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The adhesion behaviour of high modulus polyethylene fibres following plasma and chemical treatment

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Previously published pull-out adhesion results have been substantiated by more extensive studies of chemical and plasma treatment. Particular attention has been paid to the affect of geometrical variables on the values of adhesion obtained. The effect of strain rate has also been examined. Most of the results can be understood on a semi-quantitative basis by a simple extension of lap joint theory.

1. Introduction

A previous publication [1] reported a study of the effect of chromic acid treatment and plasma etching in oxygen on the surface adhesion of ultra-high modulus polyethylene (UHMPE) fibres [2] to an epoxy resin. The adhesion was determined by pull-out tests, and showed a significant improvement for both acid and plasma treatments. Different mechanisms of failure were observed, and these will be discussed further in the present paper, which describes the adhesion of monofilaments subjected to a much wider range of treatment. The previous publication [1] mentioned the effect of geometrical variables and loading rates, and these are now examined further. Finally, lap joint theory is applied to several semi-quantitative aspects of the pull-out experimental results.

2. Experimental details

2.1. Materials

Two polyethylene homopolymers were used, Unifoss 2912 ($\bar{M}_w$ = 224 000, $\bar{M}_n$ = 24 100) and Alathon 7030 ($\bar{M}_w$ = 115 000, $\bar{M}_n$ = 28 000). These were melt-spun to monofilaments of $\simeq$ 1.4 mm and $\simeq$ 1.0 mm diameter, respectively, and stretched at a high temperature to a nominal draw ratio of 30, to give drawn monofilaments of $\simeq$ 0.26 mm and $\simeq$ 0.19 mm diameter, respectively. Further details of the processing are given by Ladizesky and Ward [1].

Ciba-Geigy XD927 epoxy resin was used throughout this work (now marketed as Araldite LY1927/GB). This is a low viscosity, room temperature curing resin. Further details are given by Ladizesky and Ward [1].

2.2. Treatment of the drawn filaments

2.2.1 Chemical treatment

The monofilaments were immersed in one of the following solutions.

(a) Standard chromic acid solution: this solution has been used in previous work [1]. The composition (by weight) is

$K_2Cr_2O_7$ – 7 parts
H_2SO_4 (concentrated) – 150 parts
H_2O – 12 parts

(b) Ceric solution: cerium ions are strong oxidants, and form relatively safe solutions to handle. Somewhat arbitrarily, we chose a composition with 0.5 N of cerium ions:

(i) 500 ml H_2O (de-ionized)
(ii) 105 g $Ce(SO_4) \cdot 4H_2O$
(iii) 50 ml of a solution made up of 10% (by weight) of H_2SO_4 in deionized water.
(iv) 15 ml of H_2SO_4 (concentrated)

Item (ii) was dissolved in item (i), and then (iii) and (iv) added in this order. This procedure was found necessary to obtain complete solubility of the cerium salt, and to avoid precipitation when the solution was heated above room temperature. The presence of H_2SO_4 increases the redox potential of the solution, i.e. increases its oxidative power.

Chemical treatments of UHMPE fibres were carried out at either room temperature (RT) or 65° C for immersion times of 1 or 10 min. Immediately after treatment the filaments were rinsed in deionized water, followed by washing in running water for 2 h. The monofilaments were then given a further rinsing in deionized water and dried overnight in an air oven at 40° C.

2.2.2. Plasma treatment

As we have given general details of the plasma treatment previously [1], it is only necessary here to point out any departure from the previous procedure.

Plasma treatment of monofilament coils was carried out in a Plasmaprep 300 unit [3]. This unit is basically similar to the Plasmaprep 100 used previously [1], except that there is a larger power supply, a larger

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reaction chamber, a capability for plasma treatment with a mixture of up to two gases, and facilities for the control (via a throttle) and measurement of the pressure in the reaction chamber.

The present experiments included treatment with four different gases. These were oxygen, found highly successful as an adhesion enhancer in pull-out tests [1] and composites research [3, 4], two inert gases, helium and argon, and Freon 14 (CF_4), the latter used by the electronic industry for etching printed circuits. In some instances treatments were carried out with a mixture of gases.

Other than possible chemical reactions, the main parameter characterising the plasma treatment is the dissipated energy. As this could not readily be monitored directly, the plasma treatment was characterised by the values of the operating parameters, namely (a) intensity (a combination of power setting and gas flow), (b) duration of the treatment, (c) throttle setting and (d) gas. After exploratory work on the interaction between these parameters in affecting the plasma treatment it was decided to adopt distinct parameter levels defined as follows:

(a) Intensity: two different combinations of power and gas flow were used. M represents a combination with values close to, but not quite reaching those which will damage the monofilaments. m represents a combination with values slightly above those which will initiate glow in the reaction chamber.

It should be noted that the conditions M and m may be satisfied for a range of power and gas flow values. However, these were found to be within relatively narrow limits, and any differences are not very significant for our purposes.

(b) Duration of the treatment: M stands for 10 minutes, m stands for 0.5 minutes.

(c) Throttle setting: M stands for fully closed throttle, giving a pressure in the reaction chamber of 35×10^{-3} Torr with no gas flow. m stands for the throttle partially open, such that the pressure without gas flow was 0.8 Torr.

It should be noted that the filaments could not be damaged by plasma treatment with helium gas, even when the intensity was a combination of power and gas flow with values close to the maximum available in our equipment. Surprisingly, these values damaged the fibres when argon gas was used, in which case condition M was obtained for a moderate reduction of the gas flow.

For completeness, Table I shows the actual values of the plasma parameters for the different gases used.

2.2.3. *Nomenclature for monofilament treatment*

The following examples illustrate the nomenclature adopted in this work to indicate the chemical and plasma treatments given to the monofilaments

(a) Chemical Treatment: "A" stands for chromic acid solution, "Ce" stands for ceric solutions.

A:1/RT = 1 minute immersion in chromic acid solution at room temperature Ce: 10/65° C = 10 minutes immersion in ceric solution at 65° C.

(b) Plasma treatment: The parameters are specified in the following order: Intensity/Duration of Treatment/Throttle Setting (Gas).

Thus, M/m/m(CF_4) represents a treatment with condition M intensity, 0.5 min exposure and the throttle partially open, using CF_4 gas.

