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A study of the adhesion of drawn polyethylene fibre/polymeric resin systems

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The effect of plasma etching and chromic acid treatment on the surface adhesion of ultra-high modulus polyethylene fibres to an epoxy resin has been studied. The adhesion was determined from pull-out tests, and showed a significant improvement for both plasma and acid treatments. The mechanism of failure, however, appeared to be different in the two cases. Untreated and acid-treated monofilaments showed a fairly smooth surface and failure of the pull-out samples involved sliding along the monofilament/resin interface. Plasma treatment, on the other hand, produced a remarkable structure on the monofilament surface, into which resin penetrated to produce a mechanical keying between monofilament and resin. Failure in the pull-out test then involved rupture within the monofilament.

1. Introduction

Among the many variables determining the properties of composite materials the characteristics of the interface between the reinforcement and the matrix can play a crucial role [1, 2]. In particular, if the mechanical properties of the reinforcement are to be effectively imparted to the composite there should be good stress transfer at the interface, which requires good adhesion between the reinforcement and the matrix.

One way to obtain satisfactory interface adhesion is for there to be a strong interaction between chemical groups on the surface of the reinforcement and the polymer matrix [3]. Usually the chemical structure of the polymer resin is such that active chemical groups are available to form strong bonds at the interface. If the surface of the reinforcement does not have suitable chemical affinity for the resin, adhesion promoters may be used with both components, thus forming a bridge at the interface [4]. Other alternatives are, for example, to tailor the chemical structure of the reinforcement for best adhesion to the specific resin [5], or to etch the surface of the reinforcement so that suitable modifications are introduced [6, 7].

To utilize fully the chemical reaction at the interface the liquid resin prior to curing should wet the reinforcement. Wettability involves more than forming the composite initially under conditions of low resin viscosity [8, 9]. To achieve the degree of intimate contact required between resin and reinforcement, the surface energy of the reinforcement should be significantly higher than the surface energy of the liquid resin.

The discovery of ultra-high modulus polyethylene (UHMPE) fibres [10] provides the possibility of producing composites which combine good mechanical properties with low specific mass. However, the considerations discussed above suggest that there are likely to be two aspects of the physical properties of these fibres which will make it difficult to achieve a satisfactory bond between them and polymer resins. First, there is the chemical inertness of linear polyethylene and the complete absence of any polar groups. Secondly, it is known that isotropic polyethylene has a low surface energy.

During the last few years considerable effort has been devoted to improving the adhesion and wettability properties of the polyolefines, polyethylene and polypropylene [6, 7, 11–19]. Both chemical treatment and plasma etching have been used, but attention was concentrated on isotropic film or films of comparatively low draw ratio, and the production of composites was not included in the aims of the research work.

In this paper we discuss attempts to improve

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the adhesion of very highly drawn polyethylene. To our knowledge our research constitutes the first attempts at this line of work.

Composites are usually reinforced with very small diameter fibres ($\sim 1\,\mu m$). Although the mechanical properties of the composite reflect the fibre–matrix adhesion, it is difficult to isolate this from other factors such as the orientation of the fibres, fibre-to-resin ratio and the method of fabrication. We have therefore monitored the adhesion between highly drawn polyethylene and composite resins by carrying out pull-out tests using thick ($\geqslant 0.2$ mm diameter) monofilaments. In a further paper the adhesion results reported here will be discussed in terms of the mechanical properties of composites and their mechanisms of failure.

2. Experimental procedure

2.1. Preparation of monofilaments

Polyethylene monofilament ~ 1.4 mm diameter was produced by melt-spinning at 210° C. A linear polyethylene homopolymer (Unifoss 2912) was chosen with $\bar{M}_w = 224\,000$ $\bar{M}_n = 24\,100$. Highly drawn samples were prepared by stretching between moving rollers which passed the monofilament through a glycerol bath at 120° C. Samples with nominal draw ratios of 8, 15 and 30 were produced, with 0.50, 0.36 and 0.26 mm diameter, respectively. The drawn monofilaments were collected on bobbins of 4 cm diameter and 12 cm length carrying ~ 12 g material. In order to remove the glycerol from the monofilaments the bobbins were immersed in water at ambient temperature for several hours, and the monofilaments were subsequently rewound on to similar bobbins, passing through a bath of de-ionized water.

2.2. Resin curing

A low-viscosity epoxy resin (Ciba-Geigy XD927) intended for high-strength composite structures was used throughout. It was cured for at least 16 h at room temperature and post-cured for 5 h at 80° C in an air oven, in accordance with the manufacturer's recommendations. To remove air bubbles introduced during mixing the resin was degassed in a vacuum desiccator.

2.3. Chromic acid treatment

For the acid treatment, the monofilaments were immersed in chromic acid at room temperature for a standard time, after which they were immediately rinsed in de-ionized water followed by washing in running water for 1 to 2 h. The monofilaments were then given a further immersion in de-ionized water and dried in an air oven at 40° C for at least 5 h. For these treatments, the standard composition of chromic acid adopted was (by weight) $K_2Cr_2O_7$ – 7 parts; H_2SO_4 (concentrated) – 150 parts; H_2O – 12 parts. In addition, in some preliminary tests a different composition $K_2Cr_2O_7$ – 0.07 parts; H_2O_4 (concentrated) – 150 parts; H_2O – 12 parts, was also employed.

2.4. Plasma treatment

The plasma treatment was carried out using the Plasmaprep 100 unit manufactured by Nanotech Ltd, Manchester, UK. This has a 100 W, 13.56 MHz radio frequency power supply with a capacitively coupled electrode discharge. The plasma carrier gas was blown axially into the cylindrical reaction chamber which is 10 cm diameter and 15 cm long. There is no means of measuring the operating pressure.

