\tau_d(t)$ express the contributions made by the mechanical interlocking, the chemical bonding and the non-polar interaction, respectively. The quantities mentioned above all will vary with the treatment time. Assume the pull-out adhesion strength, $\tau(t)$, at any time during treatment is given by

$$\tau(t) = \tau_m(t) + \tau_c(t) + \tau_d(t) \qquad (3)$$

2. The mean depth of etched pits increases with the treatment time (see Fig. 18), so mean depth, e, should be expressed as $e(t)$ which is the mean depth for treatment time t. The mechanical interlocking will be considered to arise from the penetration of resins into pits. When the treated UHMW-PE fibres are pulled out from the matrix, shear stresses along the direction of the fibres will act on the resins penetrating into the pits. This is just the adhesion strength $\tau_m(t)$ produced by the mechanical interlocking. Obviously the magnitude of $\tau_m(t)$ is related to the size of the penetrating resin, i.e. to the size of pits. It was found by SEM observation that the dimension of the size of pits is approximately equal to the depth of pits. So the size of the pits can be represented by $e^2(t)$. Therefore the contribution made by the mechanical interlocking can be expressed as

$$\tau_m(t) = k_m e^2(t) \qquad (4)$$

where k_m is a coefficient.

3. It can be seen from Fig. 19 that the polar component, γ_s^p, increases linearly with the content of oxygen-containing groups (when the carbon/oxygen ratio reduces). Thus, the contribution of the chemical bonding produced by the oxygen-containing groups to the pull-out adhesion strength can be expressed as

$$\tau_c(t) = k_c \gamma_s^p(t) \qquad (5)$$

4. Fig. 7 shows that the non-polar component, γ_s^d, is mainly constant during treatment. So the adhesion strength produced by the non-polar interaction is $\tau_d(t) = \tau_d =$ const. When $t = 0$ (i.e. for untreated fibres), because of the absence of etched pits and the zero approximate value of the polar component of surface energy (see Fig. 7), $\tau_m(0) = 0$, $\tau_c(0) = 0$ can be considered tenable. According to Equation 3 it is evident that

$$\tau(0) = \tau_0 = \tau_d \qquad (6)$$

That is, the adhesion of the untreated fibres is produced by the non-polar interaction.

Equation 3 can be written as follows, if Equations 4–6 are used

$$\frac{\tau(t)}{\tau_0} - 1 = \frac{k_m}{\tau_0} e^2(t) + \frac{k_c}{\tau_0} \gamma_s^p(t) \qquad (7)$$

5. Since $\tau_m(t)$ and $\tau_c(t)$, and consequently $\tau(t)$, vary with the treatment time the percentages of the contributions of the three factors to the adhesion strength should vary with the treatment time. The adhesion strength for 300 s satisfies

$$\frac{\tau(300)}{\tau_0} - 1 = \frac{k_m}{\tau_0} e^2(300) + \frac{k_c}{\tau_0} \gamma_s^p(300) \qquad (8)$$

Make

$$\left(\frac{\tau(t)}{\tau_0} - 1\right)\left(\frac{\tau(300)}{\tau_0} - 1\right)^{-1} = E_\tau(t)$$

$$\frac{e^2(t)}{e^2(300)} = E_e(t)$$

and

$$\frac{\gamma_s^p(t)}{\gamma_s^p(300)} = E_p(t)$$

Thus

$$\left(\frac{\tau(300)}{\tau_0} - 1\right) E_\tau(t) = \frac{k_m}{\tau_0} e^2(300)\, E_e(t) + \frac{k_c}{\tau_0} \gamma_s^p(300)\, E_p(t) \qquad (9)$$

It can be seen from Figs 4, 18 and 7 that $E_\tau(30) = 0.591$, $E_e(30) = 0.093$, $E_p(30) = 0.803$, and using Equation 9

$$0.591\left(\frac{\tau(300)}{\tau_0} - 1\right) = 0.093\frac{k_m}{\tau_0} e^2(300) + 0.803\frac{k_c}{\tau_0} \gamma_s^p(300) \qquad (10)$$

Combining Equations 8 and 10, and solving them

$$\frac{k_m}{\tau_0} e^2(300) = 0.299\left(\frac{\tau(300)}{\tau_0} - 1\right) \qquad (11)$$

and

$$\frac{k_c}{\tau_0} \gamma_s^p(300) = 0.701\left(\frac{\tau(300)}{\tau_0} - 1\right) \qquad (12)$$

i.e.