2.3. Pull-out tests

Pull-out adhesion was measured as described previously [1] by embedding one end of a length of

TABLE I Values of plasma parameters

Gas	Intensity			Throttle setting	
	Power (W)	Flow ($cm^3\ min^{-1}$)	Nomenclature	Pressure during Treatment (Torr)*	Nomenclature
O_2	60	20	M	0.6	M
	52	60		1.8	m
	30	10	m	0.3	M
	30	10		1.0	m
He	200	60†	M	1.6	M
	200	60†		2.3	m
	20	20†	m	0.2	M
	20	20†		1.0	m
Ar	200	40	M	0.5	M
	20	10	m	0.1(5)	M
	20	10		0.9	m
CF_4	40	50	M	0.6	M
	100	50		1.3	m
	20	10	m	0.2	M
	60	10		0.9(5)	m

*The Torr values are those read on the Pirani gauge. They are not true pressures because the gauge is calibrated for air or nitrogen only.
†These are the markings read on the flow meters. They are not actual flow in $cm^3\ min^{-1}$ because no calibration was available for helium gas.

monofilament ($\simeq 20$ cm) in a disc of resin and measuring the force required to pull the filament out of the disc. The pull-out adhesion was defined as

$$\frac{\text{Failure load}}{\text{Interface area}} = \frac{\text{Failure load}}{\pi DL}$$

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

2.4. Scanning electron microscopy (SEM)

All the scanning electron micrographs were taken with a Cambridge Stereoscan 150 MkII. In addition to the filaments, the holes left in the disc of resin after pull-out were also examined, when they become grooves. In some cases a few micrometres of the monofilament skin remained in the resin groove after pull-out. This skin was either observed directly, or dissolved before observation (dissolved grooves). Further experimental details have been given previously.

2.5. Miscellaneous experimental details

All measurements were carried out at room temperature, namely 21 $\pm$ 2° C. Unless otherwise stated, the following nominal values apply throughout this work.

Monofilament diameter: 0.26 mm

Immersion length: 4.5 mm

Loading rate: Between 0.9 N min^{-1} and 3.4 N min^{-1}, where loading rate is defined as

$$\frac{\text{Maximum load}}{\text{Time to reach maximum load}}$$

It should be noted that the load against time curves obtained with the pull-out experiments in the present study were almost linear.

The experimental errors experienced in the pull-out adhesion measurements were discussed previously [1] where it was reported that the maximum scatter for nominally identical samples was $\pm$ 14%.

A problem was encountered when studying the effect of the filament diameter on the measured pull-out adhesion of plasma treated fibres using the standard nominal immersion length of 4.5 mm. For the thinnest monofilament, with a diameter of $\simeq 0.19$ mm, the pull-out load was close to the tensile failure load of the fibre. Thus, the fibre often broke before pull-out. Taking into account the relative insensitivity of the pull-out load to the immersion length, as will be shown below, these tests were therefore performed with a substantially reduced nominal immersion length namely 1.5 mm.

It was then necessary to ensure that the method of preparation of samples with substantially reduced immersion length does not introduce new failure mechanisms in the pull-out tests. This was investigated by preparing samples with 1.5 mm nominal immersion length in two different ways. Samples with 1.5 mm and 4.5 mm nominal immersion length were prepared with the standard technique, as shown previously [1], namely by pouring into the mould the correct amount of resin. The samples with 1.5 mm nominal immersion length were tested without modification, and in Table II these are referred to as moulded samples. The samples with 4.5 mm nominal immersion length were milled along a full diameter, such that the immersion length remains at a nominal 1.5 mm. These samples are referred to as milled. Table II shows that the method of preparation had no significant effect on the pull-out adhesion, suggesting that for plasma treated monofilaments the conclusions obtained from a study of the smaller immersion length samples are also applicable to pull-out tests with standard samples. The errors in Table II are the standard deviation for at least five samples.

3. Results and discussion

3.1. The effect of different chemical and plasma treatments

The main pull-out results are shown in Table III, and, for convenience are summarized in a simplistic fashion in Table IV. In the latter case, strongest plasma treatment indicates M/M/M parameters. Any other combination of parameters is referred to as weak plasma treatment.

It may be seen that the lowest adhesion is obtained with untreated fibres, and for fibres treated with cerium solution. A moderate increase in adhesion is produced by chromic acid treatment and all plasma treatments with CF_4 gas, and weak plasma treatment with argon gas. A further increase in adhesion is only apparent for plasma treated fibres, i.e. all treatments with helium gas (but only marginal improvement), the strongest treatment with argon gas and the most weak treatments with oxygen gas. Higher still adhesion is only observed for plasma treatments using oxygen gas, all for 10 minutes exposure. The strongest plasma treatment with oxygen gas gave the best adhesion by a significant margin.

In some cases plasma treatment was carried out with a mixture of two gases, but these experiments did not provide unexpected results and are not included in Tables III and IV. The only noteworthy feature occurred when one of the gases was oxygen, in which case the resultant adhesion was broadly determined by the parameters associated with this gas.

TABLE II Pull-out tests of plasma treated monofilaments with different diameters

Sample	Radius (mm)	Pull-out adhesion (MPa)	Average pull-out load (N)	Average pull-out tensile stress (MPa)
Moulded	0.13	9.6 (From Fig. 9b)	11.8	222
Milled		9.6 $\pm$ 0.5		
Moulded	0.095	13.3 $\pm$ 1.0	12.4	437
Milled		14.5 $\pm$ 1.0		

TABLE III Effect of monofilament treatment on the pull-out adhesion

Treatment		Pull-out adhesion (MPa)
Untreated		0.6
A: 1/*RT*		0.8
A: 1/65° C		1.4
A: 10/65° C		1.7
Ce: 1/*RT*		0.7
Ce: 1/65° C		0.6
Ce: 10/65° C		0.7
O_2	M/M/M	4.4
	M/M/m	2.9
	M/m/M	2.4
	m/M/M	2.5
	M/m/m	2.0
	m/M/m	3.7
	m/m/M	1.8
	m/m/m	2.7
He	M/M/M	1.9
	M/M/m	1.9
	M/m/M	1.9
	m/M/M	2.0
	m/m/m	1.8
Ar	M/M/M	2.3
	M/m/M	1.2
	m/M/m	1.6
	m/m/M	1.1
CF_4	M/M/M	0.9
	M/M/m	0.7
	M/m/M	0.8
	m/M/M	1.1
	M/m/m	0.9
	m/M/m	1.3

Prior to the presentation and analysis of the SEM observations, it is convenient to summarise here some of the conclusions reached in the previous work [1]. It was found that the untreated fibres, showing the lowest adhesion, had a fibrillated surface structure which remained virtually unchanged after pull-out. Failure of these samples occurred along the interface, and the resin produced a good replication of the original fibre surface. Chromic acid treatment left this situation largely unchanged, except for a moderate increase in adhesion. A rigorous plasma treatment with oxygen gas gave rise to a strongly pitted surface topography, which was penetrated by the resin. This resulted in an interlocking mechanism which is largely responsible for the high adhesion observed. Failure of the pull-out samples occurred by peeling-off of the filaments, and this took place in two stages, namely initiation and propagation of the failure. The initiation occurred in the immersion region near the meniscus, where the force is applied, and was visually characterized by a rough appearance owing to tear of the fibrils. The failure then propagated through the rest of the immersion region. This appeared relatively smooth, and it is likely that shear inside the filament, along the fibrils, makes a substantial contribution to this stage. It was also shown that the resin surface is an accurate replica of the original surface of the plasma treated monofilament.