For treatment a 1 to 1.5 m length of monofilament was wound into a coil of about 5 cm diameter and suspended in the reaction chamber. Usually two such coils were treated at one time, and the plasma carrier gas was oxygen. It was found initially that the monofilaments readily melted and kinked during treatment, owing to the presence of impurities remaining from the drawing process in the hot glycerol bath. It was therefore essential to clean the monofilament surface either by rubbing the monofilaments with cotton wool damped with de-ionized water or acetone, or by 1 min immersion in chromic acid. The cleaned monofilaments could then be plasma-treated without any problems provided that the operating parameters were kept within certain limits, particularly with regard to gas flow. This is discussed further in Section 3.

2.5. Adhesion measurements

The monofilament-resin adhesion was measured by the pull-out technique [20], adapted to our requirements. As shown in Fig. 1, one end of a length of monofilament (~ 20 cm) is embedded in a disc of resin which rests on the horizontal platform of a loading device attached to the load cell of an Instron. The monofilament passes freely through a slot in this platform and the other end is wound round a capstan grip attached to the Instron base. The upper grip is designed to ensure

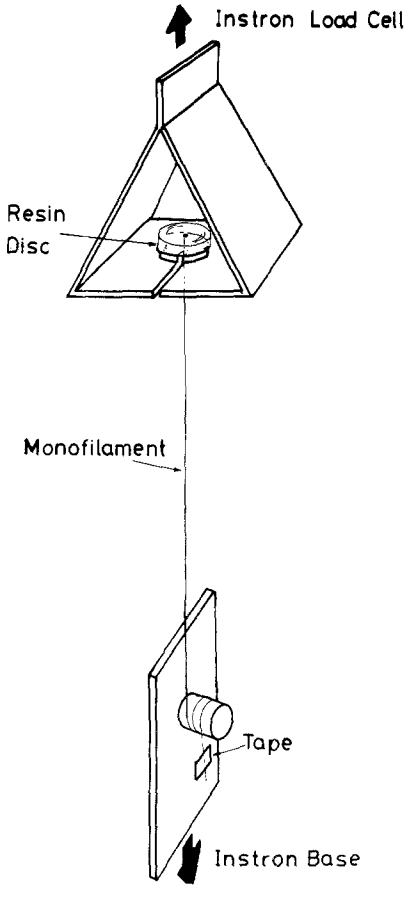

Figure 1 Pull-out test.

that the disc of resin remains horizontal during the pull-out test, and both grips are designed to allow ready axiality of the monofilament during the test.

A possible technique for embedding monofilaments in a disc of resin involves suspending a monofilament vertically with its free end touching the bottom of the mould and pouring in liquid resin, which is then cured. In the case of polyethylene monofilaments this procedure was not suitable because (a) polyethylene tends to float on the liquid resin, (b) the filaments have a comparatively low bending stiffness and therefore do not remain vertical. We therefore used Metaset (Metallurgical Services) polypropylene cylindrical moulds of 3 cm i.d. with a detachable base in which a hole was drilled. The monofilament could then be threaded through this hole and any leak of the resin prevented during curing by sealing the hole with a silicon rubber compound (Dow Corning Silastic 9161 RTV). The hole in the base of the mould produces a protuberance in the disc of resin which has to be removed to ensure accurate measurement of the immersion length. The protuberance was removed to better than 0.1 mm using a surgical blade and working under x 5 magnification. To remove the disc from the mould a cut was made along the length of the side wall of the mould and sealed with the silicon rubber compound. After curing the resin the mould can then be easily sprung open by inserting a knife blade in the cut, after which the disc of resin is easily removed.

The pull-out adhesion was defined as

$$\frac{\text{failure load}}{\text{interface area}} = \frac{\text{failure load}}{\pi D l},$$

where D is the filament diameter and l the immersion length.

The maximum scatter in the pull-out adhesion of identical samples was found to be ± 14%. This compares with estimated errors in the determination of D of ± 2% and in l of ± 9%*. It was found that the pull-out adhesion depended on the average loading rate (failure load/time), which is determined by the cross-head speed, the length of the monofilament and its stress–strain characteristics, as well as the failure load itself. Preliminary experiments showed that for plasma-treated monofilaments of low draw ratio (8:1) a decrease in loading rate from 3.4 to 0.9 N min^{-1} produced a 35% increase in pull-out adhesion. These monofilaments are most sensitive to loading rate because their stress–strain curves show the greatest departure from linearity and, for high draw ratios (i.e. the most useful technological materials) the effect of loading rate is less significant. To standardize the loading rate within narrow limits would require a considerable number of preliminary experiments. Instead, we used monofilament lengths of between 15 and 20 cm and cross-head speeds of 3, 2 and 1 mm min^{-1} for draw ratios of 8:1, 15:1 and 30:1 monofilaments, respectively. These conditions gave average loading rates varying between 2 and 4 N min^{-1}, depending on the given combination of draw ratio and treatment.

2.6. Measurement of monofilament tensile strength

For tensile strength measurements both ends of a

*The pull-out adhesion, as defined by the above equation, should be independent of l. In practice, this is not always so and an explanation for this behaviour may be seen in Section 4. The above error quoted for l is mostly due to its variability among our samples. For a single sample, l is measured within ± 0.5%.

monofilament were held by capstan grips attached to the Instron clamps. The gauge length was 10 cm and the strain rate (cross-head speed) was 2 cm min^{-1}. The tensile strength is failure load/initial filament cross-sectional area. The maximum scatter on the tensile strength of identical samples was ± 6%.

2.7. Scanning electron microscopy (SEM)

Most of the scanning electron micrographs (SEMs) were taken with a Cambridge Stereoscan 150 Mk II, with some occasional use of a Jeol JSM 15. In addition to the monofilaments, the holes left in the disc of resin after pull-out were also examined. The holes were exposed by the sequence of operations shown in Fig. 2. First the disc, as seen in Fig. 2a, is sawn close to the hole (Fig. 2b), and then microtomed a few microns at a time until finally the hole is exposed and appears as a groove (Fig. 2c). It is the grooves which are subsequently examined by SEM, and we shall refer to them as such henceforth.

