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SCANNING ELECTRON MICROSCOPY OF HIGH-MODULUS POLYETHYLENE FIBRES

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Abstract

Scanning electron microscopy (SEM) examination of high modulus polyethylene (HMPE) fibres gives rise to a number of artifacts which are here recognized. Antistatic agents may be successfully used for the observation of the woven fibres, but only in conjunction with an intermediate metallic coating. For isolated threads superior results are obtained with the metallic coating alone.

New SEM evidence suggests that the high density of surface cracks produced by plasma treatment of HMPE fibres is associated with an aging process. This can also be activated by mechanical energy or storage at room conditions.

Key Words: scanning electron microscopy, polyethylene fibres, surface cracks, plasma treatment, acrylic resins, adhesion, accelerating voltage, charging, conductance, antistatic agent.

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Introduction

Scanning electron microscopy (SEM) is now a well established technique for the study of the surface topography and texture of polymeric materials, either natural or man made. SEM advantages over light microscopy include a substantial increase in depth of focus and resolution. However, the correct sample preparation and choice of parameters for SEM observation are still a matter of concern. The technique presents numerous pitfalls, particularly for low conductivity materials such as polymers [11]. Some of the problems, e.g., charging of the sample, may be recognized and often corrected, but it is also possible to have artifacts which are not readily perceived as such, leading to false interpretation of the object under study [7].

These matters are examined in relation to high modulus polyethylene (HMPE) fibres, a recently developed material with an interesting array of properties, namely: high stiffness and strength, proven biocompatibility, white translucent appearance, hydrophobicity, etc. [3, 4, 22]. A variety of uses have been demonstrated, including the reinforcement of polymeric resins for structural and clinical application [2, 14, 15, 17].

Fibre material should bond to the matrix which is intended to reinforce in order to resist stresses that may be applied [1, 5]. Polyethylene has low surface energy and consequently poor wettability. However, it has been shown [16, 18] that plasma treatment of HMPE fibres (i.e., bombardment with highly ionized gas [6]) produces a high density of surface cracks into which the resin penetrates, giving rise to a substantial increase of the interface adhesion.

The crack dimensions are on the micrometers scale and have been the object of considerable attention, particularly using SEM techniques [16-18]. The present work includes new evidence on the origin of the cracks, as well as an assessment of suitable experimental conditions for observation.

Experimental

Materials

HMPE fibres with a draw ratio 30:1 were used throughout, either plasma treated or untreated. The

geometry, however, varied and included monofilaments ($\approx 3 \times 10^{-4}$ m in diameter) as well as multifilament bundles made with fibres of $\approx 15 \times 10^{-6}$ m diameter. The latter material was also studied in a woven form. Plasma treatment was carried out with either 50 watt or 120 watt input power, applied for 10 minutes or 2 minutes respectively. The first set of parameters has been used in previous studies [16, 17] and it was ascertained that the new treatment conditions do not affect the observations reported here. The characterization of the fibres and woven texture, as well as further details of the plasma treatment were reported previously [16, 17].

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Some of the experimental details will be presented in the following sections. However, a number of parameters have been maintained constant throughout the work and these may be summarized as follows.

The fibres were mounted on stubs (25 mm diameter) using a colloidal carbon dispersion as a conducting and adhesive medium. Two types of coatings were used, either gold or an antistatic agent (Duron Spray, Hansa Textilchemie GmbH, Bremen, Germany), referred to as Duron®. Unless otherwise stated, all samples were prepared following the procedure listed in Table 1. In a few cases, the whole length of the fibres was adhered to the stub with double sticky tape and the distance between carbon points reduced to about 8 mm. These conditions did not affect the observations reported here, but helped to eliminate charging or movement of the samples during examination with high accelerating voltage at high magnification.

Gold coating was applied in a JEOL JFC-1100 ion sputter coater operated at 1.2 kV, 5 mA in two periods of 4 minutes each to minimize heating of the sample, rotating the stub 180° during the interval. This resulted in a 25 nm thick coating. Duron was sprayed for about half a second at a distance of 300 mm, with the sample on a vertical plane and level with the spout of the aerosol can. These spraying conditions were broadly similar to those used by Sikorski *et al.* [20] and Wegener *et al.* [23], although these authors recommended spraying equipment for critical examination. However, they also concluded that application of Duron directly from the can, as in the present work, is fully adequate for an initial assessment.

The specimens were examined in a JEOL JXA-840 SEM equipped with a tungsten filament to produce electrons by thermionic emission. The filament current, i_f, was adjusted to operate in the initial stage of the i_β versus i_f plateau (saturation condition), where i_β is the emission (beam) current. This was selected at an optimum value of 6×10^{-11} amp, giving minimum probe beam diameter (d) compatible with satisfactory brightness. The working distance was kept at about 14 mm and the accelerating voltage varied between 5 kV and 30 kV. With the above conditions, and taking into account the various aberrations in the electron optical system, the probe beam diameter (d) is found to be in the 50 nm scale [10a].

TABLE 1. Standard Sample Preparation

Type of sample	Mounting	Coating
Monofilament and multifilament fibres (non-woven)	One carbon paint strip at each end, separated by ~20mm	Gold
Woven multifilament fibres (20mm x 20mm)	Carbon paint over all edges of the sample	Gold followed by Duron. Two days drying at room conditions

Results

Ladizesky *et al.* [16, 17] showed that the surface of untreated fibres is fairly smooth except for some longitudinal striations. Plasma treatment changes this topography, producing a high density of cracks. These past studies were performed on fibres a year old or less before examination. The same batches have now been re-examined, seven years later and plasma treated fibres continue showing a high density of surface cracks (Figure 1a). On the other hand some of the untreated fibres now show a cracked surface (Figures 1b and 2a) while others maintain their original appearance (Figures 1c and 2b). The cracked topography appears frequently on untreated multifilaments but is seldom seen on untreated monofilaments.

The appearance of woven fibres is, on the other hand very consistent, namely the surface is covered with a high density of cracks whether the weave is plasma treated or untreated (Figure 3). The occurrence of cracks in the untreated material is somewhat unexpected, but was further confirmed by the observation of isolated threads removed from the woven texture. Their surface was also cracked, as shown in Figure 4.

The micrographs shown in Figures 1-4 have all been taken at 5 kV accelerating voltage. Increasing this parameter resulted in a significant loss of detail, as indicated in Figures 5a, 5b and 5c corresponding to an untreated fibre with cracked topography. These photographs, taken at 5 kV, 10 kV, and 20 kV, respectively show a gradual reduction of surface details even though the apparent sharpness actually increases. Thus, examination of the sample at 20 kV would give no indication that important features of the surface are being missed, unless complimentary observations are also made at lower accelerating voltages. Examination of plasma treated multifilament fibres gave rise to similar effects.

A further artifact has occasionally been observed with fibres having a high density of cracks, namely plasma treated or threads removed from the weave. This may be referred to as a "transformation" whereupon a single fibre in a stub was initially seen without cracks, contrary to expectations. However these cracks appeared after examining other fibres on the same stub, all

showing cracks, and then returning to the "odd" uncracked one. In other cases all the fibres on the stub were initially seen without cracks. Removing the stub from the SEM and replacing it again produced the appearance of the expected cracks.