TABLE IV Summary of the effect of monofilament treatment on the pull-out adhesion

Adhesion level	Limits (MPa)	Treatment
Low	0.4 – 0.7	Untreated All Ceric Solutions
Medium	0.8 – 1.7	All Chromic Acid Solutions All Plasma Treatment with CF_4 Gas Weak Plasma Treatment with Ar Gas
High	1.8 – 2.8	Strongest Plasma Treatment with Ar Gas All Plasma Treatment with He Gas Most Weak Plasma Treatment with O_2 Gas
Very high	2.9 – 3.7	M/M/m (O_2) m/M/m (O_2)
Maximum	4.4	Strongest Plasma Treatment with O_2 Gas

The present results fully confirm and complement the conclusions summarized above. Highest adhesion with chemical treatment is obtained with A : 10/65° C. Some minor but noticeable roughness is observed in the immersion region near the meniscus, as shown in Fig. 1. Elsewhere in the immersion region the original surface topography of the treated filament remains unchanged. Thus, it appears that the two stage failure proposed in our previous work [1] for plasma treated filaments is also applicable to a rigorous chromic acid treatment. However, in the latter case the failure occurs largely along the interface.

Treatment with cerium solution produces a small enhancement of the fibrillar structure of the filament. However, no increase of adhesion is observed, and the immersion regions of the filaments are identical to the non-immersed regions. Fig. 2a shows the immersion region of a filament treated with cerium solution for 10 min at 65° C, and Fig. 2b shows the corresponding groove.

The present studies with the M/M/M (oxygen) treated filaments do not need to be presented here in detail, since they are consistent with those obtained previously [1]. For completeness, Fig. 3 shows the plasma treated surface obtained with the equipment used in this work, i.e. Plasmaprep 300.

Figure 1 Immersion region of A: 10/65° C treated monofilament near meniscus.

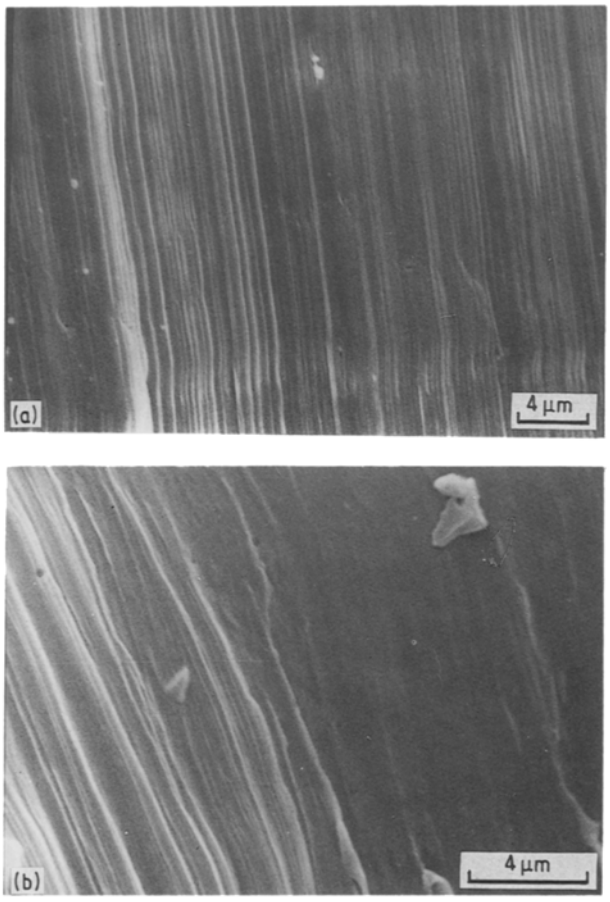


Figure 2 (a) Immersion region of cerium: 10/65° C treated monofilament away from meniscus. (b) Groove from cerium: 10/65° C treated monofilament.

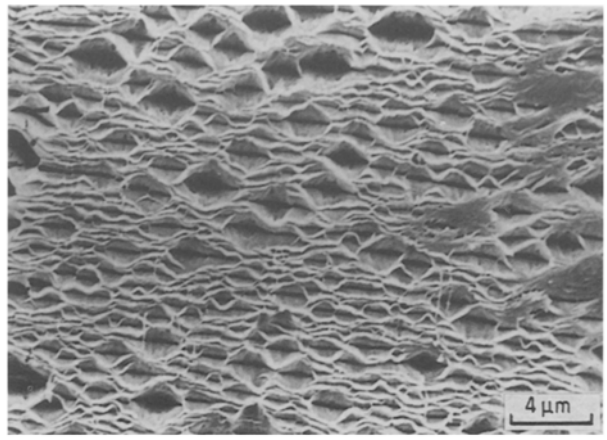


Figure 3 M/M/M (oxygen) treated monofilament.

It is of interest to examine two other filaments plasma treated with oxygen gas, namely M/M/m (oxygen) and m/m/m (oxygen). The former represents a plasma treatment with maximum intensity and time of exposure, but carried out at a relatively high pressure. The latter treatment has also been carried out at high pressure, but the filament was exposed for minimum time, and the intensity was just sufficient to maintain glow.

Fig. 4a shows the filament with M/M/m (oxygen) treatment. The surface is extensively pitted, but the pits are smaller than those produced by M/M/M (oxygen). As a consequence, the fibrillated surface topography is still discernible. The resin gives an excellent reproduction of the fibre surface (Fig. 4b), and the expected peel-off mechanism has taken place, with initiation of the failure near the mensicus (rough section near the meniscus, Fig. 4c) and a propagation stage giving a smoother section in the rest of the immersion region, as seen in Fig. 4d.

Table III shows that the adhesion obtained with M/M/m (oxygen) treatment is significantly smaller than the maximum adhesion. This is due to the smaller pit size, leading to a thinner peel-off skin. A similar situation was observed in the previous work [1] when comparing the pull-out adhesion of plasma treated filaments with different draw ratios. It was found that lower draw ratios were associated with smaller pits and lower adhesion. The present results indicate that the pressure during treatment is also an important parameter, and a possible explanation would invoke a reduction of the mean free path of the bombarding particles, which will then acquire less energy before reaching the sample, and produce smaller pits.