In some cases a few microns of the monofilament skin remained in the resin groove after pull-out. This skin was either observed directly, or melted or dissolved before observation. Melting was carried out by heating the preferred groove for 15 min at 150° C, while dissolving required 2 min immersion in about 50 ml xylene at 130° C, using moderate agitation. The "dissolved groove" was then washed with a spurt of ethanol, and dried for 1 h in an air oven at 40° C.

When spun (i.e. undrawn) monofilaments were immersed in resin, pull-out could not be carried out. The cutting and exposure of the groove was still performed as above, but it remained full of polymer. The interface was then exposed by immersion in xylene at 130° C for 20 min with moderate agitation, followed by a rinse in xylene at 100° C, a spurt of ethanol, and drying as above.

Gold coating of the samples was generally carried out using a Polaron 500 Vacuum Coating Unit, run at 1.2 kV and 10 A for 8 min, to obtain a 20 nm thick layer without heating the specimen. For large resin samples where moderate heating was not a problem, the current was raised to 20 A for 6 min to obtain a 30 nm layer.

During SEM observation and photographic work the polymer samples may be damaged by the electron beam. The two most important parameters are the electron beam accelerating voltage and the magnification. We chose to limit the former to obtain optimum resolution without damage to the samples.

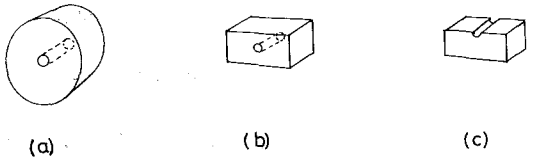

Figure 2 Preparation of a filament socket for SEM observation: (a) after pull-out, (b) after sawing, (c) after microtoming.

3. Results

3.1. Preliminary experiments: general considerations

Prior to the main experiments which will be described in detail below, a wide range of preliminary pull-out tests were carried out on monofilaments of draw ratio 30:1. We will now summarize the conclusions of these preliminary experiments which were important in defining the subsequent more detailed investigation.

It was found that chromic acid treatment improved the adhesion of the monofilaments and that there was a systematic increase as the treatment became more drastic, either by increasing the length of time of treatment or the $K_2Cr_2O_7$ concentration. However, it soon became apparent that the improvements obtained were much less than those obtained by plasma treatment. For this reason most of the effort has been concentrated on plasma treatment.

Although as a general rule the adhesion was improved with the rigour of the plasma treatment, the main variable was found to be the flow of gas, followed by the time of exposure. The power input appeared to be only of secondary importance, provided that the glow had been initiated.

TABLE I Pull-out adhesion ($T = 19.5 \pm 1.0$° C) and tensile strength, σ_u ($T = 20.5 \pm 1.5$° C)

Draw ratio	Treatment	Pull-out adhesion (MPa)	Final tensile strength (GPa)
8:1	None	0.6	0.30
	Acid	2.4	0.31
	Plasma	2.6	0.31
15:1	None	0.5	0.70
	Acid	2.2	0.71
	Plasma	2.7	0.64
30:1	None	0.5	0.98
	Acid	1.4	0.85
	Plasma	4.9	0.58

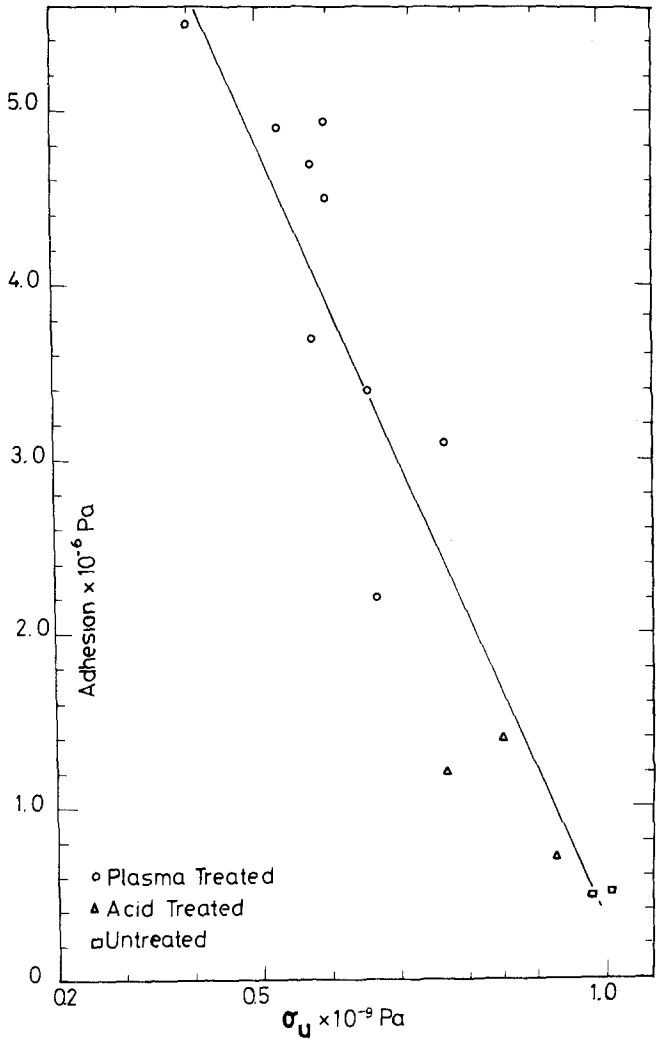

Figure 3 A plot of pull-out adhesion against tensile strength for a draw ratio of 30:1 monofilaments.

