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The crystallization and interfacial bond strength of nylon 6 at carbon and glass fibre surfaces

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The nucleation and crystallization of nylon at the interface in glass-fibre and carbon-fibre reinforced nylon 6 composites has been investigated by electron microscope studies of sectioned and etched bulk specimens and solution cast and melt crystallized thin films. The fracture energies of the composites were obtained from tensile strength tests and the interfacial bond strengths were calculated from fibre pullout measurements. The fibres are shown to nucleate a columnar structure at the interface with marked differences between the structures nucleated by glass fibres and by carbon fibres and also between that nucleated by type I and type II carbon fibres. The structure around glass fibres was non-uniform and influenced to some extent by the presence of the size coating on the fibre surface. In the carbon-fibre composites the columnar structure was due primarily to physical matching of the graphite crystallites. Surface treatment of the carbon fibres to improve chemical bonding is shown to have a significant effect on bond strength which cannot be explained in terms of the columnar structure at the fibre surface. The treated fibres gave rise to only small amounts of fibre pull-out and low fracture energies whereas the untreated fibres showed extensive pull-out which was reflected in high fracture energies.

1. Introduction

The mechanical properties of fibre-reinforced plastics depend to a large extent on the ability of the matrix to transfer stress to the high strength fibres. This depends in turn on the physical nature of the fibre surface and the fibre to matrix interfacial bond. Recently it has been proposed [1, 2] that improvements in the mechanical properties of the composite may result from changes in the morphology and crystallinity of the polymer matrix in the interfacial region. In preliminary work [3, 4] we have shown that in polyamides the presence of reinforcing fibres can produce a directional crystallization with a significant difference in the crystallization around type I and type II carbon fibres and E glass fibres. The directional crystallization consisted of an inner zone, the initial nucleation region adjacent to the fibre, and an outer zone, the columnar growth region, which extended to the spherulitic structure of the matrix. The width of the inner zone was greater in the case of the type I fibres. The extent and morphology of the columnar growth region around the type I and type II fibres were similar, irrespective of fibre manufacturer. Similar columnar structures have also been observed in polypropylene nucleated at carbon fibres [5, 6] and at copper wires [7]. The morphology and molecular orientation relationships of the polymer lamella within the columnar zone is similar to that along the radius of a spherulite or a "row" nucleated structure, which has been discussed in detail by Keller [8, 9]. However, the nucleation of polymers on substrates is complex and may be influenced by factors such as supercooling, thermal conductivity, surface tension, surface energy and polymer flow rates. In many cases the nucleation of polymers has been considered in terms of the epitaxial matching of the crystal lattices of the polymer and substrate where, in the initial nucleation, the molecular chain axis of the polymer is oriented parallel to the substrate surface [10–14]. Experiments using graphite surfaces have shown that the polyethylene unit cell is oriented with its (1 1 0) plane parallel to the substrate and has a lattice mismatch of less than 4% [15].

Chemisorption has also been proposed as a nucleating mechanism which may aid epitaxial crystallization. The nucleation of polypropylene [5], nylon 6 [15] and nylon 66 [16] onto graphite surfaces has indicated that there are strong interactions between the polar groups of the macromolecule and the graphite crystallites. The chemisorption of atomic hydrogen, carbon, nitrogen and oxygen are believed to be of particular importance, and it has been demonstrated that the most stable configuration for carbon and nitrogen is that in which the atoms are situated directly over the bond connecting nearest carbon atoms in the graphite substrate [17].

In composite systems consideration must also be given to the type of carbon fibre used since it has been shown by Hobbs [5] that polypropylene films containing type II carbon fibres do not generate a columnar growth, whereas type I fibres have pronounced nucleating ability. This is attributed to the difference in graphite crystallite size in the type I and type II carbon fibres and it is suggested that for nucleation a minimum graphite crystal size of 50 Å is required [5].

The purpose of the present work is to investigate the factors affecting the nucleation and the structure of the columnar growth of anionically polymerized nylon 6 around carbon fibres, and to show how the presence of the columnar structure affects the interfacial bond strength of the system, as measured by the fibre pull-out from the fracture surfaces.