It should be emphasized that the "transformation" referred to above is a rare event, observed only with the JEOL JXA-840 equipment used during the past three years. The artifact occurred at accelerating voltages of 5 kV and 10 kV, although this might be coincidental because these were the values used for most of the SEM observations. Other features of the "transformation" are that: **a**) it could not be reproduced at will; and, **b**) it has never been observed in the reverse sense, namely from a cracked to an uncracked surface topography. Figures 4 and 6 give an example of such phenomena, observed on a thread taken from untreated weave.

Woven HMPE fibres could not be observed with gold coating alone, owing to significant charging occurring at any magnification and accelerating voltage combination. This is standard occurrence in SEM observation of textile materials and the problem has been overcome by the application of an extra layer of antistatic agent such as Duron (a technique used for many years on "difficult" fibres and fabrics by Sikorski *et al.* [20], at Textile Physics Laboratory, Univ. of Leeds, England). When Duron was applied directly over non-woven HMPE fibres the results were unsatisfactory except for very cursory observation. Figure 7 shows specks and a thin coating of Duron on the surface of an untreated monofilament. Magnifications above x1000 produced damage and/or charging of the samples. The texture of woven fibres could be examined at low magnifications (Figure 8a), but the observations at higher magnification were again unsatisfactory, as shown in Figure 8b.

Spraying Duron on top of a gold coated specimen gives different results according to the type of fibre being studied. The surface of non-woven untreated fibres show significant contamination, but this is not apparent when spraying is carried out after plasma treatment (Figure 9). High magnification observation of woven fibres can only be achieved with a combined coating of Duron on top of gold, in which case surface cracks are seen up to a magnification of x15000 and above with no indication of electron beam damage nor Duron contamination, (Figure 10).

Discussion

Considerations of Irradiation Damage of HMPE Fibres During SEM Observation

Polymeric materials suffer a number of changes when observed under the electron microscope owing to inelastic interactions between the electron beam and the sample [11]. It is then necessary to assess the possibility of radiation damage as a contributory factor to the results presented in the previous section.

The energy associated with the incident beam is given by the charge passing per unit surface (flux) multiplied by the accelerating voltage. Following the definition of coulomb (charge carried by a current of 1 ampere passing for 1 second), the flux in C/m^{-2} is obtained with a beam current i_β multiplied by the exposure time, and divided by the cross-sectional area of the beam. For SEM, the beam (probe) scans the sample and the exposure e_1 for each point of a line scanned once in a time t_1 is $e_1 = [t_1/(a/d)]$, where a is the width of the observed area and d the probe beam diameter (in the 50 nm scale, as stated in the "Experimental" section). The above relation may be deduced by assuming discrete scanning, that is, the probe stops for the corresponding exposure time before jumping instantly to the next adjacent position. It follows that the *flux* is given by [(beam current * exposure time) / cross-section area of the probe], i.e.,

$$flux = 4\ [(i_\beta t_1) / (\pi a d)] \qquad (1).$$

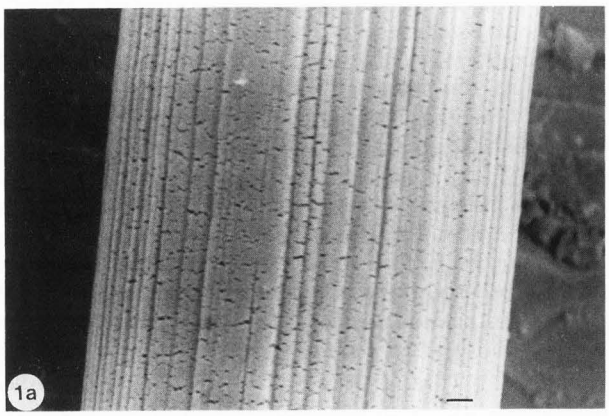
Table 2 gives the scanning times t_1 for observation and photography. The width of the scanned area can be obtained by measuring the length of the scale cursor at each magnification and the dimensions of the screen. The corresponding fluxes calculated using above relation (1) are given in Table 3, together with other parameters of interest.

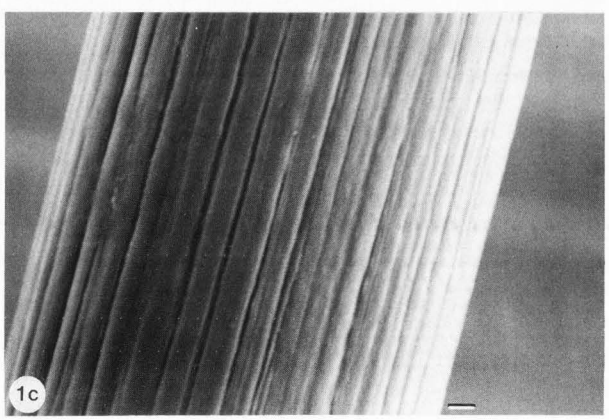
The above considerations may be used to obtain the incident energy. However, only a fraction of this is associated with radiation damage, namely the energy absorbed by the specimen. A further complication arises because inelastic scattering takes place at deeper levels as the accelerating voltage increases [10b]. It appears reasonable to assume that any damage which might affect the observations reported in the "Results" section should take place at, or very close to the surface of the fibres. These regions, therefore, absorb higher fractions of the incident energy as the accelerating voltage decreases.

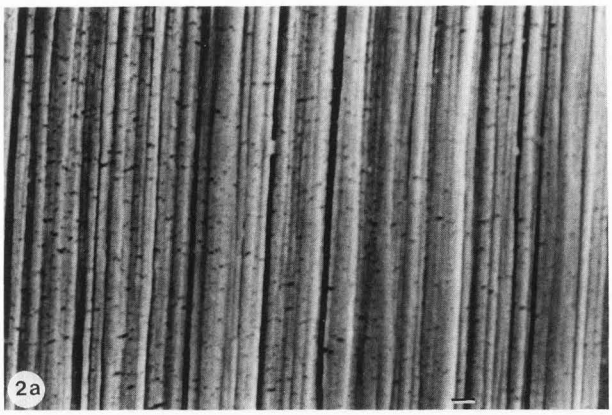
Notwithstanding the above comments it is still possible to make some comparisons between the incident energy (or flux) involved in the present research and data on radiation damage of polyethylene available in the literature. It was shown [11] that polyethylene single crystals are destroyed at room temperature by a dose of about 4000 Mrads, a dose obtained with an electron flux of 100 C/m^{-2} at 100 kV. The calculated fluxes in Table 3 are at least one order of magnitude smaller than this value. In particular, a large proportion of the evidence reported here was obtained at a magnification of x5000, and Table 3 shows that the flux for 10 seconds observation is 2.45 C/m^{-2}, that is, 1/40th of the value required to produce destruction of polyethylene single crystals when working at 100 kV.