Finally, and of great practical importance, gas flows above 10 cm^3 min^{-1} were likely to produce kinking and localized melting of the monofilaments.

Some monofilaments were acid treated before or after plasma treatment. The resultant adhesion was generally determined by the plasma treatment, but if this was weak a previous application of acid treatment significantly improved the adhesion performance to levels which were close to those obtained with a stronger plasma treatment.

When only one type of treatment was used, an increase in adhesion was usually obtained at the expense of a decrease in monofilament tensile strength. Fig. 3 shows the general trend observed in this respect, and we have neglected any distinction other than the type of treatment.

A few pull-out tests were carried out with a polyester resin (Scott Bader Crystic 272). The adhesion values obtained were marginally lower than those for epoxy resin, but gave very similar trends with variation of treatment.

3.2. Main experiments: summary of key results

Following the preliminary experiments, the following treatments were adopted to obtain the comparative behaviour of the different draw ratio monofilaments:

(a) chromic acid treatment: 1 min in the standard composition acid at room temperature;

(b) plasma treatment: 10 W input power for 10 min with 10 cm^3 min^{-1} gas flow.

Table I shows the results of the pull-out tests and tensile strength measurements. Results for untreated monofilaments are included for comparison.

It can be seen that both acid and plasma treatment produce significant increases in the pull-out

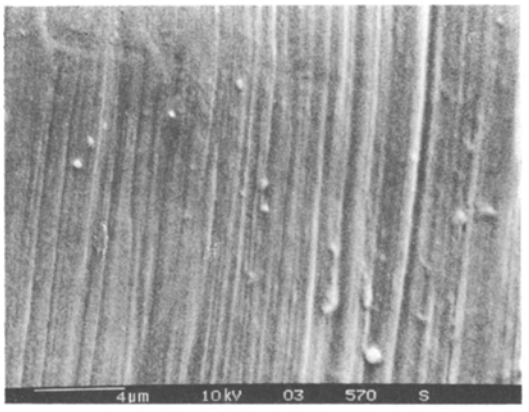

Figure 4 Untreated monofilament, draw ratio 30:1. × 3000.

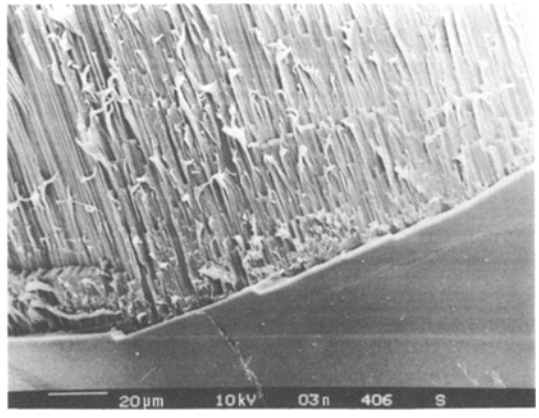

Figure 6 Immersion region of plasma treated monofilament near meniscus, draw ratio 30:1. × 600.

adhesion over the very low values obtained for the untreated monofilaments. In general terms the acid treatment is most effective for lower draw ratio material whereas the plasma treatment is most effective for the highest draw ratio monofilament where an improvement by a factor of about ten is obtained. The effect of plasma treatment on the adhesion of lower draw ratio monofilaments is only marginally greater than that produced by acid treatment.

As the draw ratio is increased there is a corresponding increase in the tensile strength of the initial monofilaments, and there is an increased sensitivity of tensile strength to the applied treatment, especially to plasma treatment. The tensile strength of the 30:1 draw ratio monofilament is reduced by about 40% by plasma treatment. Acid treatment has a smaller effect which is only significant at the highest draw ratio.

4. Discussion

4.1. High draw ratio monofilaments

Because the highest draw ratio material is of greatest scientific and technological interest this will be discussed first.

A scanning electron micrograph of an untreated monofilament of draw ratio 30:1 is shown in Fig. 4. It can be seen that the surface is fairly smooth, except for longitudinal striations which indicate the possible presence of fibrils, as reported in a previous publication [21]. Plasma treatment produces a dramatic change, as shown in Fig. 5. A highly developed cellular structure has now replaced the longitudinal striations, with pits varying in diameter and depth in the range 1 to 4 μm. Next we examine at lower magnification the immersed region of a plasma-treated monofilament. In Fig. 6 it may be seen that the meniscus of the disc of resin remains on the filament after

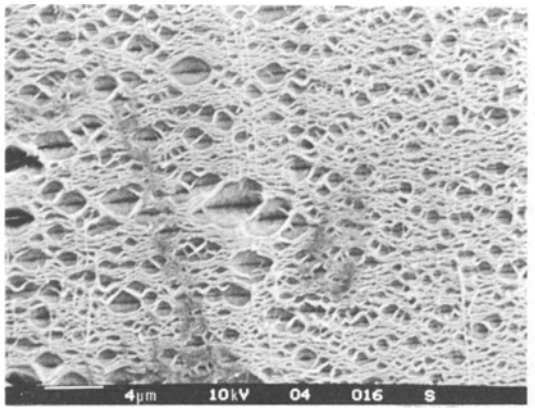

Figure 5 Plasma-treated monofilament, draw ratio 30:1. × 2850.

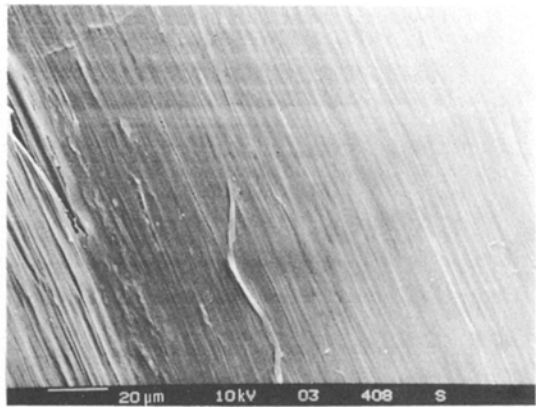

Figure 7 Immersion region of plasma-treated monofilament away from meniscus, draw ratio, 30:1. × 600.