2. Experimental

The anionic polymerization of nylon 6 using sodium hydride as catalyst and acetyl caprolactam as initiator has been described fully elsewhere [18]. Cast thin nylon films containing single fibres were prepared for optical microscopy by placing individual filaments on degreased carbon-coated glass slides. A small drop of liquid monomer, catalyst and initiator was placed on the slide and a second slide placed on top to disperse the solution into a film. Polymerization was allowed to take place under nitrogen in an oven maintained at the required polymerization temperature.

Films containing single filaments for examination by electron microscopy were prepared by melt crystallizing a solution cast thin film. A thin layer of polyamide was deposited onto a clean and degreased glass slide from a solution of 2% nylon in formic acid. After evaporation of the formic acid small lengths (less than 1 mm) of either carbon or glass fibres were deposited onto the slide. The nylon, with the fibres on the film surface, was then melted at 535 K (260° C) for 8 min in an atmosphere of nitrogen and allowed to crystallize in silicone fluid for 15 min at 453 K (180° C). The spherulitic film containing the fibres was stripped from the slide using polyacrylic acid and floated onto electron microscope grids.

Tensile tests were performed on an Instron testing machine using unidirectional continuous fibre composites prepared in a modified leaky mould. The polymerization of the nylon was carried out *in situ* around the fibres; details of the fabrication of the composites and the preparation of tensile specimens has been previously described [4]. An estimate of the fibre–matrix bond strength was made from the mean length of pulled out fibres protruding from the fracture surface [19]. The length of fibre was measured from scanning electron micrographs of the fracture faces.

3. Results

The columnar structure around the filaments in the thin films was examined using polarizing optical microscopy and transmission electron microscopy. Thirteen different types of carbon fibres from six different manufacturers, and "E" glass fibres having a polyamide compatible coupling agent in the size coating were examined.

Optical polarizing microscopy has primarily revealed that there is a significant difference between the columnar structures surrounding the type I and type II carbon fibres and the glass fibres [4]. When viewed between crossed polars the columnar region consisted of an inner zone, adjacent to the fibre, with a fine speckled structure and an outer zone with a fibrillar structure extending to the spherulitic matrix. For the type I carbon fibres the width of the inner zone was greater than around the type II fibres. The extent and morphology of the columnar regions around the type I and II carbon fibres were similar irrespective of fibre manufacturer. "Modmor I", "Rigilor AG" (type I) and "Grafil HM-S" (I) gave similar structures and "Modmor II", "Rigilor AC" (type II) and "Grafil A" also produced similar structures [4].

No marked differences in the columnar growth were observed with fibre surface treatments and similar columnar morphologies were seen to surround treated and untreated "Hitron HMG-50" carbon fibres [4]. This similarity was also observed in films containing treated and untreated "Modmor I" and "Modmor II" carbon fibres.

Reduction in the matrix spherulite size had a significant effect on the extent of the outer fibrillar zone of the columnar growth region around both type I (Fig. 1) and type II (Fig. 2) carbon fibres. It can be seen that decreasing the mean spherulite diameter from 25 μm to about 3 μm has resulted in the elimination of the outer zone in both cases. The inner white zone was unaffected indicating that it is independent of the nucleation and crystallization rates within the spherulitic matrix.

The ability of the glass fibres to nucleate columnar growth is less than that of the carbon fibres and the columnar structure around the glass fibres was not apparent at all in some places along the same glass filament (Fig. 3).

The different nucleating ability of the carbon and glass fibres was also apparent in bulk composite sections. The carbon fibres were always at the central nucleation position of each columnar unit [4]. The glass fibres, however, tended to be randomly positioned with respect to the spherulite or columnar structures. Fig. 4 shows a mechanically polished and etched section of a glass fibre composite in which many fibres intersect the structural boundaries.

