Letters

Affine deformation of linear polyethylene during stretching and affine transformation to the original shape in the liquid state

It has been well known for some years that thin films of recrystallized polyethylene are built up of spherulites, which are partially destroyed if the film is stretched but may reappear in the original shape when the sample is allowed to retract, provided that the stretching ratio is less than five times [1]. The authors supposed that this phenomenon can be explained by a rubber-like elasticity of an amorphous matrix in the melt-crystallized material.

Starting with the melt-crystallized Lupolen 6001H (BASF) we found that polyethylene, hot or cold-stretched, always shows a stretching ratio of about 10 if the material leaving the shoulder is not heated (Fig. 1a). The deformation is an exactly three-dimensional affine transformation down to colloid dimensions.

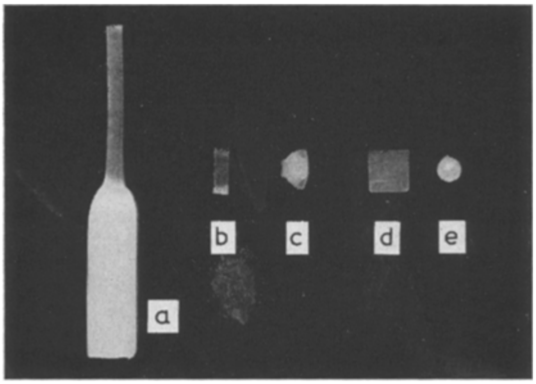

Figure 1 Linear polyethylene (Lupolen 6001H from the Badische Anilin- & Soda-Fabrik AG) and its affine deformations.

This was proved in three different ways.

(*a*) From a block material of a platelet 4 mm thick, a rod was cut with a cross-section 4 × 4 mm^2. A family of parallel straight grooves was pressed by the holder of the stretching machine into the rod surface. After stretching, the grooves were still straight on the surface of the extended rod and had a spacing 10 times larger in the direction of stretching, $\sqrt{10}$ smaller orthogonal to this direction (Fig. 2).

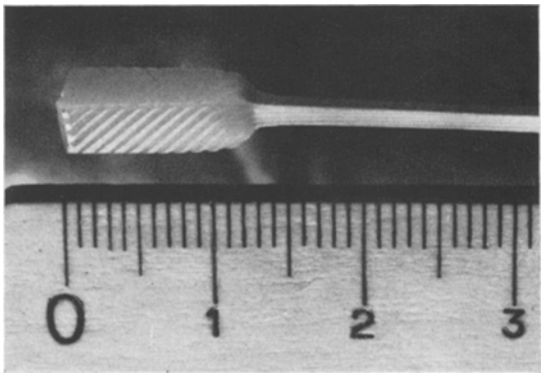

Figure 2 The family of linear parallel grooves before and after affine deformation of the rod of Lupolen 6001H.

(*b*) The cross-section of the stretched rod had kept its square form with side length $\sqrt{10}$ times smaller than 4 mm.

(*c*) A part of the stretched region of Fig. 1a is cut off (Fig. 1b). Floated in glycerine some degrees higher than the melting point this part becomes a platelet with the same shape and dimensions of cross-section as the original material (Fig. 1d).

Precise transformation to the original shape takes place which can only be explained by a three-dimensional affine deformation both in the stretching and in the melting process. From small and wide-angle X-ray analysis we found that each crystalline domain of the melt-crystallized material transforms during stretching, on the average, into about twenty smaller crystallites which lie like a string of pearls, all chains parallel to the direction of stretch. They build up segments of the ultrafibrils. The positions of the centres of gravity of all these segments in relation to each other can be obtained by affine transformation of the positions of the centres of the crystallites in the original material. These crystalline domains can be compared with the branching points of molecules in a rubber-like structure and are connected to each other by a number of "non-individual" chain molecules (tie molecules). Inside the crystalline domains they are connected with other "non-individual" 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.

Acknowledgment

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References

1. I. L. HAY, and A. KELLER, *Kolloid-Z.&.Z. Polymere* **204** (1965) 43.
2. N. KASAI and M. KAKUDO, *J. Polymer Sci.* **A2** (1964) 1955.
3. R. CORNELIUSSEN and A. PETERLIN, *Makromol. Chem.* **105** (1967) 192.

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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 × 10^{17} n/cm^2 ($E > 1$ MeV) and then decreasing at fluences somewhere above 1 × 10^{18} n/cm^2 for

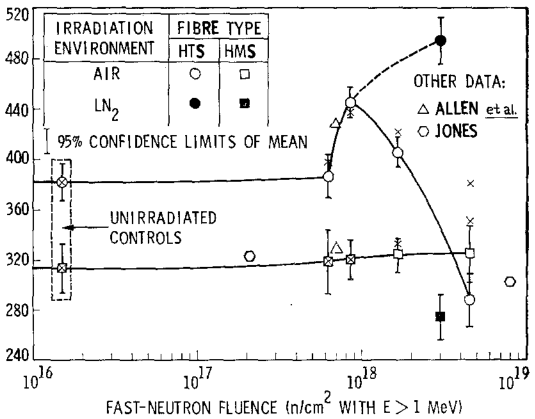

Figure 1 Tensile strengths of carbon fibres for various radiation exposures.