

---

## Interface in Composite Materials [and Discussion]

P. Ehrburger, J. B. Donnet, A. R. Ubbelohde, J. W. Johnson, M. O. W. Richardson and R. A. M. Scott

*Phil. Trans. R. Soc. Lond. A* 1980 **294**, 495-505  
doi: 10.1098/rsta.1980.0059

---

### Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

---

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

---

## Interface in composite materials

BY P. EHRBURGER AND J. B. DONNET

*Centre de Recherches sur la Physico-Chimie des Surfaces Solides,  
24, Avenue du Président Kennedy, 68200 Mulhouse, France*

[Plate 1]

The mechanical characteristics of a fibre–resin composite depend primarily on the mechanical properties of the combined materials, the surface of the fibre, the nature of the fibre–resin bonding as well as the mode of stress transfer at the interface.

These two last points are related to the surface properties of the fibres. The various types of bonding that may occur between fibrous materials (carbon, glass and organic fibres) and organic polymers, including the relevant theories, are briefly reviewed.

In order to optimize the fibre–resin interactions, it is often essential that the interface should be chemically modified. The various possible treatments may be classified under three headings: chemical surface modification of the fibre, sizing and polymer fixation (grafting).

The major factors that influence the interactions between high-performance fibres and organic resins will be established and discussed, as illustrated in a few selected examples.

## INTRODUCTION

It is a well known fact that unidirectional composites reinforced with high modulus fibres exhibit excellent characteristics in the direction of the reinforcement. However, their weak point lies in their moderate shear strength. This may be aggravated by the decrease in strength of the composite during weathering, which renders the problem of the coupling between fibre and matrix even more intricate.

Interfacial stresses in composites are due to the shrinking of the resin and the difference in elasticity modulus between matrix and reinforcing agent. The stress transfer at the interface therefore requires an efficient coupling between fibre and matrix. It is, however, important to optimize the interfacial bonding, since a direct linkage between fibre and matrix gives rise to rigid, low impact resistance material.

Among the many factors that govern the characteristics of composites involving a fibrous material and a macromolecular matrix, it appears certain that the adhesion between fibre and matrix plays a predominant part. Although the different authors do not always agree as to the nature, the intensity and the properties of the interfacial bonding (physical or chemical, reversible or irreversible) it seems clear that one of the main criteria is the absence of interfacial defects, i.e. the existence of a smooth interfacial adhesion.

Many models have been suggested, but only those with a direct bearing on composites will be dealt with in the first part. As to the influence of surface chemical functions in carbon fibres–epoxy resin composites, attention will be paid to them in the second part.

[ 87 ]

## FIBRE-RESIN INTERFACIAL BONDING

As a rule, in composite materials, mechanical bonding is distinguished from specific bonding.

*Mechanical bonding*

This model consists of a linkage phenomenon, a mechanical anchoring of the polymer into the pores and the unevenness of the fibre, after hardening of the polymer. The interpenetration of two solids is, in fact, a mechanical factor which promotes the adherence between two bodies. Wake (1959) has shown that the adherence to fabrics based on continuous but variously shaped yarns is proportional to the surface area of the fabrics. However, the rugosity is a positive factor only in so far as the substrate is perfectly wetted by the liquid. As a matter of fact, if the liquid cannot penetrate into the asperities of the substrate, the hardening of the resin is accompanied by the formation of interfacial cavities which are liable to initiate the failure of the interfacial bond.

In this model, the adherence and wetting criteria are therefore closely related. Thus, in the case of a good wetting, an increase in the specific surface area of graphite fibres, achieved by nitric oxidation improves the interlaminar strength (i.l.s.s.) of the corresponding composites (table 1) (Donnet *et al.* 1974).

TABLE 1

fibre (type I)	$S_{B.E.T.}$ (fibre)/(m <sup>2</sup> g <sup>-1</sup> )	i.l.s.s. (carbon fibre-epoxy composite)/MPa
non-treated	0.4	22
nitric acid treated	1.4	43

It is also worth noting that pitting the surface of carbon fibres by oxidation in air at 870 K significantly increases the shear strength of the resulting thermosetting composites (Clark *et al.* 1974).

*Physical coupling*

In this model, the forces of interfacial bonding are so-called secondary or van der Waals forces. They include mostly London dispersion forces, dipolar interactions and hydrogen bonding. Their energy is usually comprised between 8 and 16 kJ/mol.

Generally speaking, these forces are involved in the wetting and adhesion phenomena (Zisman 1963). In the case of composite formation, this model stipulates that strong adhesion may only be achieved if the materials facing each other are in close contact. In this connection, it is worth noting that the shear strength has been related to the wetting angle between resin and carbon fibre (Yamamoto *et al.* 1971).

*Chemical coupling*

In the chemical bonding model, the adsorption of chemical groups and the formation of true covalent bonds between fibre and matrix are assumed. The forces of interfacial bonding are, in this case 'primary forces' of high energy (40-400 kJ/mol) i.e. covalent, ionic or metal bonds. Chemical groups that give rise to such bonding are seldom available on a surface, and the aim of surface treatments is to insert them at the interface.

For glass fibres the surface is treated with coupling agents, mainly of the silane type, described among others by Plueddemann (1970). The bonding between fibre and resin involves the

formation of hydrogen bonds between the silanol groups of the fibre and the partly hydrolysed silanes according to the scheme shown in figure 1, where R is a group compatible with the resin.

An overall interpretation of the characteristics of the coupling agents according to the theory of the chemical bond is however not completely satisfactory. Other theories have been proposed, more particularly an enhanced ageing resistance of the composite in a humid atmosphere (Outwater & Murphy 1970).