The solution cast and melt crystallized thin films which were examined using transmission electron microscopy also demonstrate the differences in the nucleating ability of the surfaces. Electron micrographs of the columnar crystallization at "Modmor I" and "Modmor II" carbon

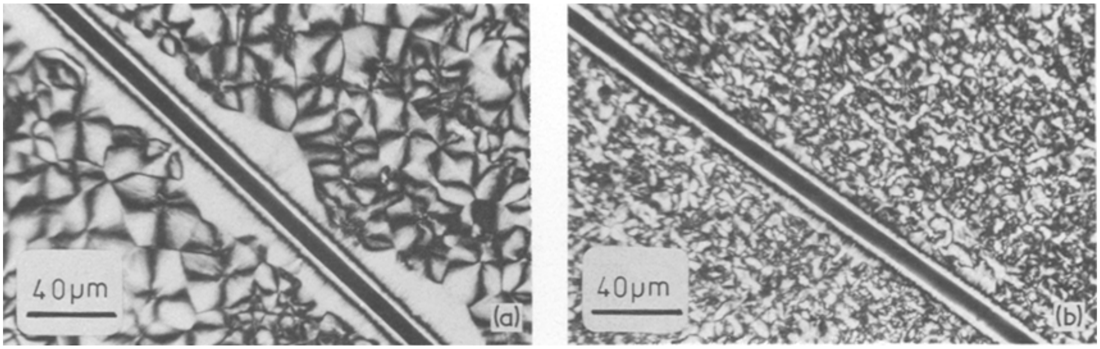

Figure 1(a) and (b) Optical micrographs using crossed polars showing the effect of reducing the nylon spherulite size on the extent of the columnar growth around type I carbon fibres.

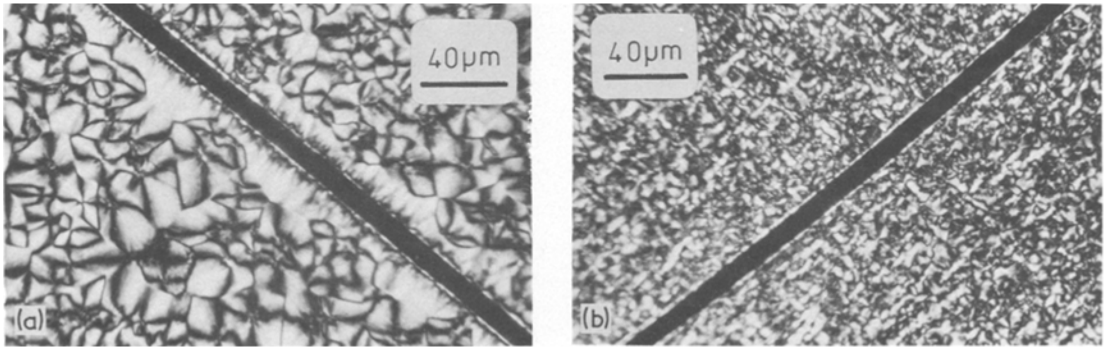

Figure 2(a) and (b) Polarizing micrographs showing the effect of reducing the spherulite size on the columnar growth around type II carbon fibres.

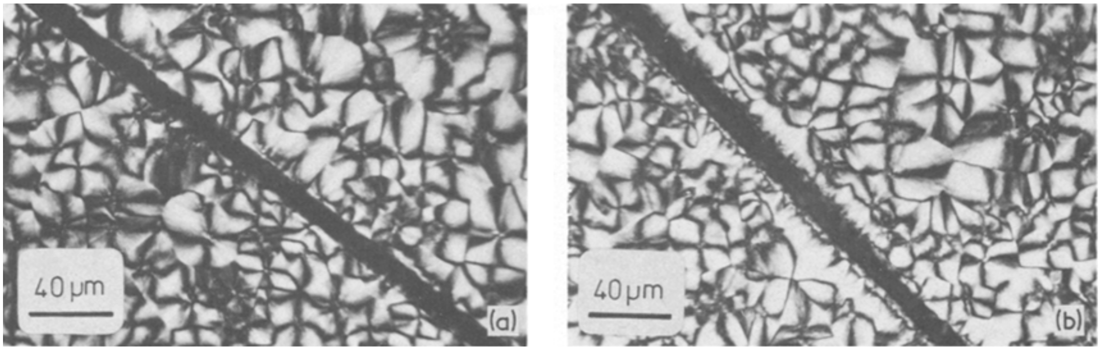

Figure 3(a) and (b) Optical micrographs of thin films of nylon 6 showing the lack of uniformity of the columnar growth around different parts of the same glass filament.

