Letters

Observations of a three-phase structure in high-modulus PAN-based carbon fibres

Several recent publications [1-4] have indicated that a consistent variation of both Young's modulus and fracture strength exists in copolymer polyacrylonitrile (PAN) based fibres, heat-treated to temperatures above 1500°C. These variations become more pronounced as the heat-treatment temperature is raised to 2500°C [2]. This effect was considered to be a consequence of the "sheath" and "core" type structure of this fibre, the difference in properties of the two zones increasing with heat-treatment temperature. A sample from the same batch of high-modulus fibres studied by Jones and Duncan [1], which has a mean fracture-strength of $\sim$ 2.0 GNm^{-2} and a Young's modulus of $\sim$ 380 GNm^{-2}, was examined by the techniques of high-resolution electron microscopy. The results indicate the existence of two distinct turbostratic graphite phases together with a small proportion of a third component

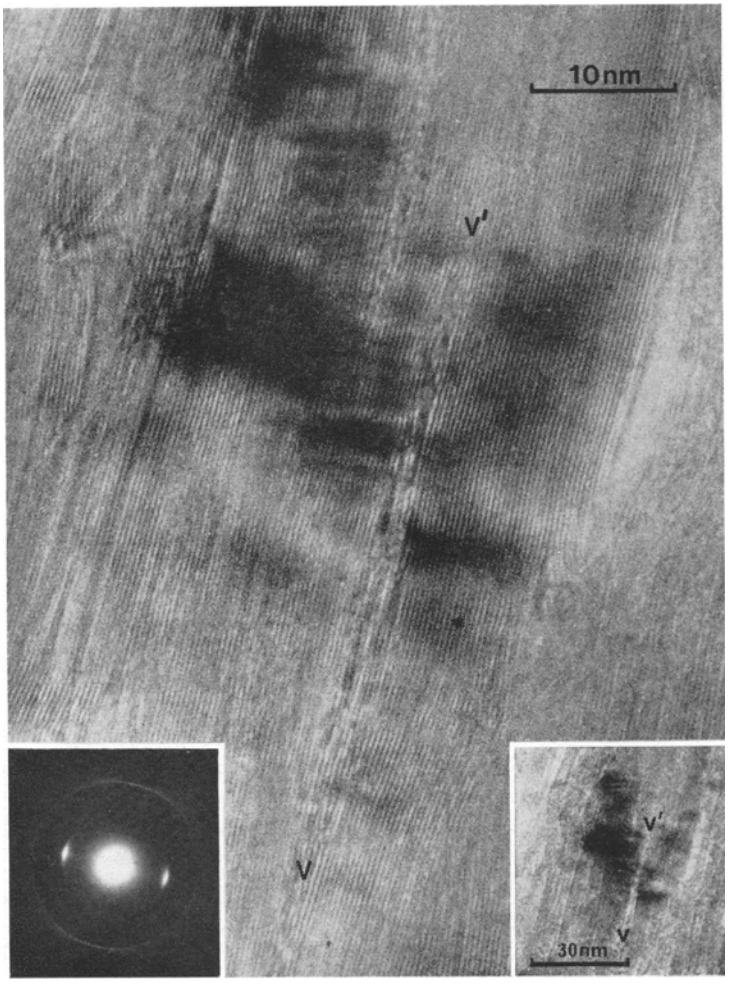

Figure 1 TI Phase of high-modulus PAN-based carbon fibre × 1900000; left insert, electron-diffraction pattern, right insert, same area at × 425000.