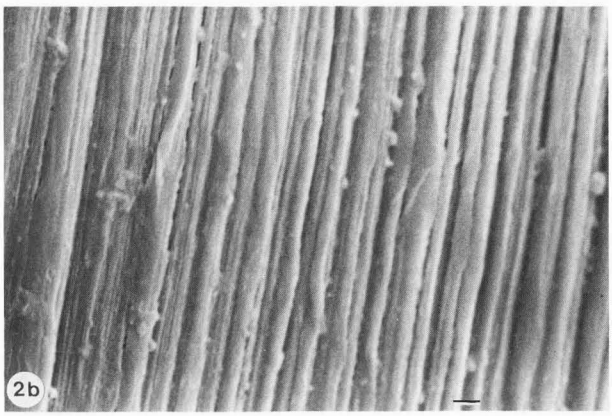
TABLE 2. Scanning Time

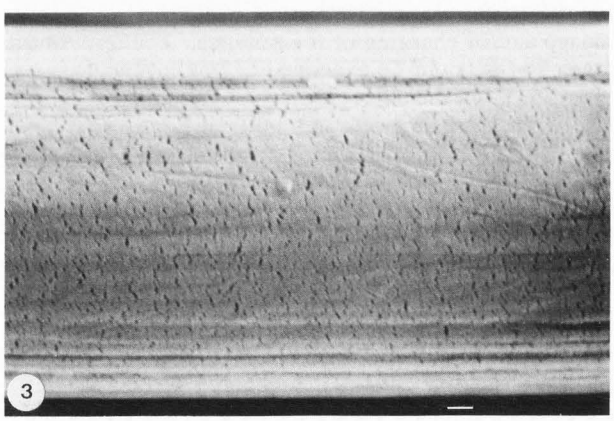
Mode	Horizontal (s/line) x 10^3	Vertical s/frame
Observation	0.127	0.033
Photography	40	100











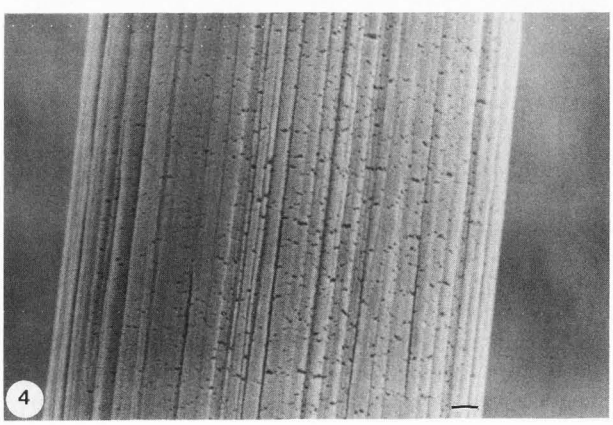
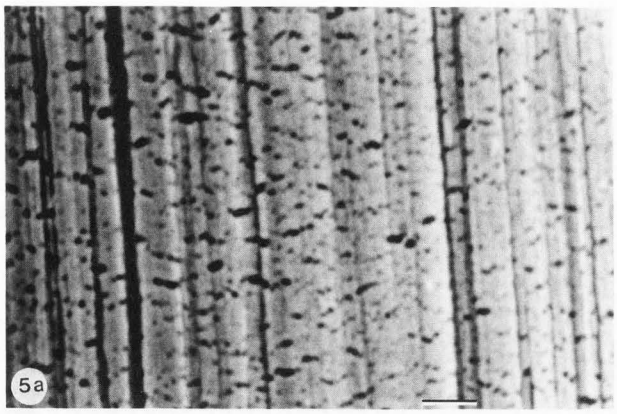


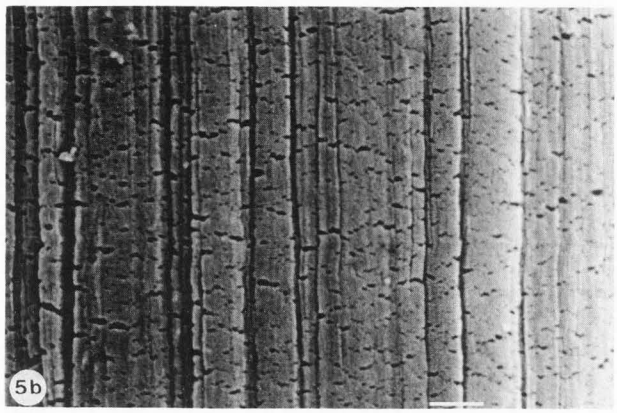
Figure 1. Multifilament fibre at 5 kV: (**a**) plasma treated; (**b**) untreated, showing striations and cracks; (**c**) untreated, showing striations only. Bar = 1 μm.

Figure 2. Untreated monofilament at 5 kV: (**a**) showing striations and cracks, (**b**) showing striations only. Bar = 1 μm.

Figure 3. Untreated woven fibre at 5 kV. Bar = 1 μm.

Figure 4. Fibre removed from untreated weave at 5 kV. Bar = 1 μm.





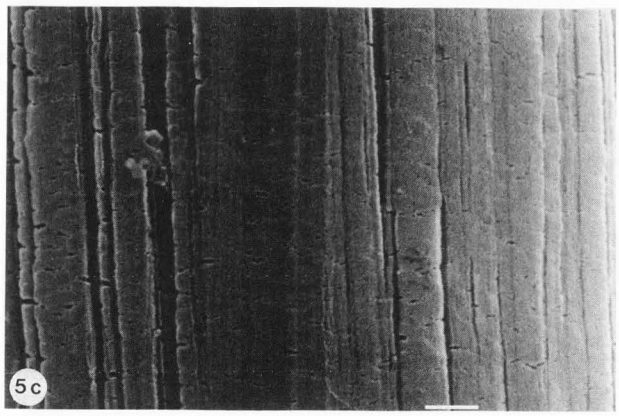


Figure 5. Cracked untreated multifilament fibre at (**a**) 5 kV; (**b**) 10 kV; (**c**) 20 kV. All photographs taken in neighboring areas. Bar = 1 μm.

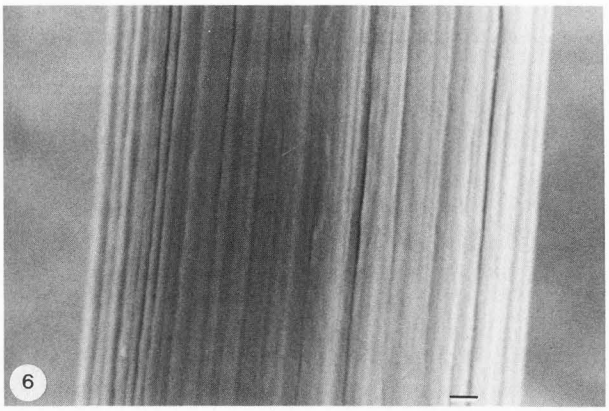


Figure 6. Fibre removed from untreated weave at 5 kV. First observation of the same fibre which a few minutes later produced Figure 4. Bar = 1 μm.