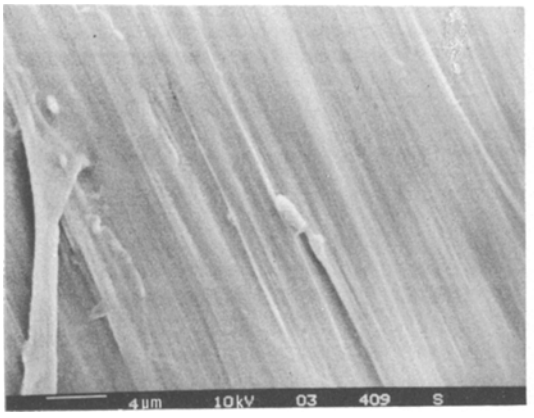

Figure 8 Immersion region of plasma-treated monofilament away from meniscus, draw ratio 30:1. × 3000.

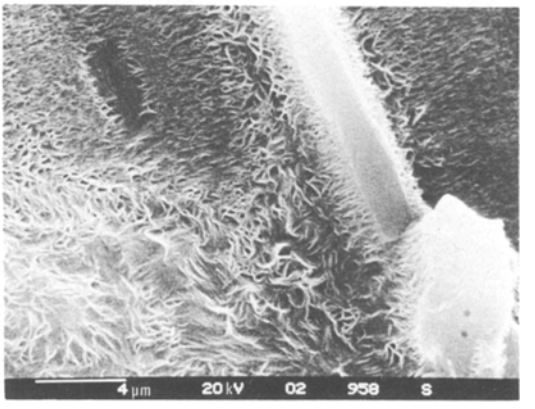

Figure 10 "Melted" groove from plasma-treated monofilament, draw ratio 30:1. × 2850.

pull-out and that the immersed region is rough near the meniscus, where the pull-out force is applied. However, Fig. 7 shows that away from the meniscus the immersed region is significantly smoother, while a higher magnification photograph of this region (Fig. 8) shows no trace of the original cellular surface structure produced by the plasma treatment.

These results suggest that during the pull-out test the samples fail within the fibre, rather than at the interface between fibre and resin. It appears that failure initiates inside the fibre, near the resin meniscus, and that the failure then propagates inside the fibre so that a skin of fibre is removed.* This peel-off mechanism is confirmed by examination of the groove left after pull-out. Fig. 9 shows that the groove is covered by what appears to be a layer of polymer, which we identify with the skin of the immersed fibre. Conclusive evidence for this was obtained in two ways. First, after pulling out the monofilament, the groove was heated above the melting point of polyethylene and examined by SEM. Under high magnification, the typical dendritic surface pattern of a polymer solidified from the melt was observed (Fig. 10). Secondly, the groove was treated with xylene at 130° C to dissolve any adhered polyethylene. The very remarkable result is shown in Fig. 11. Not only has the polymer layer apparent in Fig. 9 disappeared, but the resulting resin surface is an accurate replica of the plasma-treated monofilament surface shown in Fig. 5.

We conclude from these SEM observations that pull-out samples including plasma treated

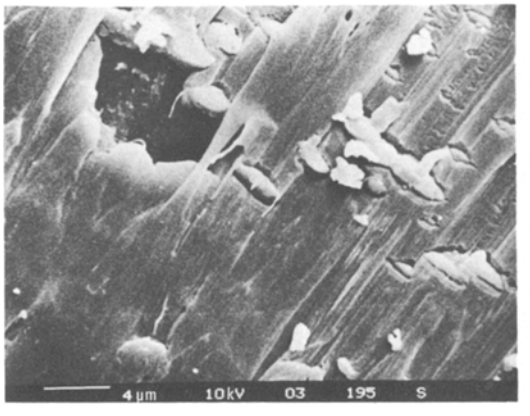

Figure 9 Groove from plasma-treated monofilament, draw ratio 30:1. × 3000.

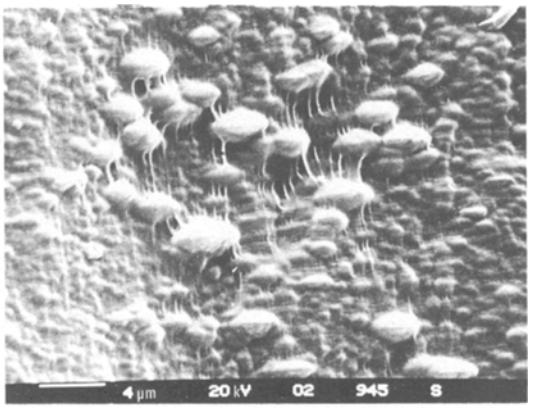

Figure 11 "Dissolved" groove from plasma-treated monofilament, draw ratio 30:1. × 2850.

*We have previously stated that in some cases the failure load is not proportional to the immersion length. This applies to plasma-treated monofilaments and the two-stage mechanism of failure provides an explanation for this result because the first stage, initiation of failure, should not be very sensitive to small changes in the immersion length.