Next, consider samples with m/m/m (oxygen) plasma treatment. Fig. 5a shows that the treatment has had little effect on the monofilament surface, although there is a suggestion that it may have produced a high density of relatively very small pits. The resin accurately replicates this finely detailed surface, as seen in Fig. 5b for a dissolved groove. The immersion region of the filament shows no trace of the pits, but, instead, a two stage peel-off mechanism has occurred. Fig. 5c shows the rough surface near the meniscus. The high adhesion obtained may be associated with the peel-off mechanism, although the very thin layer involved produced adhesion lower than for the M/M/M (oxygen).

The SEM results for pull-out samples made with M/M/M plasma treated filaments using helium, oxygen or CF_4 gases relate well to the corresponding adhesion levels shown in Table I. CF_4 produces adhesion levels similar to chemical treatment, and Fig. 6 shows that this treatment leaves the filament surface virtually unchanged. Examination of the immersion regions and the grooves indicates a failure mechanism broadly similar to that discussed for the untreated and chemically treated filaments, namely sliding of the filaments along the interface. Plasma treatment with both helium and argon gases produces some minor but noticeable pitting on the surface of the monofilaments as shown in Fig. 7 for helium gas. This accounts for both the high adhesion levels seen in Table IV and a minor degree of roughness observed in the immersion region near the meniscus. Fig. 8 shows that the small pits on the treated filaments, in this case produced using argon gas, has been reproduced by the resin.

It can, therefore, be concluded that the treatments M/M/M (helium) and M/M/M (argon) and possibly m/m/m (oxygen), produce a minor but noticeable degree of pitting on the surface of the filaments, leading to a two stage peel-off mechanism and adhesion values within the 'high' level (see Table IV). However, Table III shows that of these three treatments, m/m/m/ (oxygen) is associated with the highest adhesion by a small but significant amount. It is, therefore, possible

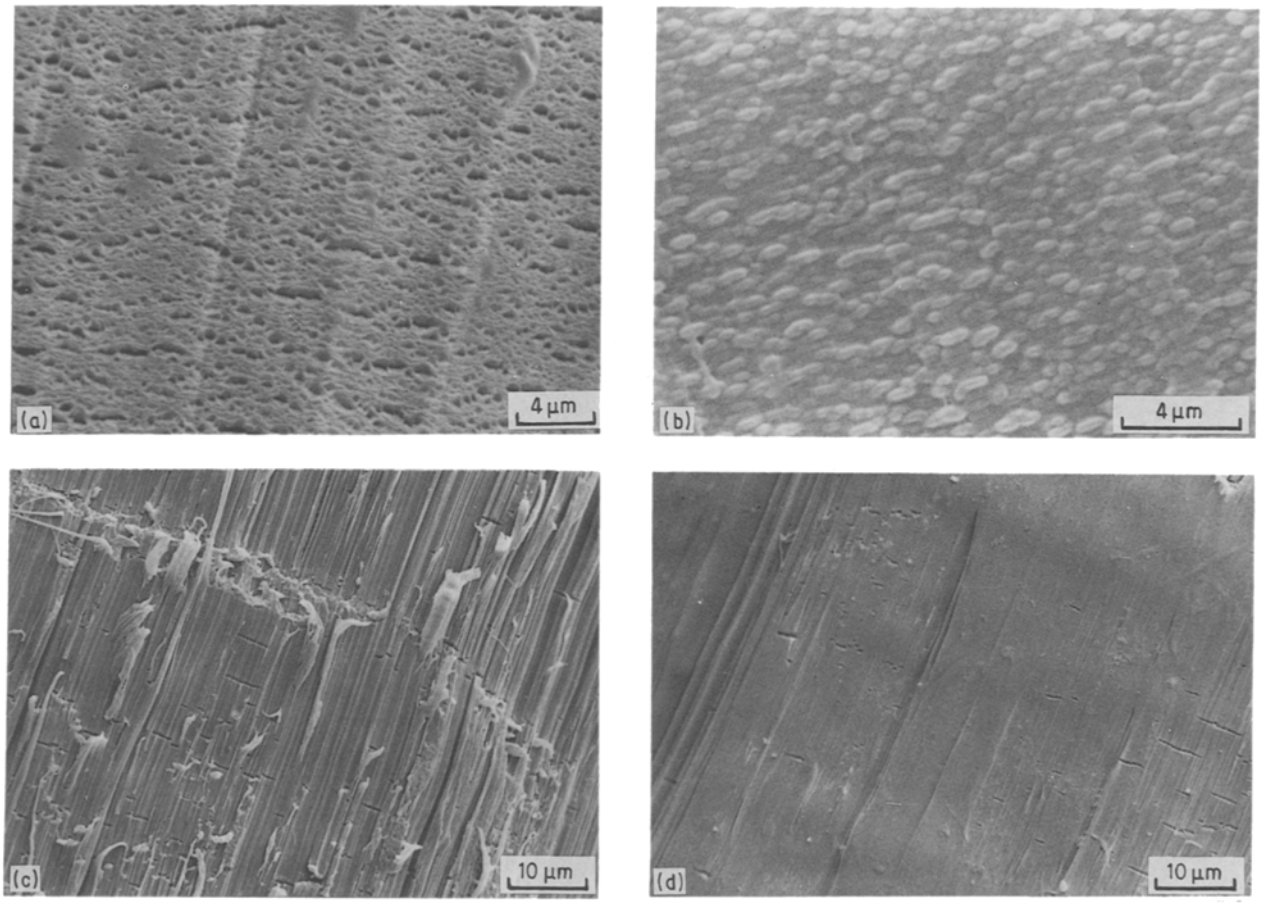


Figure 4 (a) M/M/m (oxygen) treated monofilament. (b) Dissolved groove from M/M/m (oxygen) treated monofilament. (c) Immersion region of M/M/m (oxygen) treated monofilament near meniscus. (d) Immersion region of M/M/m (oxygen) treated monofilament away from meniscus.

that the adhesion of filaments subjected to plasma treatment with oxygen gas has a chemical contribution which is absent when the other gases are used.

Plasma treatment with helium or argon often produces a significant amount of debris, namely particles smaller than 1 μm diameter (see Fig. 7). This debris was not observed on filaments subjected to any other treatment, or left untreated. It is possible that some contaminants were present in the helium and argon gases, but it is surprising that the effect was only apparent when using the inert gases.