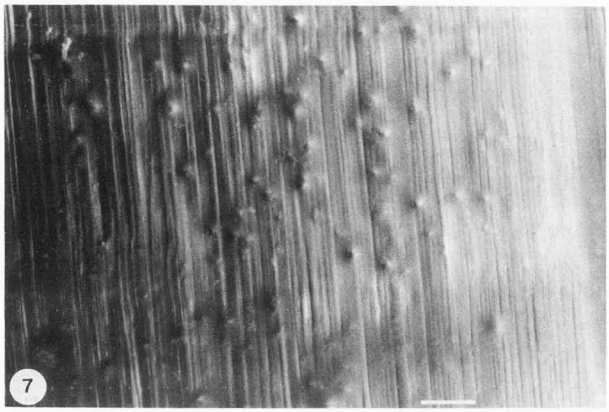
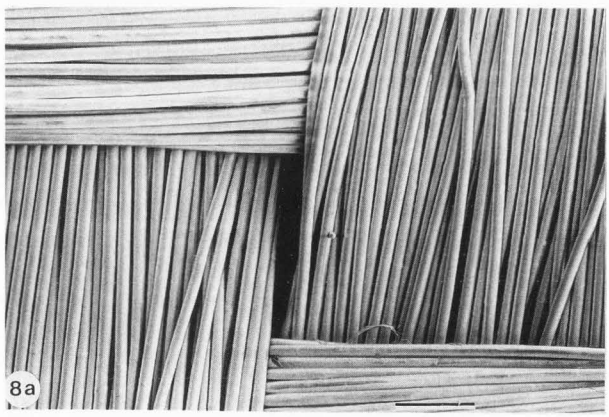


Figure 7. Untreated monofilament coated with Duron only at 5 kV. Bar = 10 μm.



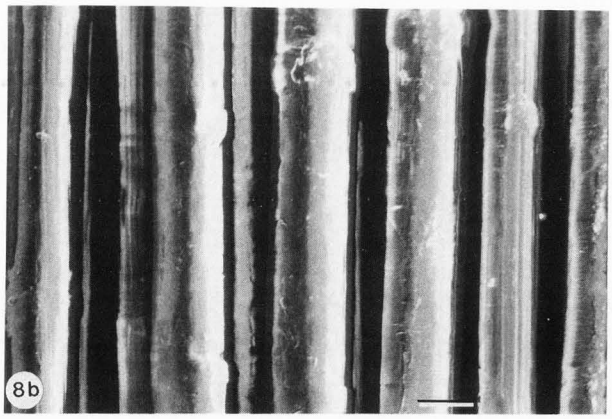
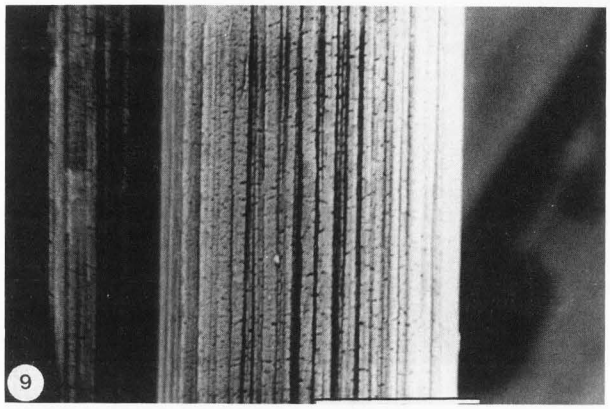
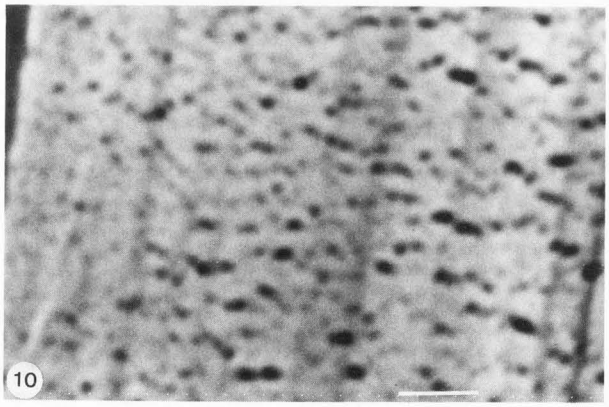


Figure 8. Untreated woven fibre coated with Duron only at 5 kV. Bar = (**a**) 100 μm; (**b**) 10 μm.

TABLE 3. Calculation of Flux on the Specimen Surface Under SEM Observation

Magnification	Width scanned on sample (m) x 10^6	Exposure for each point after one scan (s)		Flux after one scan (Cm^{-2})		Flux after 10s observation (Cm^{-2})
		Observation x 10^8	Photography x 10^6	Observation x 10^4	Photography	
X 500	240.00	2.6	8.3	8.1	0.25	0.25
X 1000	115.00	5.5	17.0	16.9	0.53	0.51
X 5000	24.00	26.0	83.0	80.9	2.55	2.45
X 10000	12.00	53.0	167.0	162.0	5.09	4.91
X 15000	7.75	82.0	258.0	250.0	7.89	7.58





On these grounds it appears reasonable to assume that the photographs presented in the "Results" section have no contribution from radiation damage. However, the effect of using relatively low accelerating voltage of between 5 kV and 10 kV is difficult to quantify because it entails lower available incident energy as well as higher fractions absorbed near the surface, where it is more likely to affect the observations.

Other factors to consider includes the metallic coating, producing a significant reduction of both the flux and the energy of the electrons owing to the high atomic number of gold [10b].

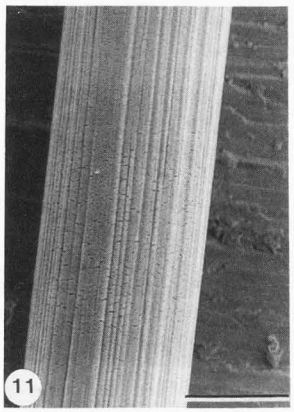


Figure 11. Plasma treated multifilament fibre at 5 kV. Taken immediately after Figure 1a without changing the area, but at lower magnification. Bar = 10 μm.

Figures 9-10 (at left). Plasma treated multifilament fibre (**Fig. 9**) and woven fibre (**Fig. 10**) coated with gold followed by Duron at 5 kV. Bars = 10 μm (Fig. 9) and 1 μm (Fig. 10).

Notwithstanding the speculative nature of the considerations above, this and other experimental evidence indicate that the SEM parameters used in this research do not produce observable irradiation damage on HMPE fibres. For example, untreated fibres without cracks were maintained for 3 minutes at 5 kV accelerating voltage and x5000 magnification, followed by three slow scans in photographic mode without changing the above conditions. Thus, these regions received over twenty times the flux corresponding to 10 seconds observation (Table 3) but no change whatsoever was observed on the surface topography. Furthermore, it should be noted that 10 seconds is, in most cases, a pessimistic appraisal of the time required to initiate examination of the chosen object area. When observing neighboring regions of the same fibre at x5000 magnification any surface change occurring after 3 seconds would be readily detected, thus reducing further the flux incident on the sample prior to observation.

While smooth fibre surfaces are very stable under the electron beam, a cracked type topography is more susceptible to changes, particularly in the photographic

mode. This is illustrated in Figures 1a and 11, showing two consecutive photographs of the same area at x5000 and x2000 magnification respectively. It is seen that the first exposure at higher magnification has produced a slight enlargement in the size of the cracks, probably due to high localized temperature arising from poor gold coating inside the cavities. Increasing the number of carbon strips from two to four and mounting the fibres with double sided sticky tape improves the stability of the cracked surfaces.