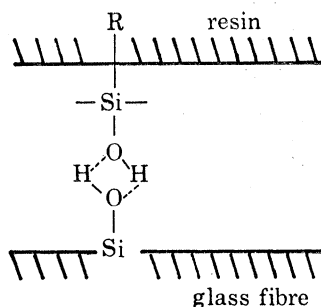


FIGURE 1. Schematic diagram of silane fixation on a glass fibre.

For carbon fibres, the presence of carboxylic and phenolic surface groups suggests the creation of covalent bonds between fibre and matrix. This last possibility was checked by causing surface groups to react with model compounds. Thus, by reacting epichlorohydrin with oxidized type I fibre, an irreversible amount of chlorine, close to the number of acidic groups, has been found (Donnet *et al.* 1974) (figure 2).

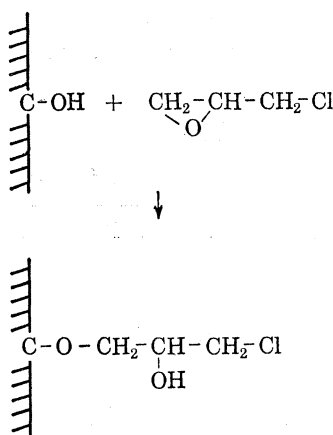


FIGURE 2. Chemical reaction between carbon fibre and epichlorohydrin.

The model of the chemical bonding, however, is only an extension of the physical coupling as suggested by Kaelble (1971). Both are dependent on a good contact and hence upon a good wetting between fibre and matrix. Only the bonding energy may vary from one model to the other even though the broad scattered spectrum of the various possible bonds (hydrogen, ionic, covalent bonds) renders their identification difficult.

*Flexible interlayer*

The insertion of a non-rigid interlayer between the fibre and the matrix constitutes another practical means of ensuring a good stress transfer. Broutman & Agarwal (1973) calculated that although the strength of the composite varies little with the modulus of the interlayer, the rupture energy of the composite passes through a maximum for a modulus lower than that of the resin used. It appears, therefore, that coating the fibres with a polymer provides a means of increasing the impact strength of the composite (Fila *et al.* 1972; Hancox & Wells 1977).

A simple process to establish such a non-rigid layer and ensure a good adherence between fibre and matrix has been employed by Riess *et al.* (1974). They modified carbon fibres by grafting a copolymer bearing flexible segments (polyisoprene, PI) and segments compatible with the matrix (styrene maleic anhydride copolymer, SMA). The bonding between the carbon fibre and the polyisoprene sequence consists of dipole-dipole interactions resulting from salified carboxylic groups, as shown in figure 3.

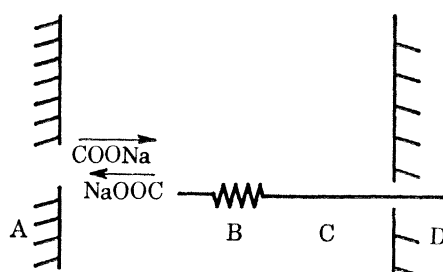


FIGURE 3. Fixation of block polymer on carbon fibre through dipole-dipole interaction. A, fibre; B, elastomer; C, SMA; D, matrix of composite (Riess *et al.* 1974).

The mechanical characteristics of thus obtained epoxy composites are shown in table 2. It appears that the impact strength has been significantly improved.

TABLE 2†

carbon fibre (type II)	carbon fibre-epoxy composites	
	i.l.s.s./MPa	resilience/(J cm <sup>-2</sup> )
non-treated	71	4.0
PI-SMA treated	80	6.3

† Riess *et al.* 1974.

The 'Kevlar type' organic fibres have likewise been polymer treated with positive results. According to Wake (1972), the fibre surface may react with an isocyanate linked polymer as indicated in figure 4.

Using polyurethane treatment, Riess & Reeb (1977) significantly improved the torsion stiffness of Kevlar-epoxy composites.

Before concluding this section, it is worth noting that the model of the flexible interlayer has also been suggested to account for the behaviour of silane coupling agents in glass-fibre based composites. In fact, Bascom (1972) reports that after hydrolysis, the silanes may have an effect on resin polymerization and hence on its physico-chemical properties in the vicinity of the

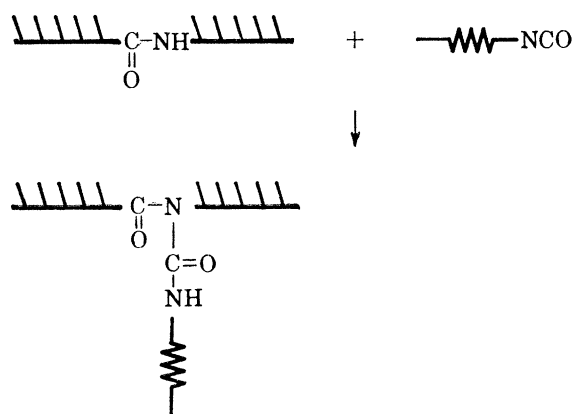


FIGURE 4. Reaction of isocyanate linked polymer with Kevlar fibre (Wake 1972).

interface. Unfortunately, the extent of this modification and the thickness of the interlayer that is affected are not well known. The thickness is estimated to lie between 5 nm and 1  $\mu\text{m}$ , depending on the composites. However, the theory of the deformable layer (Kenyon 1968) appears to be general and to apply to various types of fibre and organic resin composites.