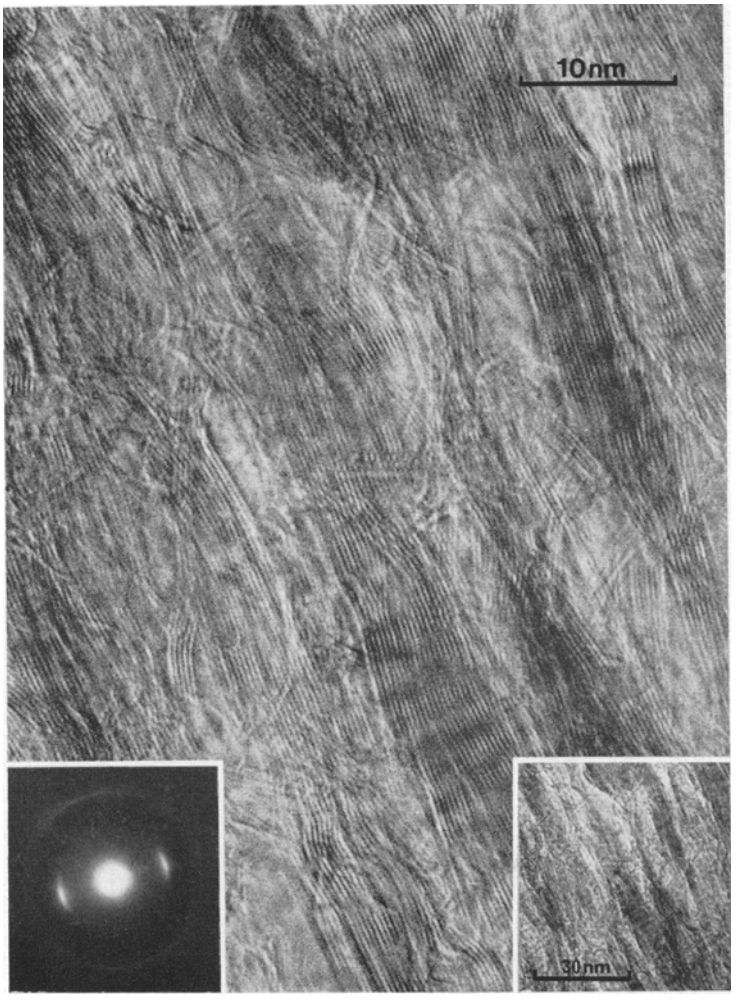

Figure 2 T2 Phase of high-modulus PAN-based carbon fibre × 2050000; left insert, electron-diffraction pattern, right insert, same area at × 425000.

composed of more perfect three-dimensional graphite.

Specimens were prepared for electron microscopy by wet grinding in alcohol/water with an Agate pestle and mortar; drops were then deposited on grids coated with thin carbon supporting membranes, and examined in a Philips EM 300 electron microscope fitted with an anticontamination device. Lattice resolution was carried out by tilting the electron beam during observation of the diffraction pattern so that the zero order and one of the 002 diffracted beams from the graphite lattice have approximately equivalent paths through the instrument. A significant increase in lattice-fringe contrast over earlier work in this field [5] was achieved after improving electron-beam coherence by means of a relatively small aperture (0.3 mm diameter) bias cap accurately aligned in the electron gun. High-resolution images were recorded at the maximum available magnification (× 600000), at an accelerating potential of 100 kV, and with the objective lens overfocused about 180 nm with respect to the background phase structure of the carbon film. Medium magnification images at × 125000 and electron-diffraction patterns were also taken for each area examined in the lattice-resolution mode. The electron-diffraction patterns were analysed on the polar table of a Joyce-Loebl microdensitometer.