Effect of Accelerating Voltage

Cross *et al.* [7] found that the amount of detail observed during examination of certain textiles under the SEM decreases with increasing accelerating voltage. They attributed the effect to increased penetration of the electron beam, but no further elaboration was offered. Similar observations have been made in the present work with HMPE fibres (Figures 5a, 5b and 5c) and additional understanding may be gained by considering the principles of SEM and the nature of electron interaction with matter, as discussed below.

The signal reaching the detector is made up of back-scattered primary electrons (BSE) and secondary electrons (SE). The latter may be produced by either the primary electrons (PE) or the BSE and will be referred to as SE-I and SE-II respectively.

BSE carry information of both the surface and deeper layers. However, the cross-section (probability of an event) for elastic and inelastic scattering decreases as the energy of the PE increases [8, 10b], an effect that is further enhanced for low atomic number elements such as those involved in polymeric materials [10b]. It follows that the information carried by BSE will be weighted towards the inner layers as the accelerating voltage increases. For example, measurements in PMMA showed that the interaction volume between the PE and the material is pear shaped with a depth of several μm [9]. This dimension was obtained with 29.5 kV and is significantly larger than the size of the cracks seen in Figures 1a and 5a. Thus, the detector receives less information on such features as the accelerating voltage increases, leading to the observed decrease in surface detail (Figures 5b and 5c).

Further enhancement of this effect is provided by processes involving SE. These account for most of the low energy emerging electrons (below 50 eV) [10b] and therefore, have a large scattering cross-section, sampling a very shallow depth of the order of 10 nm [19, 21]. However, while SE-I are emitted from an area equal to the probe cross-section, SE-II are affected by the interaction volume and emerge over a much larger area, carrying less detailed information on the surface. An increase of the accelerating voltage (indicating larger interaction volume) produces a decrease of SE-I and an increase of SE-II, leading to a further loss of surface detail.

Other factors may also influence the signal, in particular the BSE generated within the metal coating. The exact coating thickness at the point of impact of PE and at the points of exit of the BSE are not known, nor are the path lengths of such electrons through the coating known. Thus these variables cannot be elaborated meaningfully.

The above considerations give a qualitative explanation for the loss of detail with increasing accelerating voltage. They cannot, however account for the "transformation" observed at relatively low accelerating voltages. The understanding of this artifact, illustrated in Figures 4 and 6, is more complex and an explanation may be suggested as follows.

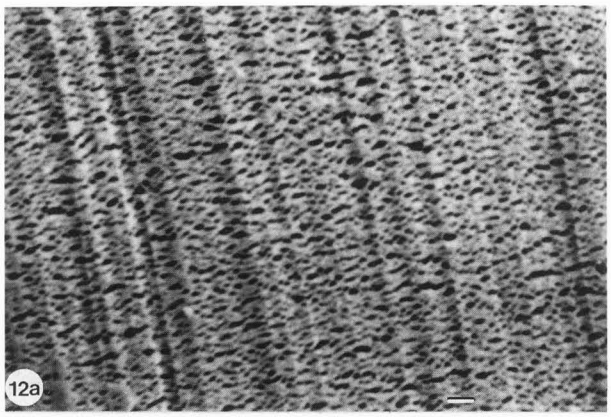
Several currents flow in and out of the specimen during SEM observation, namely the probe current i_β, back scattered current $i_{\beta S}$, secondary emission current i_{SE}, and specimen current to ground i_{SC}. It should be remembered that all electrons are equivalent irrespective of energy because current is passage of charge per unit time. Charging does not occur if the number of electrons arriving at the object is equal to the loss of electrons, a condition which is usually stated with the following relation [10c].

$$i_{SC} = i_\beta - (i_{\beta S} + i_{SE}) \qquad (2)$$

Charging of the specimen implies an excess of surface electrons, increasing its potential relative to ground. Thus, the flow of electrons through conduction i_{SC} also increases. A high state of charge may damage the sample and/or change the trajectory of the primary beam [7] to such an extent that the observation conditions become unstable. However, instability may not occur if the higher potential of the sample produces a sufficient increase of i_{SC} to establish the balance given by equation (2). Therefore, this may be looked upon as a condition for charge stability, of which zero charge is a particular situation.

The above considerations can now be used as the basis to provide an explanation for the observed "transformation". It is postulated that HMPE fibres mounted and coated (as described in Table 1) require a state of charge before stable conditions (equation 2) can be attained. The excess of negative surface charges is generally small and have no significant effect on the quality of the image, but may still be instrumental in restraining the penetration of the primary beam and/or the emission of electrons from deeper layers. Under these conditions, the information to the collector arrives mainly from the sample surface, which is then faithfully reproduced on the screen.

Nevertheless, statistical variations of the experimental parameters may give rise to an occasional sample with exceptionally good conductance to ground. The resultant reduction in the state of charge will be accompanied by increased penetration of the electron beam and a consequent loss of surface detail (Figure 6). Movement of the fibre produced by the primary beam,



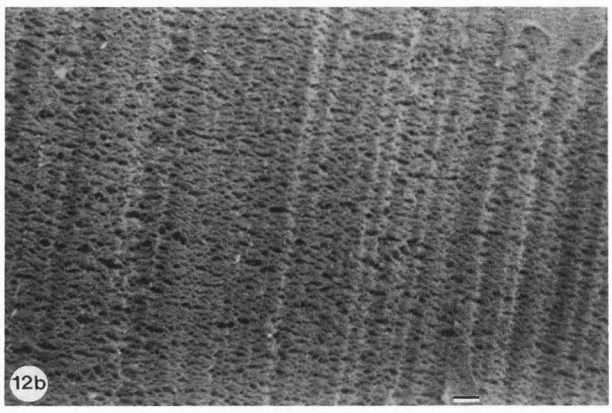


Fig. 12. Plasma treated monofilament mounted with four carbon paint strips. Operated at (**a**) 5 kV; (**b**) 30 kV. Bar = 1 μm.

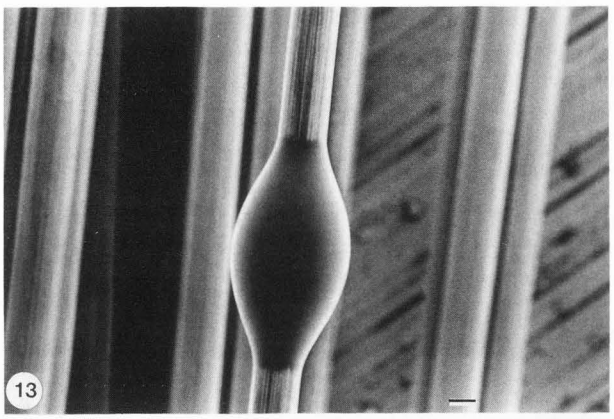
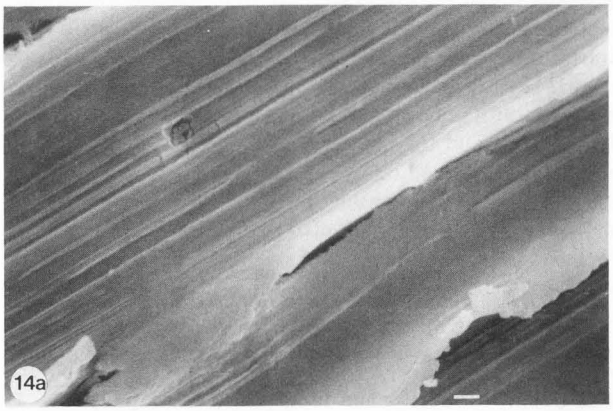


Fig. 13. Droplet of Duron on a plasma treated multifilament fibre. The antistatic agent was sprayed on top of gold coating. Operated at 5 kV. Bar = 10 μm.