#### INTERFACIAL PROPERTIES OF CARBON FIBRE-BASED COMPOSITES

It is well known that the interlaminar shear strength (i.l.s.s.) of carbon fibre-based composites may be increased significantly by oxidation. Generally, the oxidation reactions bring about a simultaneous increase of the fibre surface and the number of surface groups. Both factors may have beneficial effects on the fibre-resin bonding. A third possible reason for the improvement of the i.l.s.s. is the removal of surface defects on the carbon fibres (McKee & Mimeault 1973).

#### *Anodic oxidation of the fibres*

In order to investigate the effect of surface groups on the fibre-resin bonding, we developed surface treatments that alter the nature and the number of surface groups without affecting the surface area. Previous studies showed that short time anodic oxidations in various electrolytes (diluted nitric acid, alkaline medium) permit the achievement of such conditions (Ehrburger *et al.* 1974, 1975).

Experiments have been carried out with carbon fibre, ex-PAN fibre (AC fibre, type II). The acidic groups were of two types: the stronger ones (carboxylic and some phenolic groups) were estimated with sodium hydroxide, whereas sodium ethanolate was used for the weaker ones (hydroxylic groups). In the latter case, all the acidic functions on the carbon surface were neutralized (Scholz & Boehm 1970). The data in table 3 reveal that the number of functions

TABLE 3

carbon fibre	$S_{\text{B.E.T.}}/(\text{m}^2 \text{g}^{-1})$	acidic surface groups neutralized with	
		NaOH/ $(\mu\text{equiv g}^{-1})$	NaOC <sub>2</sub> H <sub>5</sub> / $(\mu\text{equiv g}^{-1})$
AC non-treated	0.3	7	10
AC-HNO <sub>3</sub>	0.3	14	20
AC-NaOH	0.3	16	17



that may be measured with sodium ethanolate is similar whatever the type of electrolyte used for the anodic etching ( $\text{HNO}_3$  or  $\text{NaOH}$ ). Yet, the treatment of the fibres in alkaline medium, AC-NaOH, yields comparatively stronger acidic groups since they may all be neutralized with sodium hydroxide. The uncertainty of the measurements is of  $\pm 2 \mu\text{equiv/g}$  for AC- $\text{HNO}_3$  and AC-NaOH fibres.

*Bonding properties of modified carbon fibres*

Unidirectional composites have been formed by using treated carbon fibres and an epoxy resin (Ehrburger *et al.* 1974). The interlaminar shear strength of the composites has been measured with the cantilever test as previously described (Donnet *et al.* 1974). The mode of failure of the composite in this test has been determined by analysing the load-deflexion diagram. In fact, the shape of this diagram reveals the nature of the bonding between the components of the material (Hanna & Steinsiger 1969). Two extreme cases may occur.

The interfacial bonding is weak; in that case 'pull out' is responsible for the rupture. As the fibres are not matrix bound, they slide in their beddings and load transfer can no longer take place (shear failure).

The interfacial bonding is strong; then the matrix transfers the load to the fibres until reaching of the breaking point. In this case, the failure is sudden and catastrophic (tensile failure).

Most cases of failure lie between these extremes, the relative importance of which depends on the interfacial bonding.

The load-deflexion diagram of composites comprising AC fibres are shown in figure 5.

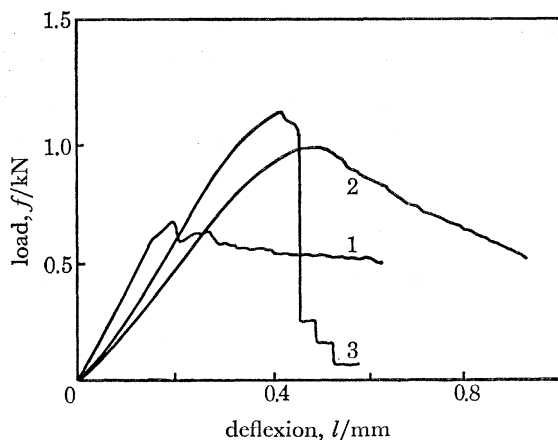


FIGURE 5. Load-deflexion diagrams for carbon fibres-epoxy composites: curve 1, non-treated AC fibres; 2, AC- $\text{HNO}_3$ ; 3, AC-NaOH.

The composites containing untreated fibres displays a shear failure mode. On the other hand, AC-NaOH fibres induce a tensile failure mode. In the case of AC- $\text{HNO}_3$  fibres, the failure mode is intermediate. The values of the i.l.s.s. as well as the mode of the failure of the composites are given in table 4.

It appears that anodic treatment results in similar improvements of the shear strength, whereas the failure modes observed are definitively different. The aspects of the fracture of the samples observed by scanning electron microscopy confirm the mode of failure (figures 6 and 7). For AC- $\text{HNO}_3$  fibres, 'pull out' of the carbon fibres is still observed, whereas with AC-NaOH fibres, the fracture surface of the composite is clean and smooth.

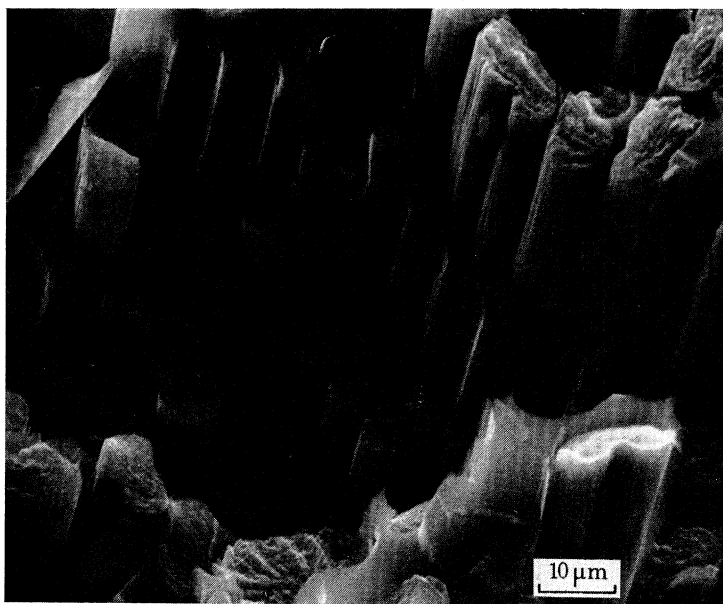


FIGURE 6. Scanning electron micrograph of the fracture of AC-HNO<sub>2</sub>-epoxy composite.