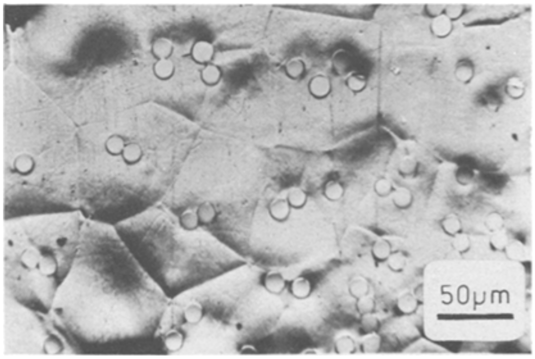

Figure 4 A bulk section of a glass fibre composite mechanically polished and etched in 10% formic acid showing the random positioning of the fibres.

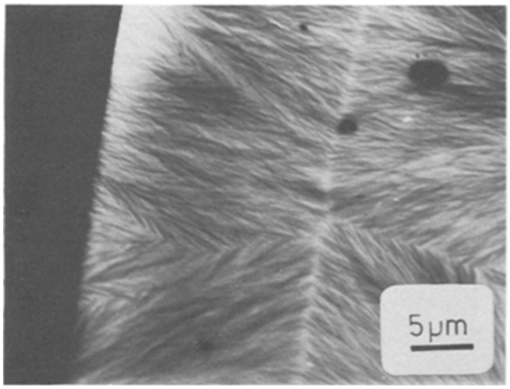

Figure 6 Electron micrograph of a melt crystallized thin film containing a type II carbon fibre showing the nucleation at the carbon surface.

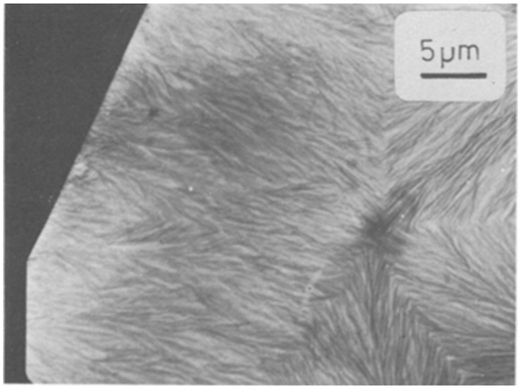

Figure 5 Electron micrograph of a melt crystallized thin film showing the nucleating ability of the type I carbon fibres.

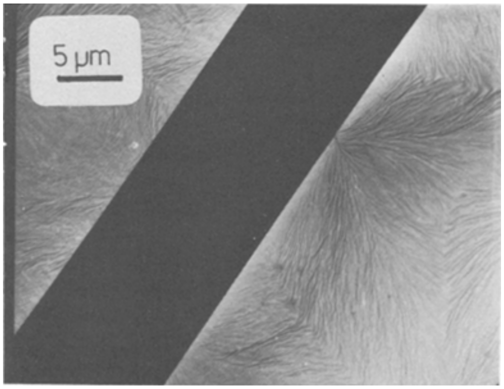

Figure 7 Transmission electron micrograph showing the nucleation around a glass fibre.

fibre surfaces (Fig. 5 and 6) show the columnar region extending out to the matrix spherulite structure. In Fig. 7 the nucleation at a glass fibre is shown and it can be observed that very few nucleation sites are apparent. This lack of nucleii produces a radiating fan-like structure initiated at discrete points along the surface, in contrast to parallel fibrillar morphology around the type I carbon fibres. There is also some tendency for the columnar zone around the type II fibres to exhibit these fan-like features indicating that there are fewer independent nucleii operating. Examination

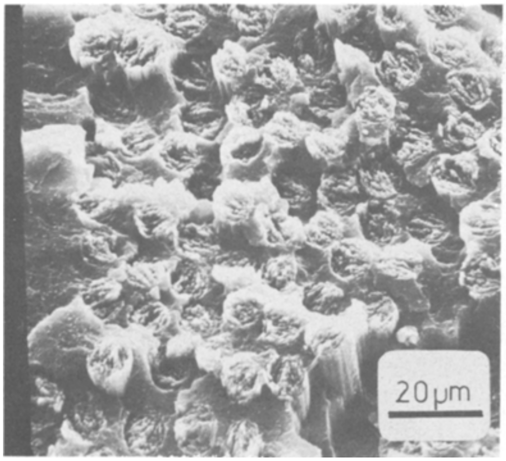

Figure 8 Stereoscan micrograph of the tensile fracture surface of a composite containing "Modmor I" surface treated carbon fibres.