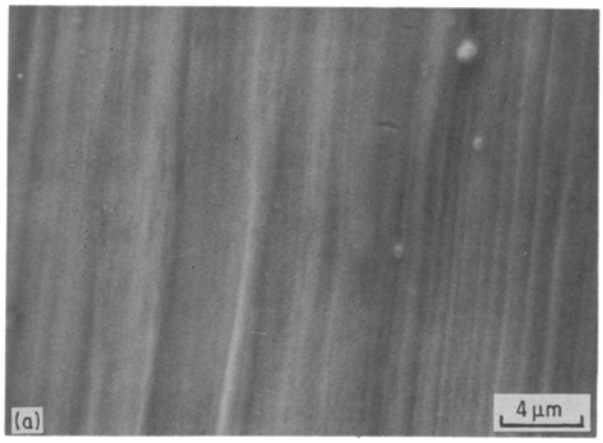
3.2. Geometrical variables

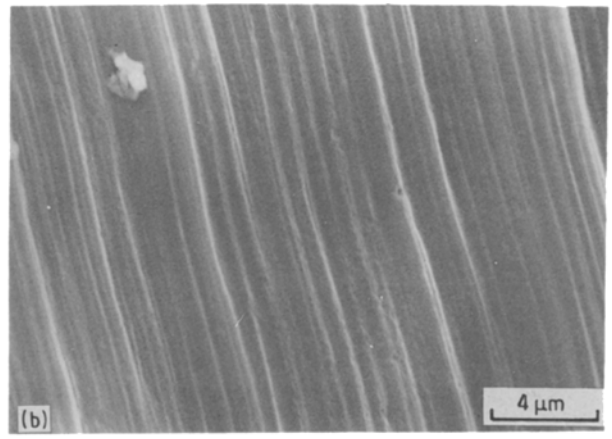
The geometrical variables are the immersion length and the filament diameter. Each will be dealt with separately.

The effect of immersion length was studied with both untreated and M/M/M (oxygen) plasma treated monofilaments of 0.26 mm nominal diameter. The pull-out immersion lengths varied between 1 mm and 10 mm and the corresponding pull-out adhesion may be seen in Figs 9a and b for untreated and plasma treated monofilaments, respectively. Plasma treated samples show a large decrease of the calculated pull-out adhesion with increasing immersion length. However, the trend becomes less pronounced as the immersion length approaches 10 mm. This result may be interpreted in the light of the two-stage failure mechanism, which was described in our previous publication [1]. The initiation of failure takes place near the entrance of the filament into the disc of resin, where the force is applied. It appears reasonable to assume that this stage will be relatively independent of immersion length, and the substantial decrease of the pull-out adhesion with increasing immersion length, particularly pronounced between 1 mm and 5 mm, indicates that a significant proportion of the energy required at failure is, in fact, expended on the initial stage of the failure.

As the immersion length increases above 5 mm the pull-out adhesion begins to level off, suggesting that an increasing proportion of the energy at failure is now being expended on the propagation stage, namely peel-off of the fibre through shear parallel to the orientation of the fibrils. This mechanism is likely to involve a failure energy broadly proportional to the interface area because higher energy will be required to shear larger areas, and/or because the polymerization shrinkage of the resin produces a compressive force on the filament.

Fig. 9a shows that the pull-out adhesion of untreated monofilaments is not affected by variation of the immersion length between 1.5 mm and 10.0 mm. It was shown [1] that failure in this case involves one stage only, i.e. sliding of the filament along the interface. This movement is opposed by the pressure arising during the resin polymerization. The force to produce failure is, therefore, proportional to the interface area or, with similar monofilament diameter, to the immersion length. However, as the immersion length is decreased below 1.5 mm the pull-out adhesion of





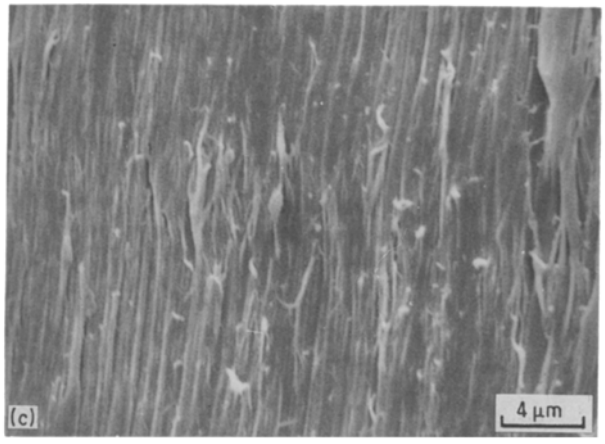


Figure 5 (a) m/m/m (oxygen) treated monofilament. (b) 'Dissolved' groove from m/m/m (oxygen) treated monofilament. (c) Immersion region of m/m/m (oxygen) treated monofilament near meniscus.

untreated monofilaments increases, indicating that a new mechanism became operative. This matter was not pursued further.

The effect of filament diameter on the pull-out adhesion was only studied with M/M/M (oxygen) plasma treated monofilaments, using a nominal immersion length of 1.5 mm (see Section 2.5). Table II shows a significant increase of the calculated pull-out adhesion for a moderate decrease of filament diameter. However, within experimental error identical pull-out loads were obtained for filaments of 0.26 mm and 0.19 mm nominal diameter.

This effect is similar in nature to the decrease of the calculated pull-out adhesion with increasing immersion length. This has been attributed to the insensitivity of the initial stage of failure to interface area, and similar considerations apply to changing the filament diameter. It therefore follows that both these geometrical parameters, immersion length and filament diameter, have to be maintained approximately constant for reliable comparative testing.

3.3. Effect of loading rate

The effect of loading rate was studied with both untreated and M/M/M (oxygen) plasma treated monofilaments of 0.26 mm nominal diameter, using an immersion length of 4.5 mm.