FIGURE 7. Scanning electron micrograph of the fracture of AC-NaOH-epoxy composite.



TABLE 4

carbon fibre	carbon fibre-epoxy composites	
	i.l.s.s./MPa	failure mode
AC non-treated	55	shear
AC-HNO <sub>3</sub>	85	intermediate
AC-NaOH	92	tensile

In order to relate the properties of the composites to those of the carbon fibres, the number of acidic groups was varied at the carbon surface through pyrolysis at 1273 K for 3 hours, in an inert atmosphere. The data are included in table 5.

TABLE 5

carbon fibre	acidic surface groups neutralized with		carbon fibre-epoxy composite	
	NaOH/( $\mu\text{eq g}^{-1}$ )	NaOC <sub>2</sub> H <sub>5</sub> /( $\mu\text{eq g}^{-1}$ )	i.l.s.s./MPa	failure mode
AC-HNO <sub>3</sub>	14	20	85	intermediate
AC-HNO <sub>3</sub> 1273 K	0	15	77	intermediate
AC-NaOH	16	16	92	tensile
AC-NaOH 1273 K	0	13	77	intermediate

It is seen that, after pyrolysis, the strong acidic groups that may be neutralized with sodium hydroxide are destroyed, whereas the weak acidic groups are only partly removed. Moreover, the nature of the acidic functions determines largely the failure mode of the composite in the shear test. The presence of strong acidic groups results in a tensile failure mode, i.e. a strong interfacial bonding. On the other hand, the failure in shear would rather correspond to weak acidic groups.

In figure 8, the i.l.s.s. of the material has been plotted against the total amount of acidic groups. A clear correlation indeed appears between the content of acidic functions and the ultimate value of the shear strength.

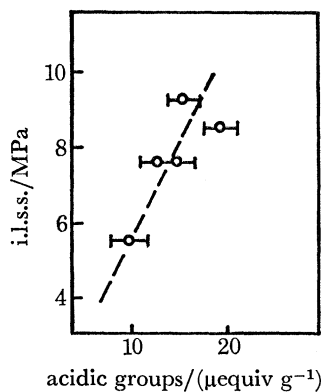


FIGURE 8. Interlaminar shear strength of the composite plotted against the amount of acidic group neutralized by sodium ethanolate.

## DISCUSSION

The data obtained with anodically treated carbon fibres clarify the predominant role played by the surface acidic groups. The presence of weak acidic functions (mainly OH groups) enhances the interlaminar shear strength without affecting significantly the mode of failure, i.e. the nature of the interfacial bonding. This would be consistent with an increase in interfacial coupling, as a result of better fibre wetting by the resin.

The presence of stronger acidic groups (COOH and OH) results in an increased adhesion between fibre and matrix. In fact, both the shear strength and the mode of failure of the composite are affected. The adhesion between fibre and matrix is thus enhanced when the surface of the reinforcing agent has the ability to form chemical bonds with the resin. A similar observation has been made with glass-epoxy composites which suggests this to be a general phenomenon (Kenyon 1968). It must be stressed, however, that the theory of the flexible layer previously exposed also permits an interpretation of these results. As a matter of fact, it has been observed that the surface of the reinforcing agent could alter the polymerization reaction of the resins with the resultant changes in their rheological and mechanical properties at the interface (Cuthrell 1967; Kenyon 1968; Bessel *et al.* 1972; Beaumont 1974). This means that chemical functions may induce polymer alterations at the time of gelation in the vicinity of the fibre, thus creating a layer with different mechanical properties. The extent of such a layer at the interface would then be dependent on the nature and the amount of surface groups. However, it is difficult to state precisely the exact nature of the alterations in the resin.

The example of the carbon fibres is a good illustration of the intricate phenomena occurring at the interface of a composite material. In this particular case it was possible to demonstrate that the nature and the amount of acidic groups play a definite part in the interfacial stress transfer. Although their mechanism of action has so far not been fully elucidated, it appears that if properly inserted on the surface, they will provide a means for optimizing the bonding between fibre and matrix.