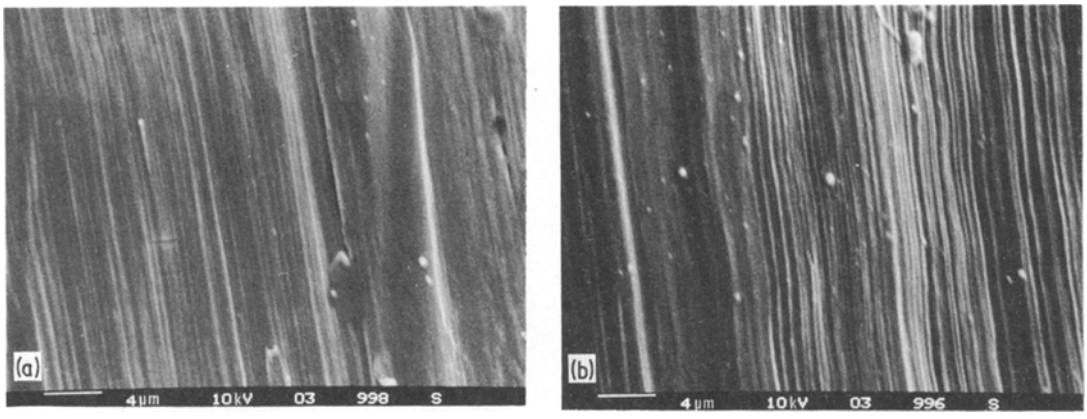

Figure 12 (a) Immersion region of acid-treated monofilament, draw ratio 30:1. (b) Acid-treated monofilament, draw ratio 30:1. × 3000.

monofilaments do not fail at the interface but inside the fibre. This is likely to be associated with the high adhesion values obtained with these systems (see Table I) and it is possible that mechanical interlinking between fibre and resin plays an important role in bringing about this drastic increase in adhesion. It is interesting to note that the liquid resin appears to wet the polyethylene surface perfectly.

In the case of acid-treated material the situation is quite different. Fig. 12a and b show the regions of a monofilament in a pull-out test which were in the immersed and non-immersed region, respectively. Fig. 13 for the corresponding groove shows that the resin again faithfully replicates the monofilament surface, and suggests that failure involves sliding the monofilament along the interface. It can be seen that in contrast to plasma treatment, acid treatment does not produce significant changes in the surface topography other than a small enhancement of the fibrillar pattern.

However, it is clear from Table I that acid treatment produces a significant increase in the adhesion. The SEM results show that, in contrast to plasma treatment, mechanical keying does not play an important role. Although there may be some increase in surface roughness, failure occurs at the resin–monofilament interface and it is likely that chemical modification of the monofilament surface occurs. Alternatively, the acid treatment could have removed a weak, low molecular weight boundary layer off the monofilament surface. This mechanism, leading to improved adhesion properties of low surface energy polymers, has been proposed by, among others, Bikerman [23] and Schonhorn and Hansen [19].

It is interesting to note that in both cases the highly oriented monofilament shows good wettability by the liquid resin. This is also true for untreated monofilament as shown by Fig. 14,

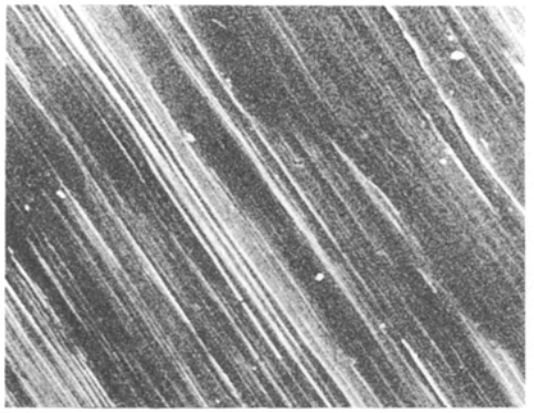

Figure 13 Groove from acid-treated monofilament, draw ratio 30:1; × 3000.

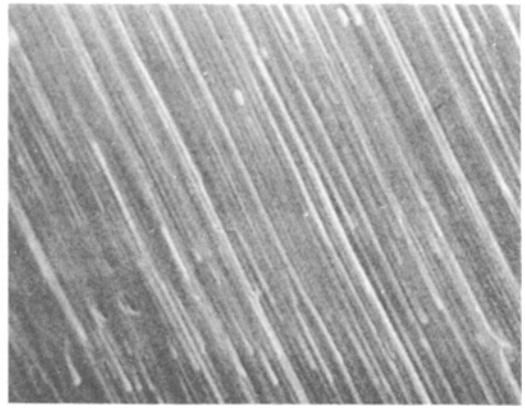

Figure 14 Groove from untreated monofilament, draw ratio 30:1; × 3000.

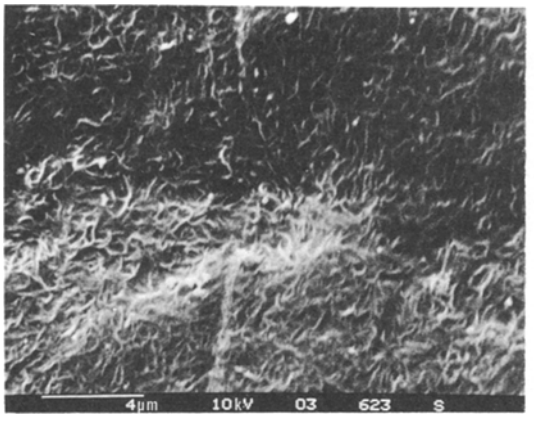

Figure 15 Untreated monofilament, draw ratio, 1:1. × 3000.

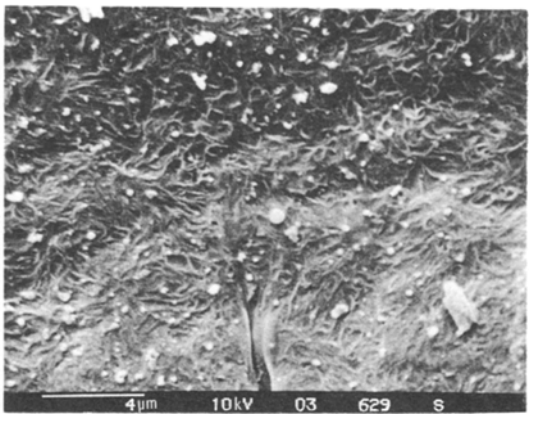

Figure 17 Acid-treated monofilament, draw ratio 1:1. × 3000.

which is the photograph of the groove corresponding to pull-out of an untreated monofilament. All the details on the monofilament surface, as seen in Fig. 4, are replicated by the resin.