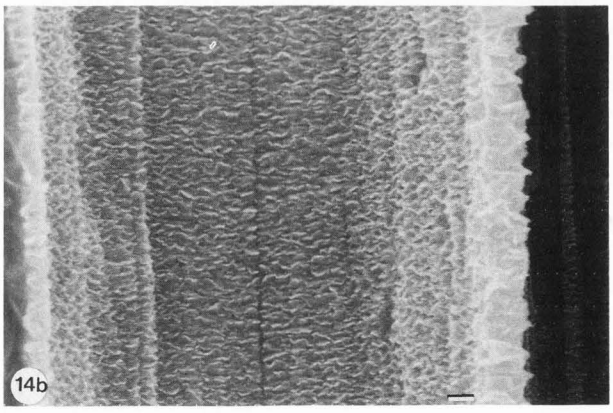


Fig. 14. Resin replication of: (**a**) untreated woven fibres; (**b**) plasma treated woven fibres. Operated at 10 kV. Bar = 1 μm.

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vacuum effects and/or vibrations associated with displacement of the stub may decrease the conductance to an "average" level, increasing the charge state and restoring the surface details as the "transformation" takes place (Figure 4).

Monofilaments are somewhat insensitive to electron beam penetration effects. Comparison of Figures 12a and 12b confirms that a large increase of accelerating voltage results in only a minor reduction of the apparent size of the surface cracks produced by plasma treatment. This may be due to: **a**) the cracks are of sufficient depth to be sampled by electrons penetrating below the surface or, **b**) the conductance of monofilaments is reduced by the large ratio of the polymeric mass to metal layer, ensuring a minimum state of charge which reduces the penetration of the primary beam and the release of back-scattered electrons carrying information from deeper layers. Therefore, the surface is faithfully reproduced on the screen even at a very high accelerating voltage.

Use of Antistatic Agent

Sikorski *et al.* [20] appear to have been the first to draw attention to the possibility of using antistatic agents and, in particular, Duron for the purpose of coating low conductivity materials prior to examination in the SEM. Wegener et al. [23] promptly followed with an exhaustive study of the chemistry and application of Duron in electron microscopy. Cross *et al.* [7] used antistatic agents (no particulars given) to study the

deformation of textiles under SEM. In all these cases the antistatic agent was applied directly on the samples either by spraying or immersion, and without an intermediate metallic coating.

Wegener *et al.* [23] mentioned three problems when using Duron on textile fibres and biological materials, namely: **a**) pool (puddles) type accumulation, **b**) decomposition of Duron by primary beam bombardment and, **c**) droplets on fibres. The three effects have been observed with HMPE fibres in the present work. Decomposition of Duron was avoided by drying the samples at room conditions for two days prior to observation. Droplets and puddles may be rinsed off by short immersion of the sprayed sample in an ether bath [23]. This procedure was not followed in the present work because the accumulation, if any, was localized and could be avoided without undue inconvenience. Figure 13 shows a droplet formed on a plasma treated multifilament fibre coated with gold followed by Duron.

Figure 9 shows a non-woven plasma treated fibre sprayed with Duron on top of gold. The typical cracked topography is clearly discernible, suggesting a suitable thin layer of the antistatic agent. When the fibres were untreated Duron acted as a contaminant, masking surface details. It is therefore suggested that the higher surface energy imparted by plasma treatment [18] increases the wettability and helps the spreading of Duron on the treated fibres, notwithstanding the intermediate gold layer. Nevertheless, the antistatic agent decreases the surface stability of non-woven fibres under the electron beam.

The excellent results obtained with woven fibres coated with gold followed by Duron may be due to large capillary forces operating within a woven texture. This should contribute to the effective spreading of the antistatic agent as a monomolecular layer, while also improving bridging between the fibres. The resultant increase in conductance virtually eliminates the large charging effects which prevent observations with gold coating alone.

The Surface Topography of HMPE fibres

Nardin and Ward [18] suggested that the high crack density on plasma treated fibres may be associated with the release of residual stresses, introduced at the manufacturing stage. The present results indicate that untreated fibres may also show a cracked topography after either **a**) several years storage (Figures lb and 2a) or, **b**) weaving procedures (Figures 3 and 4). Thus, plasma treatment and weaving both provide the activation energy required for the release of internal stresses and associated surface cracking, an effect which may be looked upon as accelerated aging.

Although the cracks on untreated and treated fibres appear to have a similar origin, namely the release of internal stresses, plasma treatment produces added surface changes. This is highlighted by the following observations.

A study [12] on the fibre/resin integration in reinforced denture bases has shown that the resin faithfully replicates the cracked surfaces of the plasma treated reinforcement. When this was untreated, the original striations were replicated, but not the cracks. The images in Figures 14a and 14b provide fresh support to the findings reported previously [12]. It follows that the liquid resin penetrates the cracks only for the plasma treated fibres, owing to their enhanced surface energy [18] and, therefore, higher wettability.

Summary

The examination of HMPE fibres under the SEM is subjected to a considerable number of artifacts. A case studied in some detail concerns the effect of electron beam penetration with increased accelerating voltage. The results indicate that high magnification observations are best started with low accelerating voltage. This may then be increased to improve resolution, as long as the features of interest are not masked by the associated increase in interaction volume. Furthermore, other artifacts suggest that the operating parameters used for the present work establish a small constant surface charge on HMPE fibres, this being a necessary condition for best observation of surface detail.

Examination of woven HMPE fibres requires an additional coating of an antistatic agent. Significantly better results are obtained when this is applied over a standard gold layer rather than directly on the fibres, in agreement with common present day practice for the observation of other textile structures. Spreading of the antistatic agent is largely controlled by capillary forces within the sample, as well as its surface energy.

It has been shown that surface cracks on HMPE fibres may appear as a consequence of prolonged storage, weaving or plasma treatment. The common factor in all these cases is the release of residual stresses stored during the manufacture of the fibre. The effect of plasma treatment may then be considered as accelerated aging plus chemical modifications on the surface of the fibres.

Acknowledgements

The authors are grateful to Professor I.M. Ward of the Department of Physics, University of Leeds, U.K., for supplying the high modulus polyethylene fibres. Thanks are also due to Miss E. Owens for her kind and skillful technical translation of German publications. The work is part of a project on dental application of materials, supported by a research grant from the University of Hong Kong, No. 335.263.0003.