## REFERENCES (Ehrburger &amp; Donnet)

- Bascom, W. D. 1972 *Macromolecules* **5**, 792-798.  
 Beaumont, P. W. R. 1974 *J. Adhesion* **6**, 107-137.  
 Bessel, T., Hull, D. & Shorthall, J. B. 1972 *Faraday Spec. chem. Soc.* **2**, 137-143.  
 Broutman, L. J. & Agarwal, B. D. 1974 *Polym. Engng Sci.* **14**, 581-588.  
 Cuthrell, R. E. 1967 *J. appl. Polym.* **11**, 1495-1507.  
 Clark, D., Wadsworth, N. J. & Watt, W. 1974 *Proc. 2nd Carbon Fibres Conference*, pp. 44-51. London: The Plastics Institute.  
 Donnet, J. B., Papirer, E. & Dauksch, H. 1974 *Proc. 2nd Carbon Fibres Conference*, pp. 58-64. London: The Plastics Institute.  
 Ehrburger, P., Herqué, J. J. & Donnet, J. B. 1974 *Proc. 4th Conf. Ind. Carbon and Graphite*, pp. 201-208. London: Society of Chemical Industry.  
 Ehrburger, P., Herqué, J. J. & Donnet, J. B. 1975 *Petroleum derived carbons*. A.C.S. Symposium Series, vol. 21 pp. 324-334. The American Chemical Society.  
 Fila, M., Bredin, C. & Piggott, M. R. 1972 *J. Mater. Sci.* **7**, 983-988.  
 Hancox, N. L. & Wells, H. 1977 *Fibre Sci. Technol.* **10**, 9-22.  
 Hanna, G. L. & Steinsiger, S. 1969 *Composite materials, testing and design*, vol. 460, pp. 182-191. ASTM Special Technical Publication.  
 Kaelble, D. H. 1971 *Physical chemistry of adhesion*, pp. 45-83. New York: Wiley-Interscience.  
 Kenyon, A. S. 1968 *J. Colloid Interface Sci.* **27**, 761-771.  
 MacKee, D. & Mimeault, V. 1973 *Chemistry and Physics of Carbon*, vol. 8, pp. 151-241. New York: M. Dekker Inc.  
 Outwater, J. O. & Murphy, M. C. 1970 *J. Adhesion* **2**, 242-253.

- Plueddemann, E. P. 1970 *J. Adhesion* **2**, 184–201.
- Riess, G., Bourdeaux, M., Brie, M. & Jouquet, G. 1974 *Proc. 2nd Carbon Fibres Conference*, pp. 52–56. London: The Plastics Institute.
- Riess, G. & Reeb, R. 1977 *D.G.R.S.T. report* 74.7.1021, Paris.
- Scholz, W. & Boehm, H. P. 1969 *Z. anorg. allg. Chem.* **369**, 327–340.
- Yamamoto, M., Yamada, S., Sakatani, Y., Taguchi, M. & Yamaguchi, Y. 1971 *Proc. 1st Carbon Fibres Conference*, pp. 179–184. London: The Plastics Institute.
- Wake, W. C. 1959 *Trans Inst. Rubber Ind.* **35**, 145–159.
- Wake, W. C. 1972 *J. Adhesion* **3**, 315–324.
- Zisman, W. A. 1963 *Ind. Engng Chem.* **55**, 19–36.

### Discussion

A. R. UBBELOHDE, F.R.S. (*Department of Chemical Engineering and Chemical Technology, Imperial College, London, SW7, U.K.*). When certain surface treatments are used to ‘improve’ the contact between carbon fibres and various matrices, it must be remembered that such fibres are often quite well graphitized. Various forms of anodic treatment in aqueous electrolytes containing (say) OH<sup>-</sup> or NO<sub>3</sub><sup>-</sup> may actually promote formation of intercalation compounds of graphite. Even if most of the intruding anions are subsequently removed, e.g. by hydrolysis, intercalation would probably involve penetration of layers in some depth, and leave a fluffier interface after subsequent treatment before contact with the resin, than if surface impurities had been merely removed by high temperature oxidation, or ion bombardment. Titration of the foreign anions with Boehm’s methods may not reveal all those present in the form of intercalation compounds, near the surface of the carbon fibre, because ‘residue compounds’ are formed.

Fibres treated anodically should thus be considered rather critically, since some anions may actually produce a fluffy interface extending inwards to some depth. Since a great variety of anions can be used for anodic intercalation, this procedure can be varied to check how far the interface has been modified in depth, by varying the anion.

P. EHRBURGER. We have indeed observed that intercalation occurs when graphitized carbon fibres are anodically treated. In fact, there is a tremendous decrease in the tensile strength of those treated fibres (Ehrburger, P., Herque, J. J. & Donnet, J. B. (1975). *Petroleum Derived Carbons, A.C.S. Symposium*, **21**, 324–334).

However, for fibres heat-treated at 1100°C, we found no evidence of intercalation.

J. W. JOHNSON (*Rolls-Royce Limited, Aero Division, Non-Metallic Laboratories, Plastics and Composite Materials Department, Alfreton Road, Derby, U.K.*). Professor Ubbelohde’s observations on the electrolytic formation of intercalation compounds in carbon fibres are very relevant and have great significance for carbon fibre composite technology. Mild anodic electrolysis of carbon fibre in a variety of aqueous electrolytes often produces thin film interference colours on the fibre surface; extended electrolysis will ultimately render the fibre completely transparent so that it can be examined in the light microscope. The electrolysis is most easily accomplished with type A or type III fibres, although the swelling accompanying the intercalation bursts the fibres along their lengths and the properties are irretrievably ruined.

Types I and II fibres, rather oddly, are more resistant to the process but are still susceptible to a large extent. Orientation is maintained in the swollen state as shown by birefringence, and details of fibre morphology are preserved (see figure 9).