The results are shown in Fig. 10a for untreated monofilaments, and in Fig. 10b for plasma treated monofilaments. In both cases it may be seen that the pull-out adhesion increases with increasing average loading rate. These results indicate the viscoelastic nature of the mechanisms operating during failure, i.e. friction for untreated monofilaments and two stage peel-off for plasma treated monofilaments. SEM was used to examine the immersed and non immersed regions of filaments tested with the lowest and highest average loading rates. The results were entirely in agreement with those presented previously [1], using similar filaments and intermediate loading rates. We therefore conclude that within the range of loading

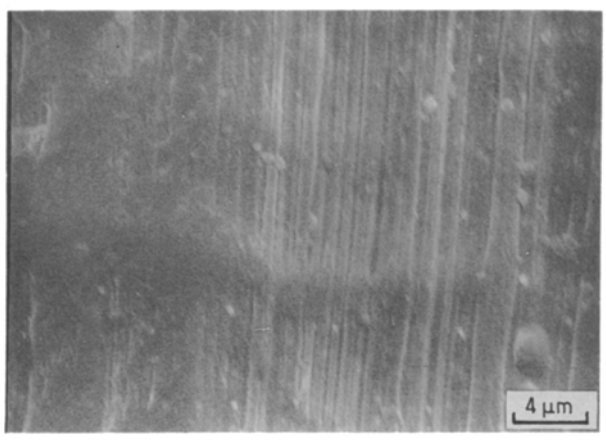


Figure 6 M/M/M (CF_4) treated monofilament.

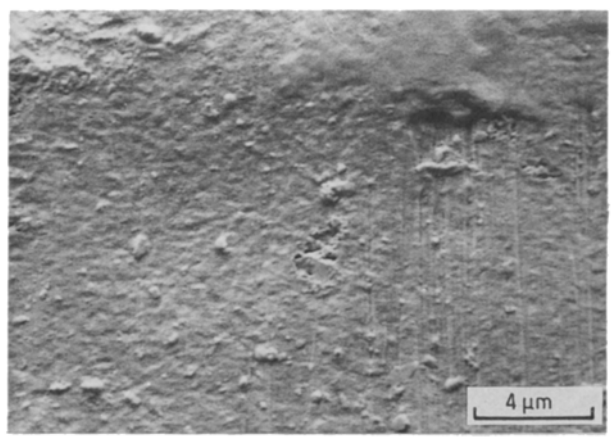


Figure 7 M/M/M (helium) treated monofilament.

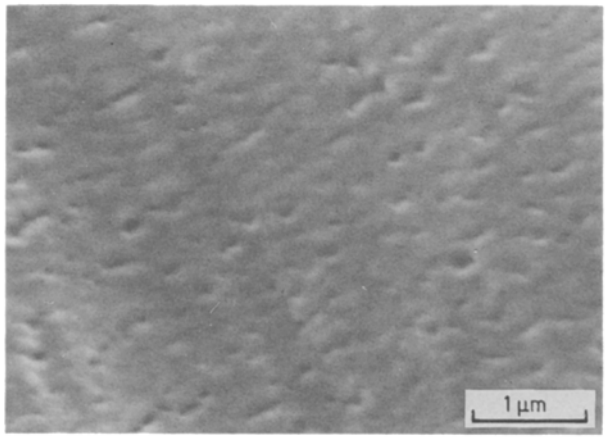


Figure 8 'Dissolved' groove from M/M/M (argon) treated monofilament.

rates shown in Fig. 10, the mechanisms of failure appear to be those identified previously.

4. Pull-out measurements: Consideration in terms of the behaviour of lap joints

In a previous publication [4] we have described the successful application of lap joint theory to several semi-quantitative aspects of the shear strength of highly drawn linear polyethylene sheets. A similar approach will now be attempted for the pull-out adhesion of the UHMPE monofilaments which were plasma treated for maximum adhesion (M/M/M/(oxygen)).

The previous publication [4] considered lap joints where bending takes place. For the pull-out experiments, however, it is clear that the correct analogy is a lap joint with no bending. The situation is illustrated by the double lap joint shown in Fig. 11. Here, L is the immersion length, h_0 the thickness of the adhesive and δ the thickness of the middle bar. The system is referred to orthogonal axes x, z, in the plane as shown, with the y axis perpendicular to the plane of the sheet.

The treatment of the double lap joint problem is originally due to Volkersen [5], and has been further discussed by Eley [6] and Bikermann [7]. These authors also considered the problem of the pull-out of an extensible thin strip glued to a rigid wall. If the thin strip is replaced by a monofilament of circular cross-section, the results obtained can be applied to the present pull-out experiments.

Returning to the double lap joint problem, Volkersen's treatment [5] may be readily adapted to a rod immersed in a wall to which it is glued. The only modifications required are those imposed by differences in geometry, which will not be summarised briefly.

Fig. 11 is still applicable, but now δ is the diameter of the bar ($=2r$). On any particular plane, z = constant, the tensile force on the rod should be exactly balanced by the shearing forces appearing in the adhesive. This condition gives

$$\frac{\delta f}{\delta z} = \frac{2\tau}{r} \tag{1}$$

where f and τ are the tensile stress in the rod and the shear stress in the adhesive, respectively. If E is the Young's modulus of the rod we have

$$\tau = \frac{Er}{2}\frac{\delta^2 l_1}{\delta z^2} \tag{2}$$

where l_1 is the displacement of any point of the rod, initially on the plane z = constant.

The solution of Equation 2 requires defining boundary conditions. For example, if the rod is a thin filament immersed in a large disc of rigid resin, the cross-section of the filament on the plane $z = 0$