$$\tau_m(300) = 0.299(\tau(300) - \tau_0) \qquad (13)$$

$$\tau_c(300) = 0.701(\tau(300) - \tau_0) \qquad (14)$$

It is shown by Fig. 4 that $\tau(300)/\tau_0 = 7.60$. Evidently,

$$\tau_0 = \tau_d = 0.132\tau(300) \approx 13\%\ \tau(300) \qquad (15)$$

TABLE II Relative pull-out adhesion strengths, polar components of surface energy and depths of etched pits for different treatment times

Treatment time (s)	$(\tau/\tau_0) - 1$	$E_\tau(t)$	γ_s^p ($\times 10^{-3}$ N m^{-1})	$E_p(t)$	$E_e(t)$	e (μm)
30	3.90	0.591	28.5	0.803	0.093	2.20
60	4.75	0.720	31.8	0.896	0.307	3.99
90	5.25	0.795	33.2	0.935	0.466	4.92
120	5.60	0.848	33.8	0.952	0.604	5.59
180	6.05	0.917	34.1	0.961	0.814	6.49
240	6.35	0.962	34.7	0.977	0.927	6.93
300	6.60	1.000	35.5	1.000	1.000	7.20

If Equation 15 is used, then Equations 13 and 14 can be rewritten as

$$\tau_m(300) = 0.259\tau(300) = 26\%\ \tau(300) \quad (16)$$

$$\tau_c(300) = 0.609\tau(300) = 61\%\ \tau(300) \quad (17)$$

Therefore, the contributions of the mechanical interlocking produced by etched pits, the chemical bonding produced by oxygen-containing groups and the non-polar interaction produced by dispersion to the adhesion are about 26%, 61% and 13%, respectively, for the plasma-treated UHMW-PE fibres with draw ratio 39.3 for a treatment time of 300 s.

6. The above discussion is based on the assumptions involved in Equations 3–6. Some of the assumptions can be justified by the experimental results and other results by intuition. In addition, they can be explained as being valid by the discussion below. Substitution of Equations 11 and 12 in Equation 9 gives

$$E_\tau(t) = 0.299\,E_e(t) + 0.701\,E_p(t) \quad (18)$$

After obtaining the values of the relative pull-out adhesion strength, τ/τ_0, and the polar component, γ_s^p, corresponding to the treatment times, the corresponding values of E_τ and E_p can be calculated (see Table II). After calculating the corresponding values of E_e using Equation 18 the corresponding values of depth e can be calculated. The curve in Fig. 18 is given in accordance with the values of depth e in Table II. The curve appears very similar to the fitted curve of the values calculated according to the theory in Section 2.5. Thus, it is believed that the above assumptions are valid.

7. The above discussion is only limited to the case in which the treatment time does not exceed 300 s. If the treatment time is too long, either too many products of small molecules are attached to the surfaces of the fibres, which will lead to the formation of a weak interface structure, or the surface layer of the fibre is peeled off at all during pulling-out. In these cases the above discussion is not significant.

4. Conclusions

1. The adhesion strength to epoxy resin of the plasma-treated UHMW-PE fibres is about ten times greater than that of the untreated fibres. For well-treated fibres failure takes place within the fibres instead of in the interface.

2. The plasma treatment increases the surface energy of the UHMW-PE fibres greatly, consequently the wettability of the resin on the fibres is increased, which is a prerequisite for an improvement in adhesion. The increase of the surface energy is due to the great increase of the polar component. This is connected with the increase of oxygen-containing groups in the surface layer.

3. After plasma-treatment, many etched pits spread all over the surface of UHMW-PE fibres. When resins penetrate into them, a mechanical interlocking structure between the fibre and resin is formed. This is a major reason for the improvement in adhesion.

4. The plasma-treatment produces varieties of polar-oxygen-containing groups in the surface layer of UHMW-PE fibres, so that it is possible to form chemical bonds between the fibre and resin. This is another major reason for the improvement in adhesion.

5. The adhesion can be considered to arise from three independent contributions which relate to the non-polar interaction, the mechanical interlocking and the chemical bonding. The contributions vary with treatment time. For a set of given specimens which are plasma-treated for 300 s, the contributions of τ_m, τ_c and τ_d to the pull-out adhesion strength are 26%, 61% and 13%, respectively. In general, for well-treated UHMW-PE fibres, the contribution from chemical bonding appears to be the most important factor. This is different from an experimental result in [8].

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