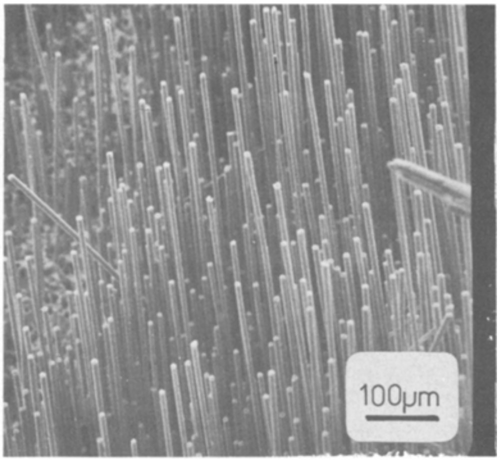

Figure 9 Stereoscan micrograph of the fracture surface of a nylon composite containing untreated "Modmor I" carbon fibres.

of the melt crystallized films (Fig. 5 and 6) did not reveal any morphological features corresponding to the inner nucleation zone in the films examined using polarizing microscopy.

To investigate the effect of columnar morphology on the bond strength of the nylon composites the tensile fracture surfaces were examined by scanning electron microscopy. A marked difference in the extent of pull-out of the fibres was observed which was most pronounced in the composites containing treated and untreated type I carbon fibres (Figs. 8 and 9 respectively). In the case of the treated fibre almost no pull-out and debonding has occurred whereas extensive debonding and pull-out has taken place in the untreated fibre composite. Such a marked effect was not observed in composites containing type II carbon fibres.

From the scanning electron micrographs the pull-out lengths were measured and using the analysis outlined by Phillips [19] values were obtained for the nylon–fibre interfacial bond strength and the fracture energies (Table I). Of particular note is the very high bond strength of the treated type I fibres and the correspondingly low fracture energy values, very little energy having been dissipated in the pull-out of the fractured fibres. The untreated type I fibres, however, can be seen to have a very low bond strength and a high pull-out fracture energy. Surface treatment of the fibres does not have such a pronounced effect on the bond strength and fracture of the composites containing type II carbon fibres and the values calculated for both type II carbon and glass fibres are somewhat similar.

TABLE I Values of interfacial bond strength and fracture energies calculated from fibre pull-out lengths

Fibre	Mean pull-out length (μm)	Bond strength (MN m^{-2})	Fracture energies (kJ m^{-2}) Pull-out γ_p	Initiation γ_i	Total γ_T
Modmor I (treated)	3.6	479	0.65	0.03	0.68
Modmor I (untreated)	84	20	12.8	0.18	13.0
Modmor II (treated)	60.5	46	12.9	0.47	13.4
Modmor II (untreated)	47	60	8.5	0.3	8.8
Grafil MM-S (I treated)	11.7	181	2.8	0.06	2.9
Glass 'E'	49.7	54	7.7	5.7	13.4

4. Discussion

The polarizing microscopy of nylon 6 thin films and sections containing reinforcing fibres demonstrates that various columnar structures exist at the fibre surface. It is apparent that the carbon fibres, particularly the type I fibres have a very great nucleating ability for the polyamide. The crystallization observed around these fibres is more pronounced than that produced by the majority of other surfaces that promote directional crystallization.

Although the columnar growth may exist

around all the fibres examined, it can be seen from Figs. 1 to 3 that several differences in columnar morphology exist. Most significant among these are, firstly, that the columnar growth around the carbon fibres is considerably more pronounced than that surrounding the glass fibres, and secondly that the structure around the type I carbon fibres is finer than that around the type II fibres. The basic reason for the different structures around the various fibres is considered to be due to the variations in the nucleating power of the different fibre surfaces. Since all the samples were prepared under identical isothermal conditions, factors such as thermal conductivity would not be expected to account for the differences observed.

The difference in the nucleating power of the type I and type II carbon fibres is best considered by examining the inner zone of the columnar growth observed in the polarizing microscope (Figs. 1 and 2). It is apparent that although the structure of this zone is similar around both fibre types, the width of the inner zone around the type II fibres is smaller than that around the type I carbon fibres. It is concluded that the inner zone is due to rapid nucleation of the nylon on the fibre surfaces. There are two reasons for this: the structure of the zone resembles that of the nylon 6 spherulite nuclei when observed between crossed polars and a decrease in the matrix spherulite diameter produces only a reduction in the outer columnar zone and not the inner zone, indicating that the zone is formed prior to any substantial crystallization in the matrix. Because of the smaller width of the inner zone around the type II fibres, it can be concluded that these fibres have less nucleating power than the type I fibres.