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Discussion with Reviewers

M.G. Dobb: Although the specimens were exposed to 1/40th of the flux required for destruction of polyethylene crystals this does not mean that the fibres have not been damaged. Some chain scission (limited depolymerization) undoubtedly occurs producing low molecular weight (M.W.) material which might "boil" off under the high vacuum in the SEM giving rise to cracks in the surface.

Authors: Irradiation of polymers in vacuum produces either chain scission (lower M.W.) or cross-linking (higher M.W.). Polyethylene belongs to the second category, namely it cross-links [11, 13]. Furthermore, the evidence presented in the text indicates that untreated fibres were observed with or without cracks, in the latter case even after long examination periods. This appears to rule out any contribution to the image of a mechanism such as proposed by the reviewer.

M.G. Dobb: (Referring to the third paragraph of section "The surface topography of HMPE fibres"). It may well be argued that the replication of pits indicates that the observed cracks seen during direct SEM examination of untreated specimens are artifacts.

Authors: As indicated in the text, cracks on untreated fibres are often seen after several years of storage as well as on all woven material. In every respect these cracks appear similar to those produced by plasma treatment, including the effect of changing accelerating voltage. All these observations have been discussed in the text and found to be consistent with the present under-

standing of HMPE fibres and electron microscopy.

The discrepancy of the replication of surface cracks seen on untreated and plasma treated fibres is presented in the paper as a further support, and a consequence of findings reported previously [18], namely the higher wettability associated with plasma treated fibres.

M.G. Dobb: Do the authors consider that the increased electron dose (associated with repeated specimen examination) might be responsible for the "transformation" observations (i.e., increased damage)?

Authors: As explained in the text, the "transformation" was a rare event which took place with fibres having a high density of cracks. In only one occasion the change from uncracked to cracked appearance occurred with the sample in a fixed position, raising the suspicion of an electron irradiation effect. In all other instances the "transformation" involved either a whole individual filament or all the filaments on a stub (see text) and was not subordinated to the repeated examination of a particular area. Thus, the effect could not be related to increased electron irradiation dose.

E. Mathiowitz: Figure 5a seemed to be out of focus and Figures 5b, 5c are more focused. Is it possible that the differences between the three Figures (5a, 5b, 5c) are due to observing the same sample but at different areas? Is it possible that on the same sample one would observe some areas full of cracks and some with fewer cracks? The argument would have been more convincing if the figures were taken at the same area but at different voltages.

Authors: The out of focus appearance of Figure 5a is due to its high magnification combined with relatively low accelerating voltage. Figures 5b and 5c maintain the same magnification as Figure 5a but were taken with higher accelerating voltage, resulting in an increased apparent sharpness as pointed out in the text.

Nominally identical fibres may show different surface crack densities, but for the short segments on a stub the variability along each individual filament is negligible when compared with the changes seen between any two of Figures 5a, 5b and 5c. The observed variability of crack density among different filaments is likely to be a consequence of a range of residual stresses introduced during the manufacturing stages of the drawn fibres (see section "The surface topography of HMPE fibres"). For plasma treated fibres, other contributory factors may include screening within the bundles in the plasma reactor.

The loss of detail with increasing accelerating voltage depends on the surface topography of the sample, but the trend is consistent. It may be observed at original magnifications as low as x2000, that is, five times lower than in Figures 5a, 5b and 5c. These Figures were selected to illustrate the effect because they combine a magnification and range of apparent sharpness which should still retain the desired information after reduction and printing. The choice of three neighboring areas on a given filament was guided by a desire to discard any doubt of a contribution to the image from damage produced by multiple exposures, involving high magnifications and accelerating voltages.

W.L. Jongebloed: Why is a tungsten filament used and not a LaB_6 source to obtain higher brightness, necessary for the 5 kV - 10 kV region? The value of 50 nm beam diameter with a coating thickness of 25 nm seems rather large for magnifications over x10,000 at the accelerating voltages used.

Authors: We agree with the possible advantages of a LaB_6 source over a tungsten filament. Nevertheless, the latter was used because it was the only one available in our laboratories. Besides, a tungsten filament SEM was used in all previous work concerning the SEM observations of HMPE fibres and fabrics [12, 16, 18], and is standard equipment for work with other polymeric textiles.

The 50 nm beam size was chosen because it gives the best balance of resolution and contrast with minimum generation of noise. We have tried various thickness of coating and found that below 25 nm the samples are liable to charging effects owing to insufficient conductivity, while coatings of 50 nm and above began to mask minor topographic details. A coating of 25 nm thickness was, therefore, chosen as providing the best compromise for the range of accelerating voltages and magnifications used in the research.

O. Johari: Please comment on how your work relates to the work of K.-R. Peters: Working at Higher Magnifications in Scanning Electron Microscopy with Secondary and Backscattered Electrons on Metal Coated Biological Specimens and Imaging Macromolecular Cell Membrane Structures, Scanning Electron Microscopy, 1985;IV: 1519-1544.

Authors: The above cited paper states (on page 1521): "Modern analytical as well as standard microscopes allow significantly improved imaging of high magnification contrasts if they are equipped with LaB_6 or field emission cathodes. It is especially for these microscopes that the imaging strategy is discussed in order to establish a resolution closely related to the beam diameters used."

The beam diameters used in Peters work are of the order of 1 nm, seeking magnification of up to x250,000. Such techniques and discussions are of undoubted value for suitable biological materials, but bear little relationship with the requirements of the work presented in our paper, namely the observation of polymeric fibres and fabrics. It was not our intention to embark on a comparison of the various electron sources.

W.L. Jongebloed: Does (ion) sputtering interfere with the existence of the cracks?

Authors: Not for coatings of the order of 50 nm or below. For coat thicknesses above 200 nm the cracks began to disappear.

W.L. Jongebloed: Would a treatment with OsO_4 (in solution or in the vapor phase) prior to Au-sputtering give an improvement in conductivity, particularly on cracked surfaces, instead of Duron spraying? What are the specks on the Duron sprayed fibre surface and why are they not visible on the cracked surface?

Authors: OsO_4 is used in biological preparations for electron microscopy observations, mainly as a fixation agent. In addition there is some evidence that the procedure results in improved conductivity of the sample. We have tried the technique (OsO_4 in solution prior to gold sputtering) on both isolated and woven HMPE fibres and found no improvement. This may be due to the fact that OsO_4 does not penetrate the cracks, nor provides an effective bridge between the fibres.

The answer to the second part of the question requires some understanding of the composition of Duron and the interactions operating in the object/Duron system. These matters have been fully discussed by other workers [20, 23] and a brief summary may be made as follows.

Duron is a solution of an active substance in 90 percent by weight of isopropanol. In an aerosol container the propellent gas is a mixture of propane and butane.