Observation revealed that this particular

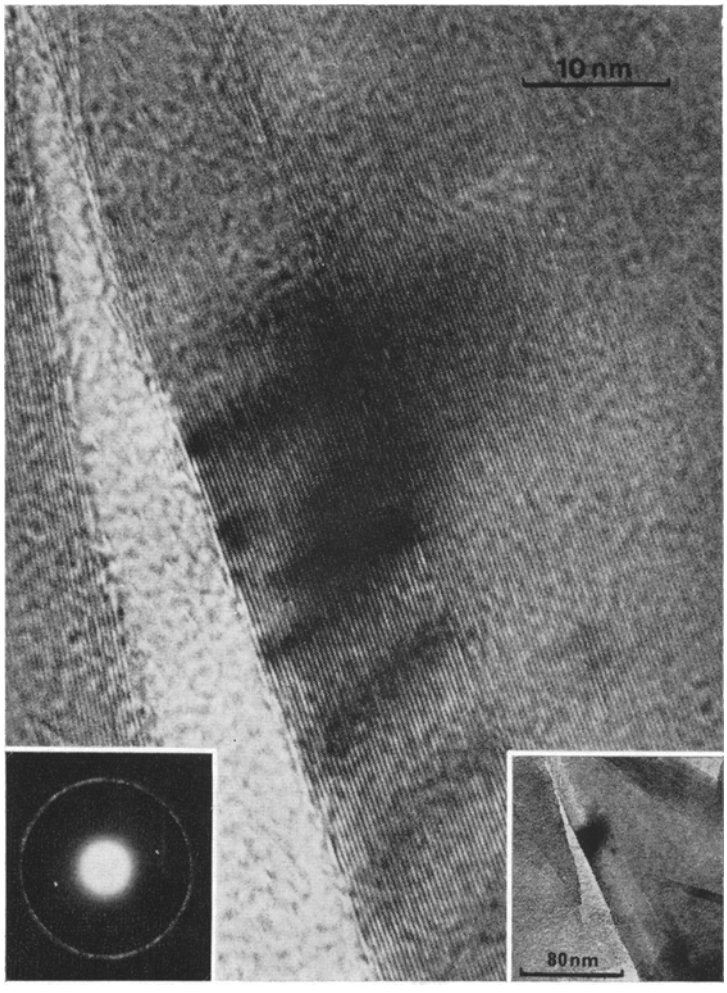

Figure 3 G Phase of high-modulus PAN-based carbon fibre × 1900 000; left insert, electron-diffraction pattern, right insert, same area at × 170000.

carbon-fibre sample comprised three distinct structural phases; a well-oriented highly-crystalline turbostratic graphite phase (designated T1) with $Z \sim 15°$, a less well-oriented less crystalline turbostratic phase (T2) with $Z \sim 24°$, and, in small proportion, a three-dimensional graphite phase (G) with $Z \sim 5°$. Z is measured in each case as the angular width of the 002 diffraction arc at half maximum intensity.

The T1 phase is depicted in Fig. 1 at medium and lattice resolution; the crystallites are part of an extensive flake formed by a complex interwoven system of "packets" of layer planes which have crystallized into regions of perfection up to 12.5 nm (36 repeats) in width. It must be stressed that this type of lattice image is an interference fringe pattern from electron waves diffracted in the crystals; fine details may be changed by tilting [6] or by a variation in focus [7], so that the position of a defect in the image does not necessarily locate exactly the position of a defect in the object. Nevertheless the presence of a large number of lattice faults can be inferred from the defects in the lattice-fringe pattern. In particular the apparent void VV[1] seen at medium resolution appears at lattice resolution to consist of an extensive region of lattice-fringe defects. This type of disturbance has not been observed previously; we might suggest tentatively that it is a manifestation of Mrozowski type cracking associated with internal stresses generated on

cooling. This type of defect has been considered by Jones and Duncan [1] and by LeMaistre and Diefendorf [8] to be responsible for reduced fracture strength in carbon fibres.

Fig. 2 is a typical example of the less-well oriented T2 phase which evidently consists of highly-interwoven fibrillar crystals enclosing many voids and containing regions of entanglement that have clearly hindered the more extensive crystallization and orientation observed in the T1 phase. Layer-planes pack together in fibrils which range in size from 0.68 to 5.1 nm (2 to 15 repeats); indeed the picture is reminiscent of the so-called "fringed-fibrillar" models of structure for cellulosic fibres which proliferated without substantiation some years ago in the field of fibre structure [9].

Finally, the more perfect G phase is illustrated in Fig. 3; this is a typical region of a type found earlier in Rolls-Royce fibres [10]. Where a suitable area is oriented parallel to the electron beam, lattice resolution reveals the perfection of the layer-plane packing in a region about 30 nm wide (90 repeats). It is of interest to note the step effect at the edge of the crystal and the extinction bands spaced at roughly 10 nm which are most probably due to a rotational Moiré effect from overlapping layer planes misoriented by about 2°.

The T1 phase observed here could well represent the highly-oriented "sheath", and the T2 phase the less-well oriented "core", as discussed by Jones and Duncan [1]. Although we have no means of identifying the location of these phases within the fibre, the data of Butler and Diefendorf [11, 12] supports the assumption that the "core" is the less well-oriented phase, T2. It would seem reasonable to conclude that the presence of this phase in a fibre would lead to a reduction in Young's modulus. The presence of the larger number of voids in the T2 compared to the T1 phase, and the fact that they have a greater chance of lying at an angle to the fibre axis and acting as stress-raisers, leads us to conclude that this phase is inherently weaker than the T1 phase. It may be that the voids, rather than the Mrozowski type cracks, are the important features in relation to fibre strength. Low-angle X-ray studies of fibre structure from the oxidation stage throughout the heat-treatment range, suggest that the voids develop around 1000°C and increase markedly as the heat-treatment temperature is raised above 2000°C [13]. This observation agrees very well with the fact that fibre strength decreases after heat-treatment at temperatures above 2000°C.