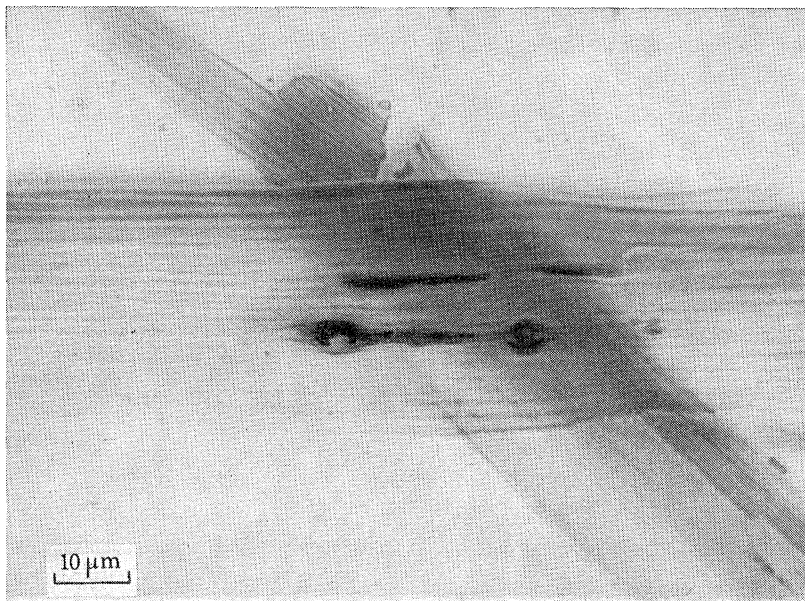


FIGURE 9. Fibres of Courtaulds Grafil A anodically electrolysed in dilute sulphuric acid. Note the internal flaw rendered visible and the general transparency of the residues. The sample is immersed in the electrolyte and viewed by Nomarski differential interference contrast in transmission.

A. R. UBBELOHDE, F.R.S. (*Imperial College, London, U.K.*). Two phenomena in the behaviour of composites warrant some discussion in terms of solid state chemistry and solid state thermodynamics:

(1) Because of their bond structure, the thermal expansion of most of the fibres under discussion at this meeting is extremely anisotropic. Parallel to the fibre spine, it will be zero or even slightly negative, but in directions perpendicular to the spine thermal expansion coefficients will tend to be exceptionally large, because of the kinds of forces holding a bundle together in any fibre. When the composite is prepared and used under more or less isothermal conditions, the very large forces resulting from non-uniform thermal expansion may not be a source of internal stress and local weakness. However, when it is intended for use at high temperatures, very different from those used in the fabrication, some intense local stresses must develop around each fibre during use. It may be possible to build in some of these stresses during fabrication, so as to compensate part of the external shock stresses the material will have to encounter. The shrinking of chilled metal into containers of different thermal expansion is a simple example of stresses built in during fabrication.

It would be helpful, and informative to molecular theory, to have data on the anisotropic thermal expansions of the principal fibres, over the widest possible range of temperatures.

(2) From remarks made by one of the speakers, one mode of effective protection of composites during use may be when the interlace layer between fibre and matrix acts as a shock absorber, cracking away so as to form a kind of shock absorbing sleeve around the strong spine within it.

If this view is correct, the question arises as to what happens to the thin layer of interface between each fibre spine, and the matrix in bulk, when the system is exposed to cyclic stresses. Solid state chemistry and thermodynamics suggest that the structure of some interface layers may be at least partly reversible, reverting to the original state, or near it, when the stress is reversed. Repeated cycles of stress would drive a partly reversible system of fibre-sleeves to an



asymptotic state, which should be detectable in the various mechanical stresses. However, some interface structures may be broken wholly irreversibly in a single stress situation. Alternatively, interface material could probably be found whose structure would be substantially reversible in each cycle. Possibilities of exploring these alternative modes of response to stress of interfaces between fibres and their matrix present some interesting opportunities in solid state thermodynamics.

M. O. W. RICHARDSON (*Department of Materials Technology, Loughborough University, Leicestershire, U.K.*). Regarding the helpful comments of Professor Ubbelohde, on the need for reversible energy absorption or modified stress transfer mechanisms at the interface of the various components of composite materials, I should like to point out that Dr E. P. Plueddemann in the U.S.A. has published some interesting theories on 'dynamic equilibrium adhesion mechanisms'. He claims that these can operate at the interface between a hydrophilic mineral filler and a polymer matrix.

P. EHRBURGER. In fact, 'reversible bonds' at the interface constitute a kind of optimization of the bonding between fibre and matrix. Thus, a covalent bond at the interface, when broken, cannot be rebuilt again. On the contrary, 'secondary forces', i.e. hydrogen bonds, can be rebuilt readily at the interface.

R. A. M. SCOTT (*Thames Polytechnic, London, SE 18 6PF, U.K.*). We have performed measurements on glass-reinforced polystyrene and have found that the usual siloxane keying agent used on the surface of the glass fibre produced composites of substantially increased strength as compared with those containing uncoated fibres. Bearing in mind the fact that polystyrene is normally considered as having saturated bonding, could Dr Ehrburger suggest any reason for this behaviour?

P. EHRBURGER. As already said, the role of the keying agent is complex and not yet completely understood. Generally speaking, the coupling agent affects the surface energetics of the fibre and plays the role of a water scavenger. In Dr Scott's case, the observed increase of strength of the composite may result from the water removal by the siloxane agent.