4.2. Lower draw ratio and undrawn monofilaments

Fig. 15 is a high magnification micrograph of the surface of an undrawn (spun) monofilament. It shows the typical dendritic surface pattern of a solidified polymer melt, similar to that seen in the "melted" groove of Fig. 10. Although it was not possible to perform pull-out tests on undrawn monofilaments because they are not sufficiently stiff, the interface can still be seen by dissolving the polymer filling the groove in a fabricated test sample. The result is seen in Fig. 16, which shows no evidence of the dendritic pattern and suggests that the resin does not wet undrawn, untreated monofilaments. This dendritic pattern is also retained by the undrawn monofilament after acid treatment, but this time it is well replicated by the resin after dissolving the polymer (Figs. 17 and 18, respectively). On the other hand, the dendritic pattern is not retained in the undrawn plasma-treated monofilament (Fig. 19) where a minutely pitted random pattern can just be resolved, and this is also well replicated by the resin (Fig. 20). It then appears that the liquid resin does not wet well undrawn, untreated monofilaments, but treatment and/or drawing improves this property to a considerable degree.

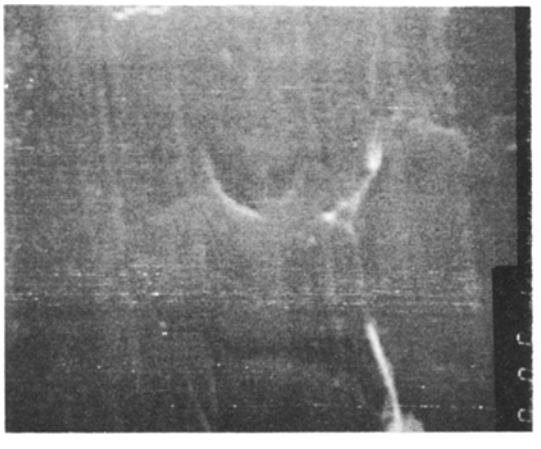

Figure 16 "Dissolved" groove from untreated monofilament, draw ratio 1:1; × 3350.

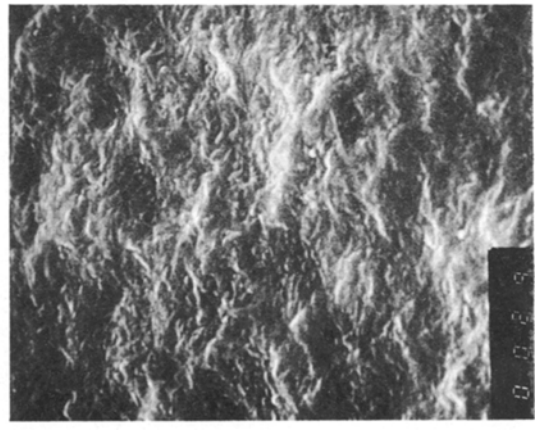

Figure 18 "Dissolved" groove from acid-treated monofilament, draw ratio 1:1, × 3200.

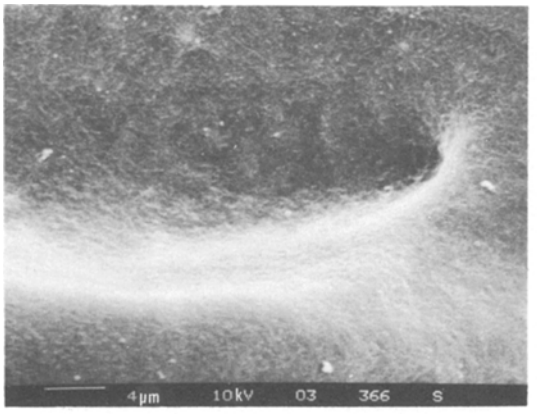

Figure 19 Plasma-treated monofilament, draw ratio 1:1. × 3000.

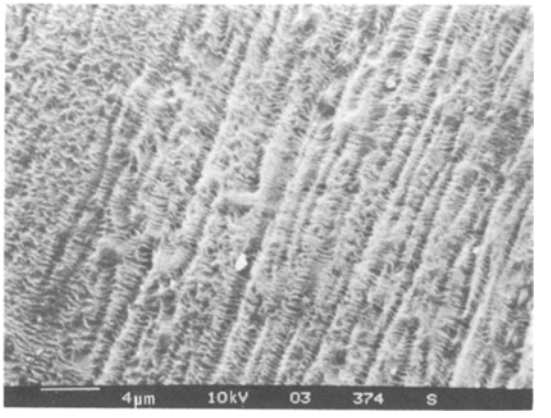

Figure 21 Plasma-treated monofilament, draw ratio 8:1. × 3000.

Turning next to the monofilaments possessing intermediate draw ratios of 8:1 and 15:1, it was found that the SEM results for both acid and plasma treatment were similar in kind to those for the highest draw ratio material. As shown in Figs. 21 and 22, which are to be compared with Fig. 5 above, plasma treatment produces a cellular surface in all drawn monofilaments, but the pit size increases with increasing draw ratio. The pull-out regions again show that failure of the immersed part of the monofilament involves peeling-off a layer of polymer, which takes place in two stages, initiation and propagation of the failure, as discussed for draw ratio 30:1. However, in the draw ratio 8:1 monofilament, the peeled-off layer is very thin, corresponding to the much finer pits on the surface produced by plasma treatment compared with higher draw material. Finally, after dissolving the polymer layer covering the grooves, it may be seen that the resin has produced an excellent replica of the surface of the plasma-treated monofilaments.