The active substance consists of various fatty acids, each molecule having both hydrophobic and hydrophilic groups. After spraying and evaporation of the isopropanol the hydrophobic groups of the sample (polymers, ceramics and some biological materials) form minimum energy bonds with the hydrophobic groups of the fatty acids, leaving the hydrophilic (polar) groups "sticking out". These interactions give rise to a densely packed oriented monomolecular layer of the active substance which may be looked upon as a pseudocrystalline arrangement. This is highly stable under vacuum and is responsible for the surfactant and antistatic properties of the coating. The molecules have lengths below 60 Å and are even smaller when looking at them from the ends. These dimensions are below the resolution of the SEM and the sample surface may be observed without interference from the antistatic agent.

The molecules of the antistatic agent achieve maximum alignment for monomolecular layers. As the thickness of the coating increases the molecular orientation decreases until the substance becomes an isotropic liquid. This will be seen as contamination under the SEM.

The explanation of the various Duron related effects presented in the main text may now be further discussed as follows.

a) *Spraying the antistatic agent directly on all types of HMPE fibres*. This gives rise to a thick layer of the active substance, which shows as contamination at about x1000 magnification. Furthermore, the specks seen in Figure 7 (untreated monofilament coated with Duron only) are produced by uneven spraying at the microscopic level. These do not spread due to poor wettability of the isopropanol solution on the low energy surface of the monofilament. The specks are not generally observed when spraying a bunch of multifilament fibres because these have much smaller diameter, giving rise to capillary forces assisting to the spreading of the coating (which, nevertheless, is still seen as a contaminating agent at about x1000 magnification).

From the above, it follows that cracks were not observed on samples coated with Duron only (Figures 7 and 8b) because: **a**) the application acted as a contaminating agent with impaired antistatic properties and, **b**) under these conditions the filaments could not be examined at magnifications above x1000.

b) *Combined coating of gold followed by Duron.* Cracks were visible on plasma treated and woven multifilament fibres (Figures 9 and 10, respectively) because these samples have higher wettability and/or capillary forces, resulting in a sufficiently thin layer of the active substance with effective antistatic properties. Thus, the contamination effect was absent and higher magnifications were possible. Further details are given in the text.

J.D. Fairing: Some of the reasons that the authors have put forward for the loss of surface detail are valid, but it is my opinion that the loss of detail is due primarily to the overwhelming preponderance of secondary electrons generated by backscattered primaries. Such electrons arising from many points on the fiber surface simply drown out the information derived from the BSEs originating at the point of primary impact.

This point is easily established; it is only necessary to observe the strength of the BSE image as the gun potential is increased. A stronger BSE signal is obtained at higher voltage indicating a greater emission of backscattered electrons. Such electrons, when near the surface, will give rise to secondary electrons and thus the total SE count will increase and the ratio of the two types of secondary electrons will alter greatly. Since there are other processes operating at the same time, this point should not be elabored unnecessarily.

My personal opinion is that in a paper of this sort where there are many variables that can neither be measured nor rigidly controlled, speculation as to the exact physical mechanisms involved may be futile. These mechanisms are exceedingly difficult to ascertain when we think that we know most of the variables involved. However, some generalized statements that the authors have made may be appropriate and help introduce some clarity to the phenomena.

More important, I feel, are what appear to be deficiencies in the technique. Two principle problems seem to exist: charging and fiber damage (possibly the result of localized heating). Charging has always been a difficult and frustrating problem in the study of fibers and textiles, but it frequently can be overcome. The following consideration, taken together, will generally produce acceptable results.

I. The path to ground (i.e., the stub) must be as short as possible. When it can be done, this is sometimes effected by placing a coat of colloidal carbon or

other conducting material on the stub, letting it partially dry, then placing the fiber on the coating. With fabrics, it is usually safe to leave the carbon somewhat wet. If wicking occurs, it frequently can be recognized and the area thus avoided.

Painting the fiber, or fabric, with strips of silver paint at frequent intervals (2-5 mm) is of considerable value. The importance of securing a good electrical contact between the back side of the specimen and the stub can not be overemphasized. For example, some types of mica (a very good insulator) can be examined in the SEM uncoated, without charging, if the back of the specimen is well cemented to the stub with a conductive glue.

II. Continuous conductivity can be aided by producing a diffuse conductive coating on the sample. My preferred method is to vacuum evaporate a carbon coating using a rather poor vacuum (about 0.1 Torr or slightly higher). Under these conditions the mean free path of the carbon atoms is rather small and they reach the sample surface from various angles. This effect is enhanced by the fact that the mass of the carbon atom is actually less than that of the gas. When doing this, the coating should be started as soon as the indicated vacuum is satisfactory; prolonged evacuation is undesirable since any residual gas near the sample surface will aid in further reducing the mean free path. Care must be taken that the sample is not heated by the increased thermal conductivity of the residual gas. A cold stage is highly desirable, the sample must be rotated, and several short exposures may be necessary. The carbon coating is, of course, to be followed by the usual gold coating. My experience in over 25 years of trials with a variety of specimens is that, except for a few isolated instances, Duron has failed to give satisfactory results.

III. Specimen damage due to heating by the electron beam can, at times, be reduced drastically by using a coating material of high thermal conductivity, such as silver or copper. Copper has worked very well and oxidation has not been found to be a problem. Copper may have an advantage over silver because of its smaller molecular volume. NOTE: if the sample contains any active halogen both silver and copper will form crystals; beautiful, but meaningless. Both metals can be evaporated easily from a tungsten basket.

Authors: Dr. Fairing singled out one of the various processes mentioned in our discussion as the main cause for the loss of surface detail with increasing accelerating voltage. We do not wish to dispute his view, which is supported by K.R. Peters (see O. Johari question above): "Only on very thin specimens of a few mm thickness the SE-I may dominate. Otherwise, on bulk specimens, the SE-II provide the majority of the signal". Seiler [19] quote the ratio of secondary electron coefficients $\Delta_{SE\text{-}II}/\Delta_{SE\text{-}I}$ as being on the order of 3 or 4. We agree with Dr. Fairing that there are other processes operating at the same time, as stated in the text.

Dr. Fairing's comments on sample preparation techniques have general application but they do not appear to address the main issues of our work. The various methods he describe to aid electrical and thermal conductivity are of interest, although there is no evidence that they will work satisfactorily with woven HMPE samples, a notoriously difficult case on which our technique (Duron on top of gold) gives exceptionally good results. Besides, our experience, with some of his recommendations, are unfortunately negative. For example, a coat of colloidal carbon under HMPE fabric produced excessive wicking and the samples were ruined. Of course, this problem should not occur when using mica, an example given by Dr. Fairing. Our attempts to use carbon coating (at high vacuum) were also unsuccessful, leading us to dismiss this techniques. Perhaps, further experiments with low vacuum might be useful as an alternative technique to using Duron for the observation of woven HMPE fibres. Dr. Fairing's suggestion of painting samples with conducting strips at frequent intervals have been tried by us and are, in fact, mentioned in the Experimental section of our text.

Dr. Fairing's statement on the usefulness (or lack of it) of Duron is at odds not only with our experience as stated in the text, but also with the following comment of reviewer Dr. M.G. Dobb: "It should be pointed out that Sikorski et al. [20] have used, for many years, combined treatments of metal and antistatic for observation of "difficult" fibres and fabrics".