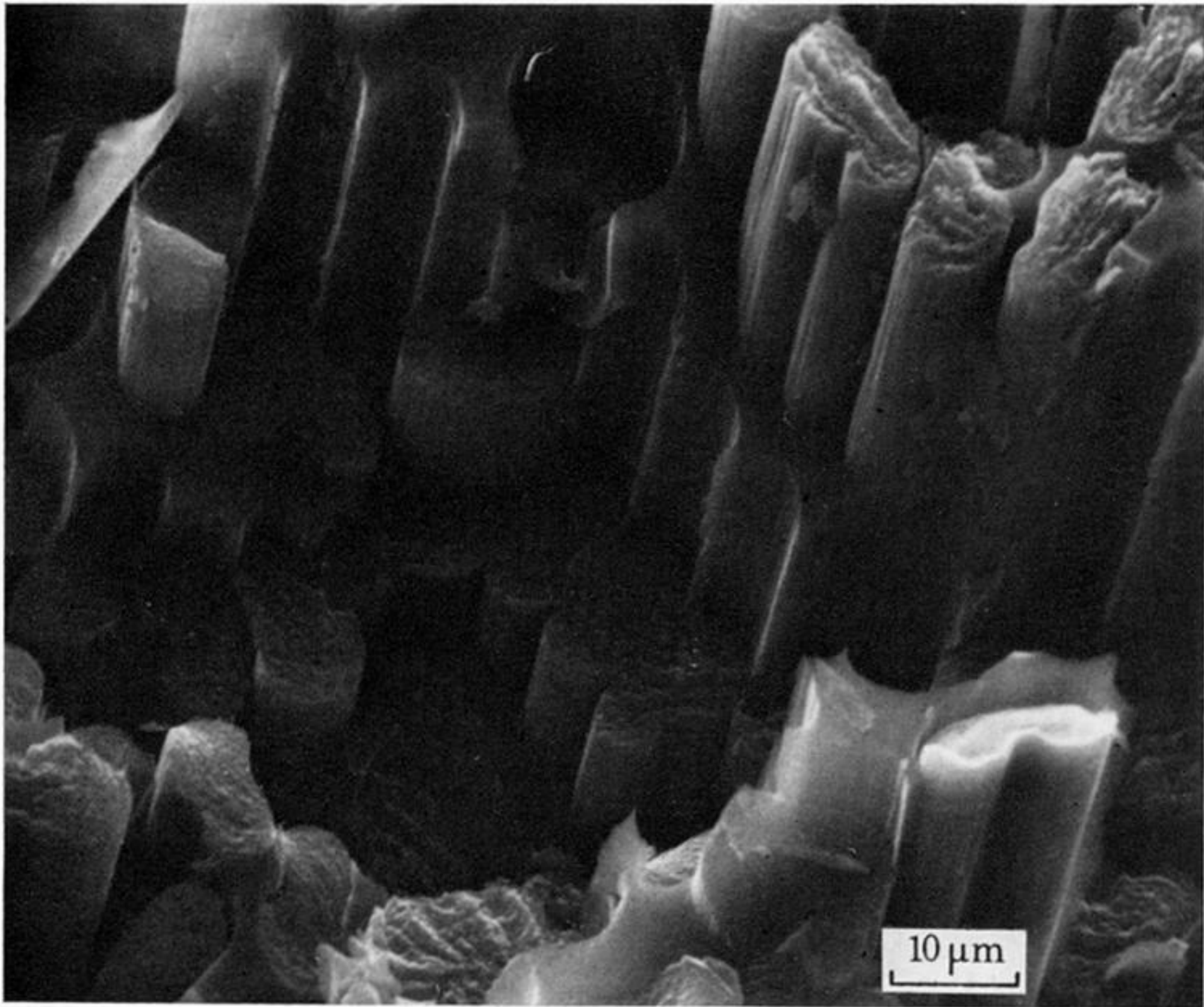


FIGURE 6. Scanning electron micrograph of the fracture of AC-HNO<sub>2</sub>-epoxy composite.