In the case of untreated and acid-treated monofilaments of lower draw ratios, the fibrillar surface structure is again moderately enhanced by the application of acid treatment. In all cases the resin has produced an excellent replica of these surfaces and there is no evidence of peeling-off, that is, pull-out involves sliding of the filaments out of the resin along the monofilament resin interface. However, while the immersed regions of the untreated monofilaments are very similar to the non-immersed regions, the immersed regions of the acid-treated monofilaments show the fibrillar structure somewhat lifted-up (Fig. 23), as if a significant degree of adhesion has to be overcome during pull-out. This effect decreases with increasing draw ratio and is fully consistent with the adhesion values seen in Table I, mainly very low adhesion for untreated samples compared with

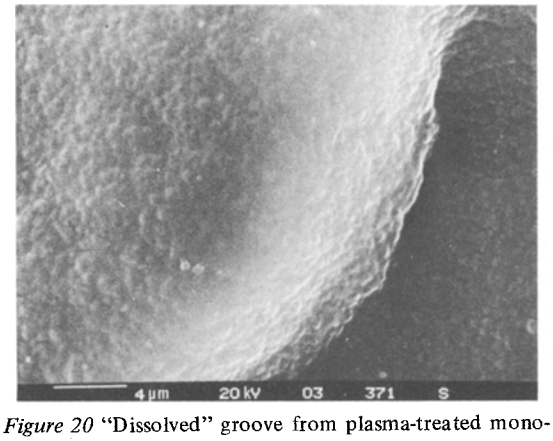

Figure 20 "Dissolved" groove from plasma-treated monofilament, draw ratio 1:1, × 3000.

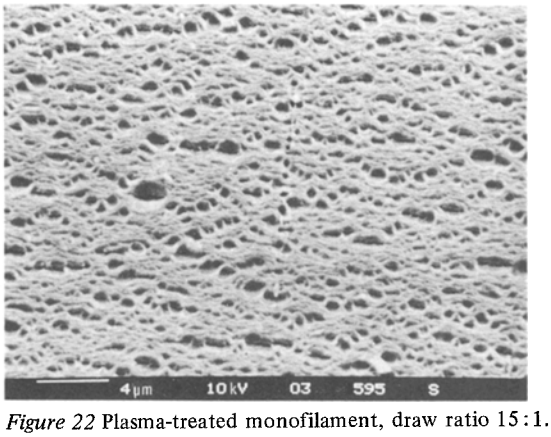

Figure 22 Plasma-treated monofilament, draw ratio 15:1. × 2850.

acid-treated samples, and the effect of acid treatment decreasing for increasing draw ratio as the monofilaments become chemically more stable [22].

From the discussion above it appears that several factors contribute to the very high adhesion values obtained with plasma-treated monofilaments with draw ratio 30:1 (see Table I). Firstly, the increase in the pit size with increasing draw ratio allows a more effective keying between resin and monofilament, and the peel-off proceeds deeper inside the monofilament as the draw ratio increases. Secondly, the initiation of the failure in the rough regions involves tensile failure of the fibrils as well as shear failure between the fibrils (see Fig. 6). Therefore, the increase in tensile strength of the fibrils with increasing draw ratio should be accompanied by a higher failure load for the pull-out system. Finally, consideration should be given to other factors more difficult to quantify. For example, the number of fibrils being broken simultaneously should depend on the pit size.

4.3. Monofilament tensile strength

The fall in tensile strength is much greater for plasma than for acid treatment. This is consistent with the SEM evidence, which shows that acid treatment does not appear to produce major changes in the surface topography, whereas plasma treatment produces surface pits which are likely to act as flaws and hence reduce the tensile strength. The increase in cellular structure with increased draw ratio relates qualitatively to the corresponding decrease in tensile strength.

5. Conclusions

(1) Although the low-viscosity epoxy resin does not wet undrawn polyethylene monofilaments, treatment and/or drawing produces good wettability characteristics, as seen from scanning electron micrographs of the grooved region in a pull-out specimen. The level of adhesion for drawn monofilaments without further surface treatment is, however, low.

(2) Chromic acid and plasma treatment both produce significant increases in the measured adhesion of drawn monofilaments. The mechanism of failure for untreated and acid-treated monofilaments involves sliding along the monofilament–resin interface. Plasma treatment produces a cellular structure on the monofilament surface into which the resin penetrates to give

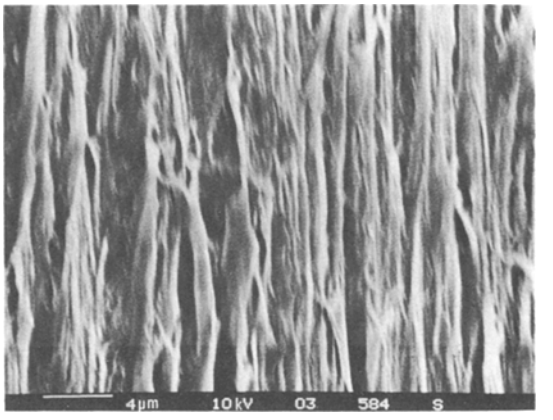

Figure 23 Immersion region of acid-treated monofilament, draw ratio 8:1. X 3000.

mechanical keying between resin and monofilament. The failure in the pull-out test then involves a two-stage rupture within the monofilament with two well-defined regions associated with the initiation and the propagation of the failures, respectively. The surface layer of the monofilament peels-off and remains attached to the resin. A combination of factors increases the pull-adhesion of plasma-treated monofilaments with draw ratio 30:1 to at least twice the value obtained with any other combination of treatment and draw ratio.

(3) Acid treatment has a very small effect, if any, on the tensile strength of the monofilaments. The most effective plasma treatment, on the other hand, produces a 40% decrease in tensile strength. This can be attributed to the production of the cellular structure on the surface which provides flaws at which failure can initiate.

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