molecules which go through to other crystalline domains. These connections can be fixed by irradiation with Co$^{60}$, to relatively small doses, in our case 12 or 30 Mrad. Non-irradiated material molten in glycerine shows the same affine transformation but after a longer annealing time it progressively loses its original shape (Fig. 1e, annealing time 1000 min at 135°C). If molten immediately above the melting point only partial transformation takes place. In Fig. 1c the rod is oriented orthogonal to the drawing plane and only its right hand part has returned towards the platelet-like shape.

The observed phenomenon proves that in nature there exist polymers which in the liquid state do not lose their macroscopic shape and have a “memory” which allows them to reobtain it if affinely deformed. By small-angle X-ray scattering it has been made evident that this transformation takes place down to colloidal dimensions, whilst on the atomic scale much more complicated transformations are observed [2, 3]. With no regard to this, the small crystalline regions act as the nodes in rubber-like networks and cause rubber-like elastic behaviour of the colloidal superstructure.

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References


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An interpretation of radiation effects on mechanical properties of carbon fibres based on a “sheath” and “core” model of fibre structure

The effects of diameter on tensile strengths and Young’s moduli of carbon fibres have recently been explained [1-3] on the basis of a “sheath” and “core” structure previously proposed for such fibres [4]. It appears that radiation effects on these mechanical properties of carbon fibres are also explainable on the basis of such a fibre structure, as will be outlined in this letter. The tensile strengths [5] and Young’s moduli [6] of high strength (HTS) and high modulus (HMS) PAN-based fibres from Courtaulds Ltd are plotted against fast-neutron exposure in Figs. 1 and 2, and percentage strains to failure are plotted in Fig. 3. Previously reported data [7-9] on neutron-irradiated carbon fibres are also shown, where these data have been normalized by factors necessary to make their control values agree with those of the figures.

It is observed that radiation exposure in air has a considerable effect on the strength of the HTS fibre and on the modulus for both fibre types, but it has very little effect on the strength of the HMS fibre. The mechanical properties that are significantly affected by radiation all behave in similar manners, first increasing with exposure above a fast-neutron fluence of about $6 \times 10^{17}$ n/cm$^2$ ($E > 1$ MeV) and then decreasing at fluences somewhere above $1 \times 10^{18}$ n/cm$^2$ for

![Figure 1](attachment:image.png)
Figure 2 Young's moduli of carbon fibres for various radiation exposures.

Figure 3 Strains to failure for irradiated carbon fibres.

air irradiations at ambient temperatures below 80°C. This rise and fall of mechanical properties of fibres with radiation exposure in air is thought to be caused by two competing processes: (1) properties increase initially as carbon atoms are displaced from their lattice sites in basal planes of tightly bound atoms and come to rest in inter-layer spaces between weakly bound planes of turbostratic graphite crystallites, but (2) properties eventually decrease as radiation-enhanced oxidation at resulting vacant lattice sites on fibre surfaces begins to dominate over displaced-atom effects.

Additional support for displacement-oxidation competition in air irradiations is provided by data for fibres irradiated in liquid nitrogen (LN₂) where oxidation does not take place, for room-temperature mechanical properties of HTS fibres irradiated in LN₂ continue to increase smoothly beyond maximum values reached for irradiations in air (dashed sections of curves). In particular, for a fluence of 3 × 10¹⁸ n/cm², the strength increases over that for unirradiated controls by 30%, the modulus by 14%, and the strain to failure by 12%. More directly still, microscopic observations show that certain sites on surfaces of highly irradiated fibres of both types are preferentially attacked in air to form "pits" as carbon atoms are lost through oxidation degassification, and this surface pitting is not found for fibres irradiated in LN₂.

Thus, there is considerable evidence that mechanical properties of air-irradiated carbon fibres are controlled by displacement-oxidation competition [5, 6], but some of the property changes of the HMS fibre do not seem to have the proper behaviour for such a mechanism. The strength of this fibre changes very little with radiation exposure, neither rising in the displaced-atom regime nor falling in the oxidation regime, the latter finding being in agreement with Johnson's etching studies [10]. Moreover, both the room-temperature strength and modulus of HMS fibres irradiated in LN₂ show a decrease rather than an increase, as for HTS fibres, but it is believed that all of these radiation effects can be explained on the basis of displacement-oxidation competition if the HMS fibre is assumed to have a flawed core whose fracture always causes fibre failure.

According to the sheath and core model [4], graphite crystallites within outer sheaths of fibres tend to be larger and better aligned along fibre axes than are crystallites within inner cores of fibres, and this duplex structure becomes more pronounced as the heat-treatment temperature (HTT) of the fibre increases. It has been suggested that thermal stresses during cooling of circular PAN-based fibres cause microcracks in these misaligned cores when the HTT exceeds ~1200°C, and that this is the reason that the strength of such fibres begins to decrease steadily with HTT above that temperature [11]. The HMS fibre (HTT > 2000°C) is known to have a sheath and core structure [12], and the misaligned core of the fibre will be assumed herein to be