Despite this modification to the theory of Jones and Duncan [1], the diameter effect on both Young's modulus and fracture strength is still explicable in terms of the proportion of weak, poorly oriented T2 material present in a specimen. In this context the origin of the different phases is of some importance. Watt and Johnson [14] showed that "sheath"-"core" effects in copolymer PAN are due to an oxidized sheath and an unoxidized core. Retrograde core formation in homopolymer PAN [15] suggests that the core can melt as a result of the exothermic nature of oxidation. In either case these and other observers [16] have shown that an unoxidized core collapses on heat-treatment to 2500°C with the formation of highly graphitic lamellar sheets. This may be the origin of the G phase material seen here, although it is well known that similar sheets can occur as a surface artifact.

We are led to the conclusion that both T1 and T2 phases derive from oxidized precursor and reflect either a sheath-core structure in the original PAN fibre, or a gradation in the degree of oxidation or stabilization from the surface to the interior of the fibre. We find no evidence for more than one phase of structure in carbon fibres heated at 1000°C, nor did earlier work on sections of PAN-based fibres differentiate between the T1 and T2 types of structure found in the fibres heat-treated at 2500°C, although it did suggest that G phase material can be found interleaved between the turbostratic crystallites [10]. It is clear that more detailed studies of fine structure at all stages of the carbon-fibre process are necessary if we are to understand completely the origins of physical and mechanical property variations in high-modulus fibres.

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Band-deformation in PVC tubes: a material or processing property?

The testing of commercial-grade materials is an essential step in the rational utilization of plastic materials. Such testing is thwart with surprises of a type not normally encountered when using custom-made laboratory materials. This note discusses observations made when a cylindrical tube specimen of a red commercial-grade PVC was subjected to a slowly-increasing internal pressure. It also demonstrates the usefulness of a technique which might, by direct analogy, be termed "metallography" of plastic materials.

Fifty-millimetre long tube specimens of 37.5 mm i.d. and 0.375 mm wall thickness, were machined from red extruded rod and subsequently deformed by slowly increasing internal pressurization at a loading rate of 30 N mm^{-2} min^{-1}. The load was applied in such a way that the specimen was subjected to a hoop stress only. Deformation was carried out under increasing hoop stress and was essentially viscoelastic until yield occurred at a strain of 2%. Further increase in hoop strain beyond 2% resulted in plastic deformation in a mode that, to our knowledge, has not been previously reported.

After yield, wide bands of plastically-deformed material exhibiting stress whitening were formed, separated by narrow linear boundaries of essentially undeformed material (Fig. 1a).

The white bands were 6.8 mm wide, parallel to the axis of the tube specimens (and also the extrusion axis) and the boundaries were at regular 20° intervals around its circumference. Fig. 2 shows a close-up of one such band in which clearly visible "chevron" type markings are evident. The chevron markings intersect in the middle of the deformation bands, along a generator of the tube at an angle of 43° ± 2°, suggesting that the material deformed by shearing.

The regular positioning of the bands suggested initially, that they were caused by some mechanical means either in the machining of the extruded rod or by regular pinning of the specimen in the experimental apparatus. The deformation bands were observed in specimens made by two different techniques on two different machines, which indicates that the bands were not produced by

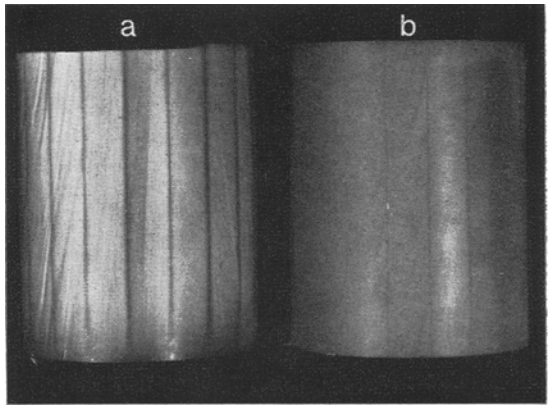

Figure 1 Band structure on (a) deformed specimen, (b) undeformed but etched specimen.