This reduction in nucleating ability is responsible for the more coarse fibrillar morphology and the formation of fan-like structures around the type II carbon fibres and glass fibres (Figs. 6 and 7). Since fewer independent nuclei would result in a reduction in the number of centres from which the nylon can crystallize, this results in a coarsening of the structure which fans out from individual nuclei.

As the number of nuclei increases the growing crystallites quickly impinge on their neighbours thus producing a more parallel fibrillar morphology and reducing the tendency to crystallize in fan type structures (Fig. 5). Apart from these differences in texture, the structure of the outer zone is similar to the radial structure of the spherulite. Similar growth rates apply since the width of the outer zone is approximately equal to the spherulite radius, and, as observed in these experiments, reduction in the spherulite diameter decreases the width of the zone.

There are several possible explanations for the differences in nucleating ability of type I and type II carbon fibres. Among these are: graphite crystallite size, crystallite orientation, surface smoothness and perfection of the individual graphite crystallites. Both Hobbs [5] and Baer *et al.* [15] have concluded that crystallite size is the most important single factor governing the nucleation of thermoplastics on to graphite fibres. Hobbs has stated that to effect the epitaxial nucleation of polypropylene a minimum graphite crystal size of 50 Å is required. It is generally acknowledged that the crystallites in the type II material are less well oriented [20, 21] and smaller [12] than those in the type I fibres. However, crystallite size alone as an explanation for columnar growth is somewhat doubtful. According to Tuinstra and Koenig [12], who determined the graphite crystal spacings using Laser Raman Spectroscopy, the apparent crystallite size of "Hitron HMG-50" and Morganite II fibres are similar, 80 and 50 Å respectively, although these fibres exhibit different columnar morphologies, the "Hitron" fibre behaving as a typical type I fibre and the Morganite fibre as a type II. The Morganite "Modmore" I fibre, which has a graphite crystallite spacing of 200 Å has a type I columnar structure similar to that around the "Hitron" fibres.

Although many fibres do show a correlation between columnar structure and crystallite size, it seems likely that the extent of epitaxial nucleation is also dependent on the orientation and defect concentration of the graphite lattice. It is known that the high pyrolyzation temperatures used in the production of type I carbon fibres promote orientation and lattice perfection within the graphite crystallites [21–23], and without exception all the type I fibres examined exhibited similar columnar structures. It is interesting to note that if crystallite size alone were responsible for the nucleation of the nylon, one would expect a greater number of nuclei on the type II fibres. This is not observed to be so, and it may be concluded that some minimum crystallite size must be present for the formation of a stable nucleus, and that the perfection and orientation of the substrate lattice also contributes to the nucleation.

The surface treatments of the carbon fibres, applied by the manufacturers to improve the interlamellar shear strengths, did not have any effect on the morphology and extent of the columnar growth [4]. Detailed examinations of treated carbon fibres have, however, indicated that the effective surface area [24] and the graphite crystallite size [12] are altered. These findings further demonstrate that these parameters alone are not wholly responsible for the columnar nucleation. Examination of the carbon fibres using stereoscan microscopy did not reveal any obvious differences in the topography of the surfaces, although as a result of oxidizing treatments both smoothing [25] and roughening [20] of the fibre surfaces have been recorded. In the work reported here both the relative smoothness of the fibre and its cross-section shape were found to have no effect on the columnar growth. Such a result is to be expected since fibre surface topography on such a large scale should not affect nucleation at a molecular level.

Although surface treatments applied to the carbon fibres did not have any apparent effect on the nucleation of columnar growth they did, in the case of type I fibres, produce a significant increase in the nylon–graphite bond strength, as measured from pull-out lengths. However, the nucleation of a columnar crystallization cannot account fully for the changes in fibre–matrix interfacial strength. It seems likely, therefore, that in the nylon–graphite interface there are two separate processes, one responsible for the nucleation of a columnar structure and a second responsible for the bond strength. As already proposed the nucleation of columnar growth appears to be a physical process involving the matching of crystalline lattices which depend upon the orientation, perfection and size of the graphite crystallites. In contrast the bond strength is considered attributable to a chemical process involving keying of side groups and chemical bonding.