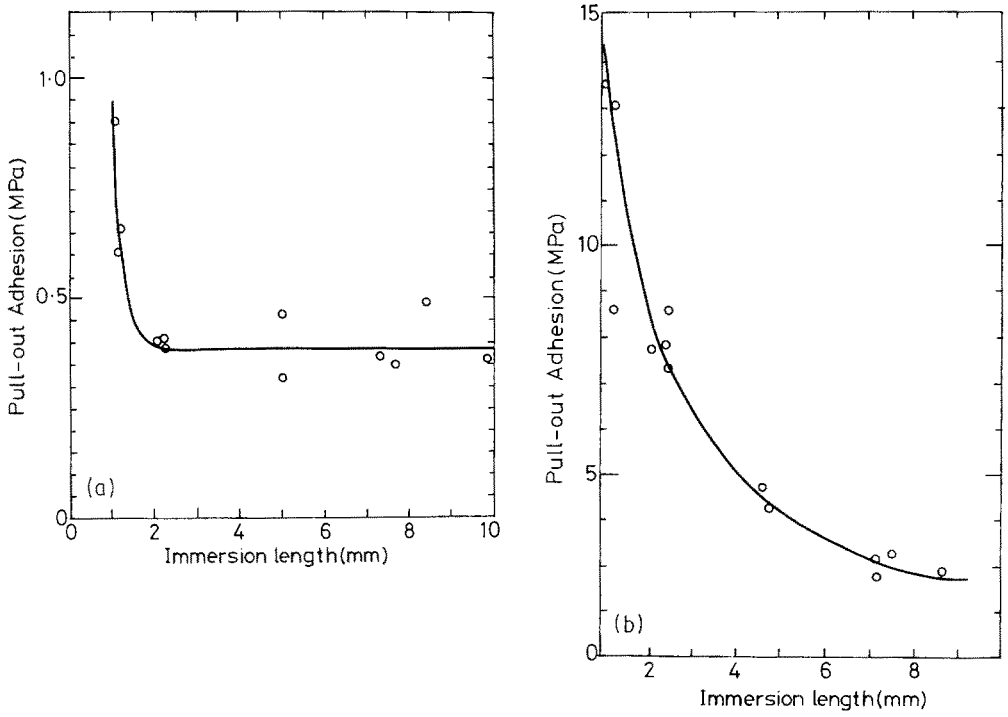
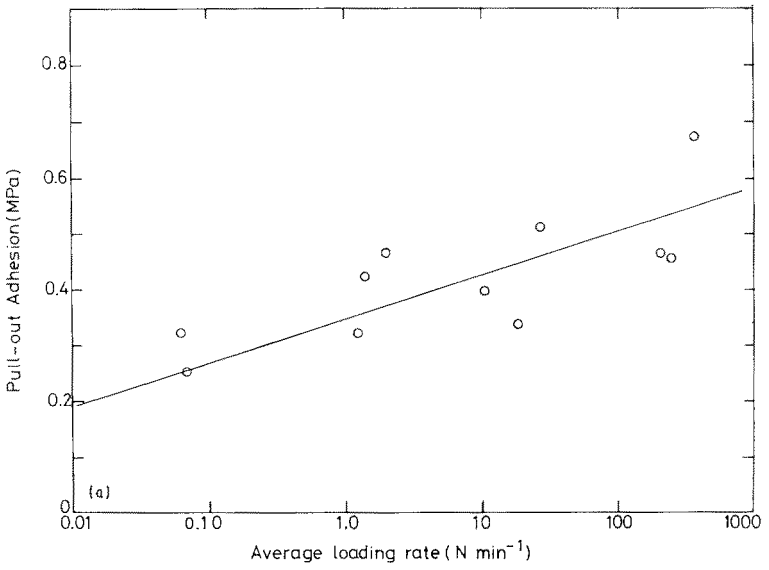


Figure 9 (a) Pull-out adhesion plotted against immersion length for untreated monofilaments. (b) Pull-out adhesion plotted against immersion length for M/M/M (oxygen) treated monofilaments.



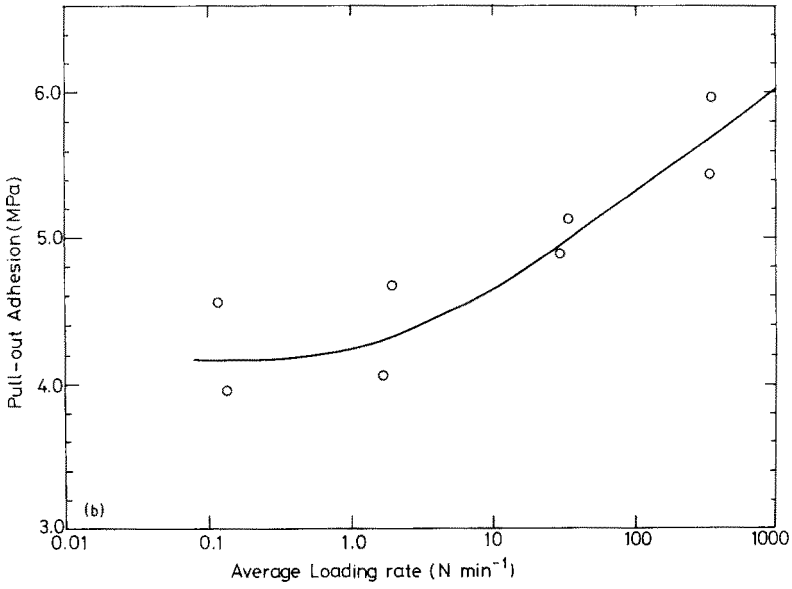


Figure 10 (a) Pull-out adhesion plotted against average loading rate for untreated monofilaments. (b) Pull-out adhesion plotted against average loading rate for M/M/M (oxygen) treated monofilaments.

retains its position as long as there is not adhesive failure. In this case the boundary conditions at $z = 0$ are given by

$$l_1 = 0 \quad f = 0 \quad \tau = 0 \tag{3}$$

Since the disc surrounding the filament is rigid, the shear strain on the adhesive is l_1/h_0 where l_1 is now the displacement of a point on the outer circumference of the filament. If G_1 is the shear modulus of the adhesive we therefore have

$$\tau = G_1 \frac{l_1}{h_0} \tag{4}$$

and combining Equations 2 and 4 we have

$$\frac{\delta^2 l_1}{\delta z^2} = \frac{2G_1 l_1}{Erh_0} \tag{5}$$

The exact solution of Equation 5 which would satisfy the boundary conditions (Equation 3) is not known. However, we are interested in the final strength of the system, that is, the tensile force F_0, or stress f_0 which will result in pull-out. From the boundary conditions Equation 3, the tensile stress is zero at $z = 0$ and rises steadily, reaching a maximum at $z = L$. A similar situation applies for the shear stress in the adhesive. It follows that the solution required should apply for the plane $z = L$, where the maximum stress concentration occurs. In this case, a solution of Equation 5 is

$$[l_1]_{z=L} = \frac{f}{E}\left(\frac{Erh_0}{2G_1}\right)^{1/2} \tag{6}$$

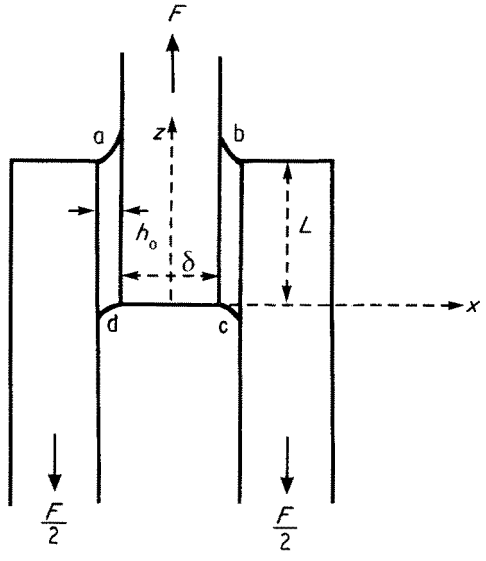


Figure 11 The double lap joint (no bending).