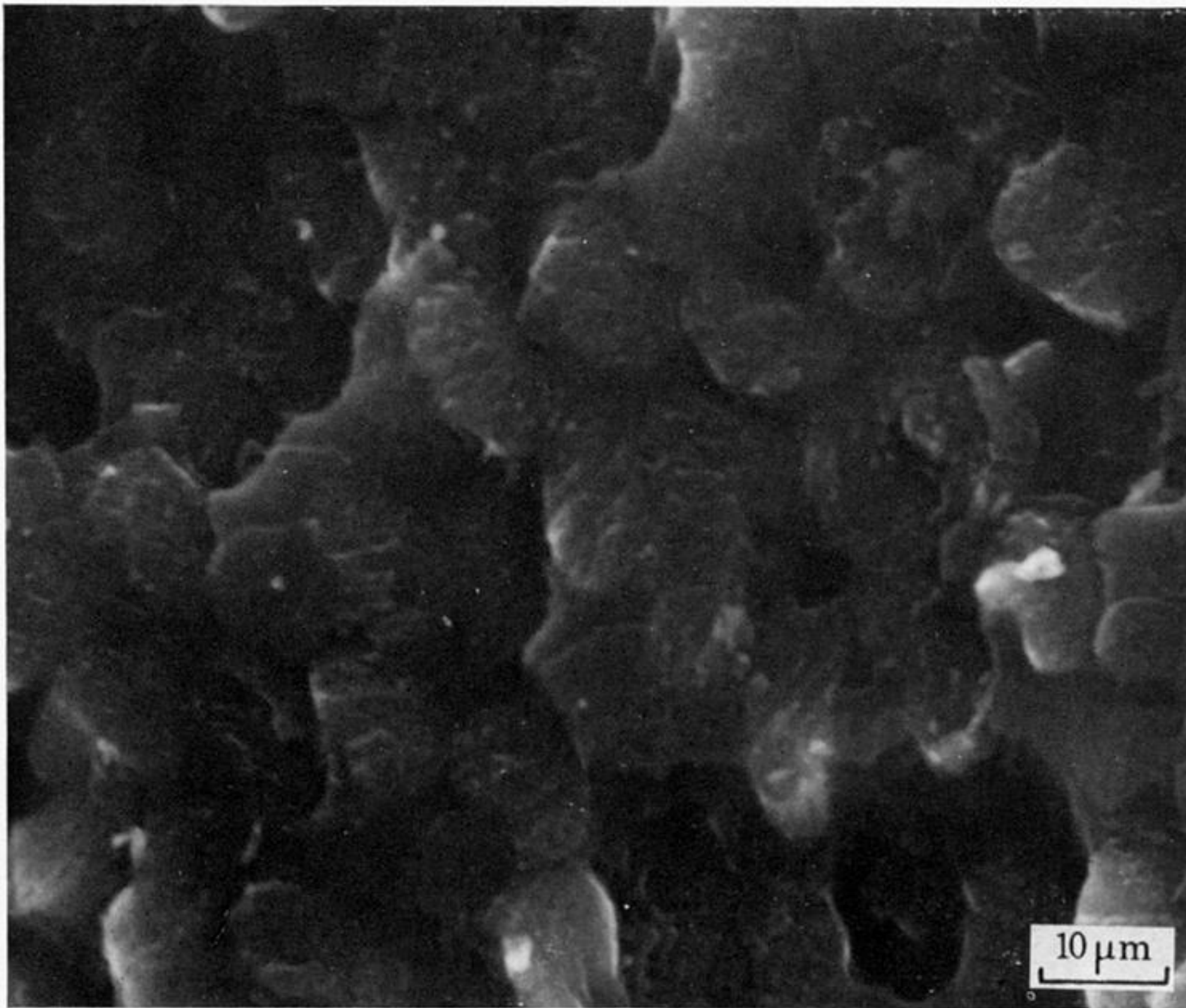


FIGURE 7. Scanning electron micrograph of the fracture of AC-NaOH-epoxy composite.



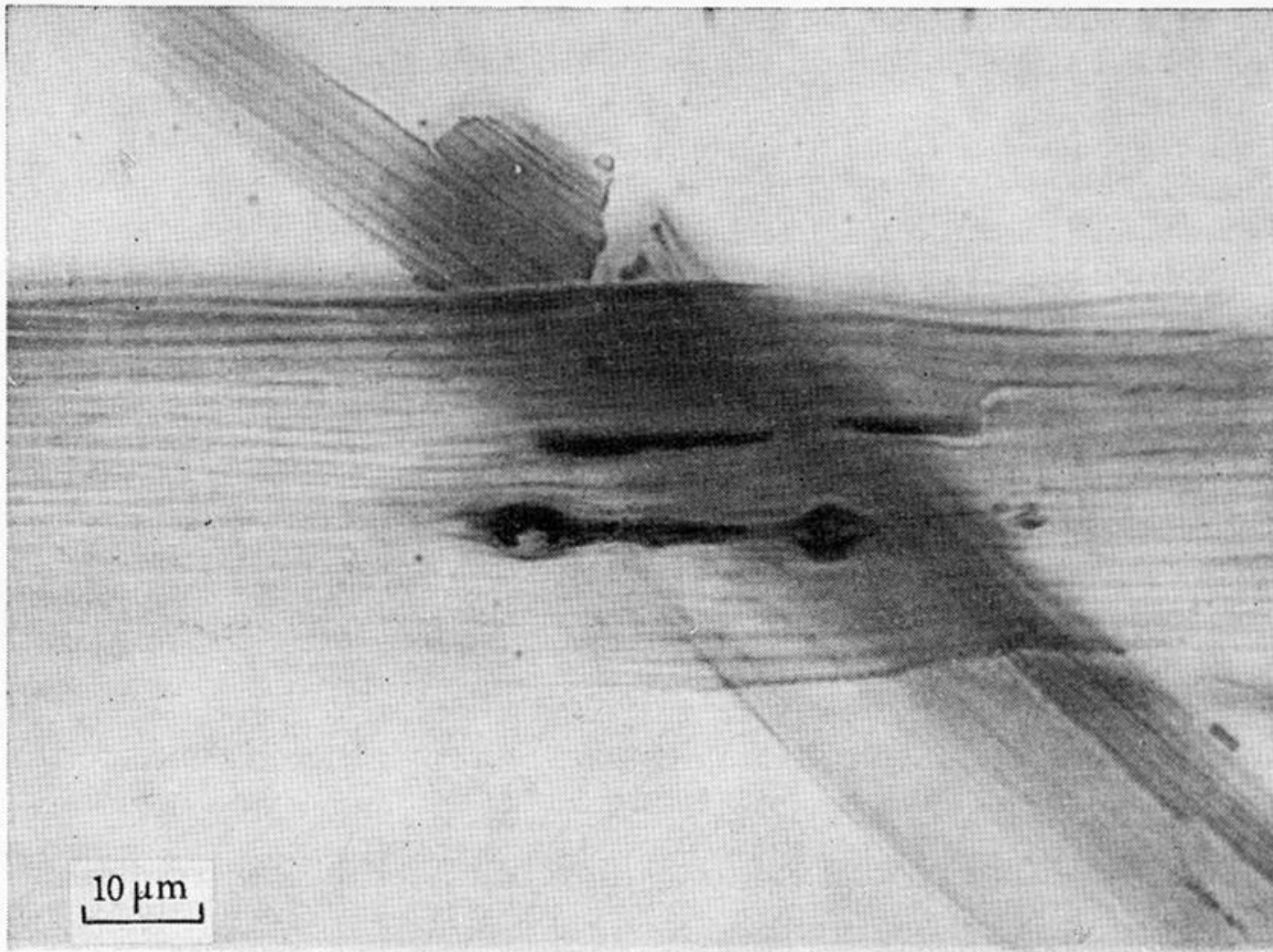


FIGURE 9. Fibres of Courtaulds Grafil A anodically electrolysed in dilute sulphuric acid. Note the internal flaw rendered visible and the general transparency of the residues. The sample is immersed in the electrolyte and viewed by Nomarski differential interference contrast in transmission.