The detailed chemistry of the interface is somewhat difficult to define due to the lack of information on the precise commercial treatments applied to the fibres. The following points are, however, considered significant.

Most commercial treatments are oxidizing in nature and are either nitric acid or perchloric acid based or involve oxidation at elevated (1273 K) temperatures. Examination of the fibres used in these studies indicate that little or no change in surface topography occurs. However, various workers [20, 24, 25] have shown either pitting or smoothing of the surface as a result of treatment. The chemistry of graphite in the presence of strong oxidizing agents, such as nitric acid and perchlorates shows that several important reactions may occur [26, 27]: (a) separation of the graphite crystal layers from 3.35 Å up to 7 to 8 Å: This product readily absorbs chemicals such as water, acetone, alcohols etc. which further increase the layer separation up to 18 Å; (b) graphite oxide may be formed, the structure of which is of the type –C–O–C, and may convert to C = O or –C–OH. These latter groups are acidic and will bond with polyamides; (c) there is also evidence that the graphite hexagonal layers become buckled. The separation and buckling of the graphite may explain the results of Mimeault [24] who suggested that the effective surface area of the fibre is tripled by treatment.

From these oxidizing reactions on the graphite surface several possible mechanisms for the nylon–carbon fibre bond may be proposed: (a) absorption of part or all of an amide molecule may occur into the enlarged graphite layers; (b) chemical bonding may also take place between the reactive acidic groups on the oxidized graphite surface and the carbonyl and imino groups of the nylon; (c) the buckling of the graphite layers may also promote a physical keying between the fibre and matrix. Thus it is considered that because of these reactions the interfacial bond strength of the type I fibres is increased by surface oxidizing treatment. Such treatments do not, however, affect the extent of columnar morphology. The effect of surface treatment on the bond strength of the type II fibres does not appear to be as pronounced as the type I material. This is probably due to the fact that the graphite content of the type II fibres is substantially less than the type I and this reduces the effectiveness of the oxidizing agent. However, the treatment of the type II fibres did noticeably increase the wettability of the fibres, giving much improved composite fabrication properties.

Therefore, although it has been proposed [1, 2, 6, 7, 28] that a modification of the matrix structure around the fibres could affect the mechanical properties of some fibre-reinforced polymer systems, surface treatment appears to have a more significant effect in the case of nylon 6 reinforced with type I carbon fibres.