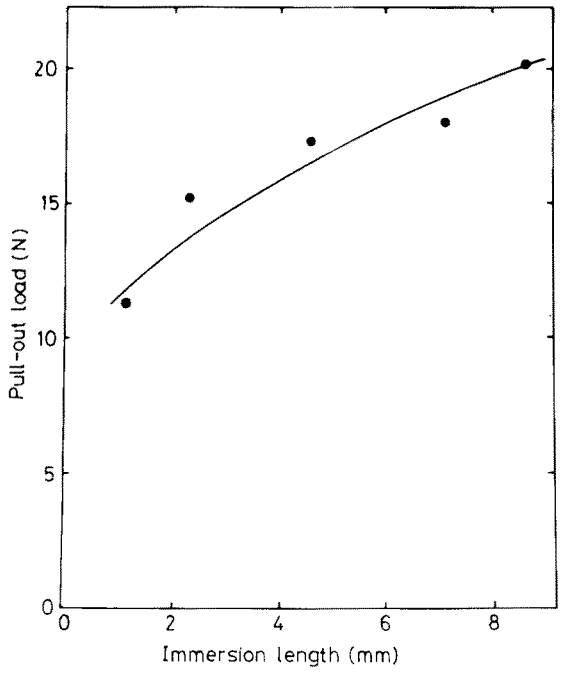


Figure 12 Pull-out load plotted against immersion length for M/M/M (oxygen) treated monofilaments (each point is the average of at least three samples).

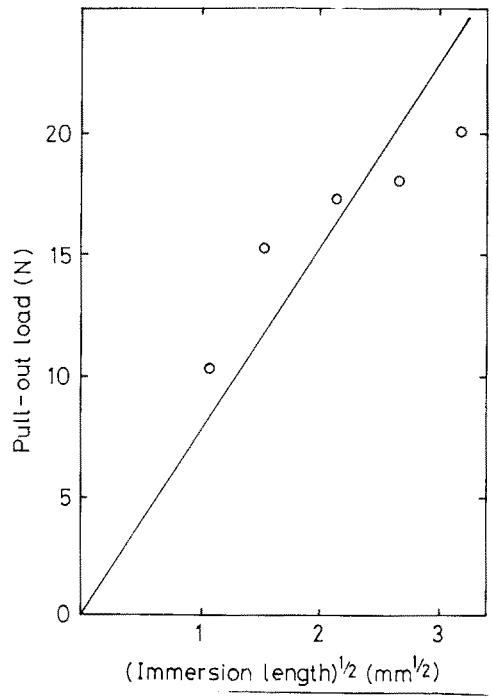


Figure 13 Pull-out load plotted against (immersion length)$^{1/2}$ for M/M/M (oxygen) treated monofilaments (each point is the average of at least three samples).

where f is the tensile stress applied to the filament. Substituting Equation 6 into Equation 4 we have

$$\tau_{max} = f\left(\frac{G_1 r}{2Eh_0}\right)^{1/2} \quad (7)$$

Next, we compare the assumptions involved in the derivations above with the experimental conditions in the present investigation. First, Volkersen [5] assumed an adhesive of constant thickness, a condition which is apparently not satisfied by the pitted surface of the plasma treated monofilaments. However, the resin has penetrated the pitted surface, and this could be considered as part of the rigid wall. In this case the adhesive would be the polymer layer of constant thickness which actually shears. The assumption of constant thickness is supported by the observation [1] that, away from the meniscus, the immersed region of a pull-out plasma treated monofilament is smooth. Considering that the pit size lies between 1 and 4 μm, it appears reasonable to consider 10 μm as the thickness of the peel-off layer, that is, the thickness of the adhesive layer.

In obtaining Equation 6 it is assumed that L is much greater than r, h_0 and

$$\left(\frac{Erh_0}{2G_1}\right)^{1/2}$$

In the present experiments L varies between 1 and 10 mm, whereas $r \simeq 0.13$ mm and $h_0 = 0.01$ mm.

Previous experimental measurements have shown that $E \sim 40$ GPa for the monofilaments [8] and that $G_1 \sim 1$ GPa for these materials [9].

It, therefore, follows that $E/G_1 \sim 40$. This gives a value for

$$\left(\frac{Erh_0}{2G_1}\right)^{1/2} \simeq 0.2\,\text{mm},$$

which is again much less than the range of L. It can be concluded from these results that the assumptions involved in deriving Equation 7 are fully satisfied by the conditions in the present experiments.

The predictions of the theory presented above will now be compared with the observations obtained from the pull-out tests on the plasma treated monofilaments. We note the following key points:

(a) Failure begins near the meniscus where the external force is applied. This observation has been discussed previously [1], and it is compatible with the boundary conditions (Equation 3), leading to maximum shear stress in the adhesive on the plane $z = L$.

(b) Fig. 12 shows the average pull-out loads for various nominal immersion lengths. It can be seen that the pull-out load is not very sensitive to the immersion length, which is consistent with Equation 7, which predicts that the maximum shear stress on the adhesive is independent of the immersion length L. Any discrepancy can be explained on the grounds that, after initiation, the failure has to propagate over the immersion length. It is, therefore, not unreasonable that the experimental results should show some dependence on immersion length.

Bikerman [7] has also reported similar discrepancies between the predictions of the theory and experimental results for the case of a strip pulled-out of a rigid wall. In particular, the tensile force at failure has been found to be proportional to $\sqrt{L}$. Fig. 13 shows that a similar proportionality applies to the present pull-out results.

(c) Pull-out occurs when the shear stress τ_{max} in the plane $z = L$ reaches the value τ_f, which is a material property independent of geometrical dimensions. It follows from Equation 7 that the tensile stress at failure should be proportional to $r^{-1/2}$ and, accordingly, Table II shows that the pull-out tensile stress increases with decreasing filament diameter. The agreement between the theory and the experimental results is,

however, only qualitative because the experimental effect is significantly more pronounced than the prediction given by Equation 7.

5. Conclusions

The pull-out adhesion of plasma treated monofilaments is significantly affected by the plasma parameters, as well as the plasma carrier gas. Maximum adhesion is obtained with oxygen gas, using the most vigorous treatment compatible with the stability of the filament. SEM studies provide the basis for a good understanding of the relationship between the adhesion values and the failure mechanism involved. In particular, there is excellent confirmation of a two-stage failure mechanism for monofilaments with pitted surfaces [1].

Comparison between different pull-out adhesion tests requires considerable care, the results being affected by geometrical variables such as the immersion length and the monofilament diameter, as well as the intrinsic adhesion at the interface. A modification of lap joint theory gives good qualitative predictions for most of these effects and also describes the two stage failure of samples with the highest pull-out adhesion values.

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