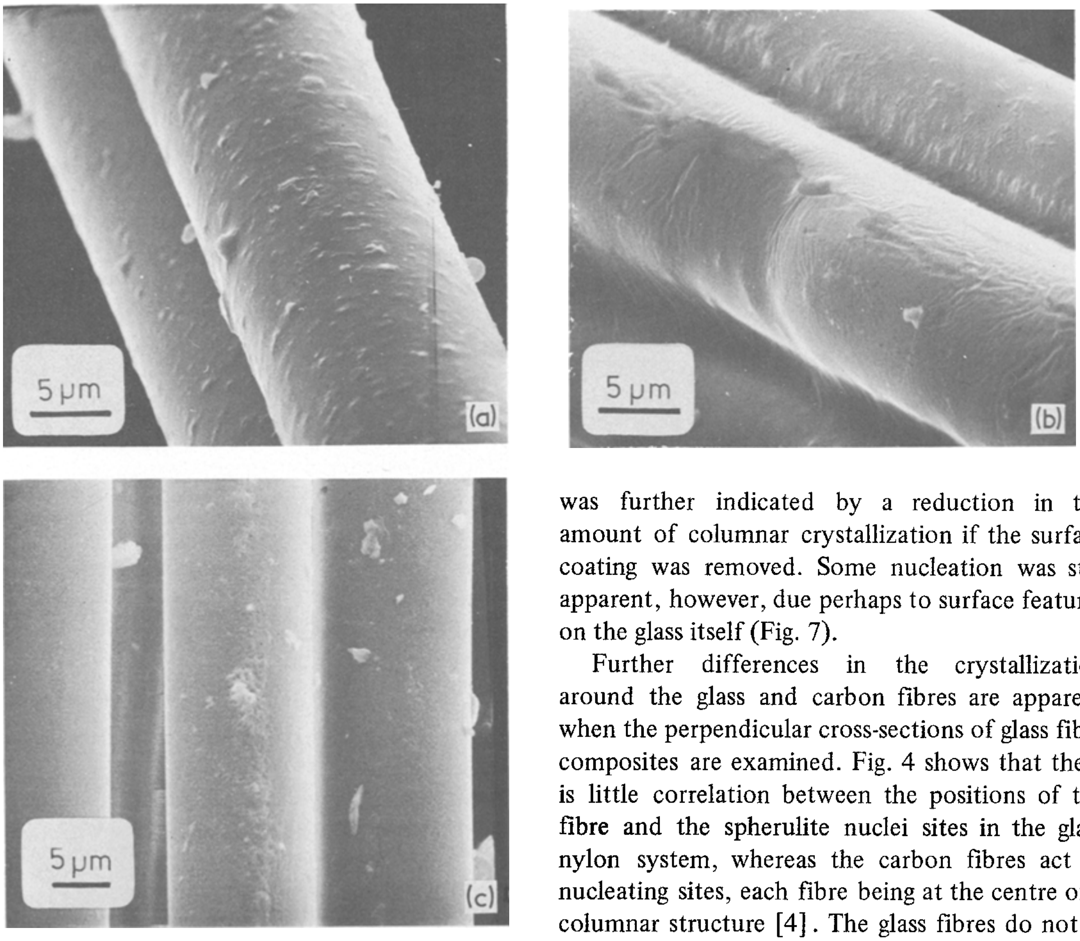

Figure 10(a), (b) and (c) Scanning electron micrographs showing the surface structures of size coupling agent on glass fibre surfaces taken from the same batch of fibres.

The nucleating ability of the glass fibres was considerably less pronounced than the carbon fibres. Apart from the overall reduction in columnar growth it was also observed that the crystallization varied in a random manner (Fig. 3). Because of the amorphous structure of the glass, the lattice matching criteria for nucleation is invalid and it can be considered that the nucleation is due in some part to the organic size on the fibre surface. The dispersion of the size was very non-uniform as can be seen in Fig. 10 which shows micrographs of fibres taken from the same batch. This could account for the irregularities in the columnar structure. The nucleation may be due to the size being locally dissolved in the polymerizing nylon (in which the temperature may reach 473 K (200° C), the dissolved size causing nucleation of the nylon. The influence of the surface coating in promoting columnar growth was further indicated by a reduction in the amount of columnar crystallization if the surface coating was removed. Some nucleation was still apparent, however, due perhaps to surface features on the glass itself (Fig. 7).

Further differences in the crystallization around the glass and carbon fibres are apparent when the perpendicular cross-sections of glass fibre composites are examined. Fig. 4 shows that there is little correlation between the positions of the fibre and the spherulite nuclei sites in the glass nylon system, whereas the carbon fibres act as nucleating sites, each fibre being at the centre of a columnar structure [4]. The glass fibres do not in general nucleate spherulites or columnar regions, and there are many self nucleated spherulites and fibres intersecting spherulite boundaries.

5. Conclusions

In the crystallization of anionically polymerized nylon 6 onto reinforcing fibres, the fibres nucleate a columnar structure. The morphology of this structure is different around the carbon and glass fibres and also around the type I and type II carbon fibres. The extent of the columnar growth decreases with decreasing matrix spherulite size and is unaffected by surface treatment. It is proposed that the nucleation of the structure is due primarily to the physical matching of the graphite crystallites.

In the case of the type I carbon fibres the surface treatments have a very significant effect on the fibre–matrix bond strength which cannot be satisfactorily explained in terms of the columnar structure. In the case of the treated fibres, very little debonding and fibre pull-out took place and very low fracture energies were obtained. In the untreated fibre composite extensive debonding and pull-out occurred and this was reflected in high fracture energies. It is, therefore, evident that in addition to the physical process responsible for the columnar growth, chemical bonding also occurs between the nylon and the oxidized graphite surface.

The crystallization of nylon onto glass fibre surfaces is non-uniform and is influenced to some extent by the presence of the size coating on the fibre surface.

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