Letters

"Hard elastic" behaviour in high-impact polystyrene

The term "hard elastic" has until now been reserved to describe highly-oriented fibres and films of a crystalline polymer which exhibit elastic behaviour at tensile strains well outside the normal elastic region of deformation [1]. The purpose of this communication is to suggest and present experimental evidence for the idea that "hard elastic" behaviour need not be limited to crystalline polymers; specifically, it is suggested that a glassy polymer with a similar geometrical structure in the strained state to that of a crystalline "hard elastic" material could also exhibit a "hard elastic" property.

Models to describe the "hard elastic" behaviour have usually attributed the restoring force which gives a "hard elastic" material its characteristic elastic property to some mechanism within the crystalline lamellae. For example, it has been proposed that the elasticity results from reversible, crystallographic shear parallel to the chain direction within the lamellae [2], or, in the "leaf-spring" model [3], that the lamellae bend elastically between fixed interlamellar tie-points. However, Miles *et al.* [4] recently proposed a model which is not necessarily restricted to crystalline material as it essentially attributes the restoring force to surface-energy effects of the fibrils interconnecting the separated lamellae (see Fig. 1a) in the strained material. The model makes no assumptions concerning the crystallinity of the material but depends only on the geometrical structure of the strained "hard elastic" fibre. The interlamellar, fibril-bridged gaps observed in strained "hard elastic" crystalline polymers [3, 4] appear similar in structure to crazes [5, 6] occurring in glassy polymers (see Fig. 1b). Thus, on the basis of the model described above, it would be predicted that a crazed glassy polymer could exhibit "hard elastic" behaviour, i.e. it could be strained reversibly beyond the normal elastic limit, the "hard elastic" restoring force being generated by surface effects of the craze fibrils.

In order to test for the predicted "hard elastic" behaviour in a crazed polymer glass, mechanical tests were performed on high-impact polystyrene (HIPS) as it is known to craze profusely and thus approximates to the geometrical structure of a strained "hard elastic" crystalline polymer. Dumbbell-shaped specimens about 3 mm wide and 16 mm gauge length were cut from compression-moulded sheet about 0.25 mm thick. The samples were first highly crazed by straining in an Instron to about 50%, and then unloaded. This was the material on which the tests were made.

Two basic types of mechanical test were performed on the highly-crazed HIPS specimens: (1) stress–strain curves were recorded for loading and unloading, in order to determine whether crazed HIPS exhibited "hard elastic" properties,

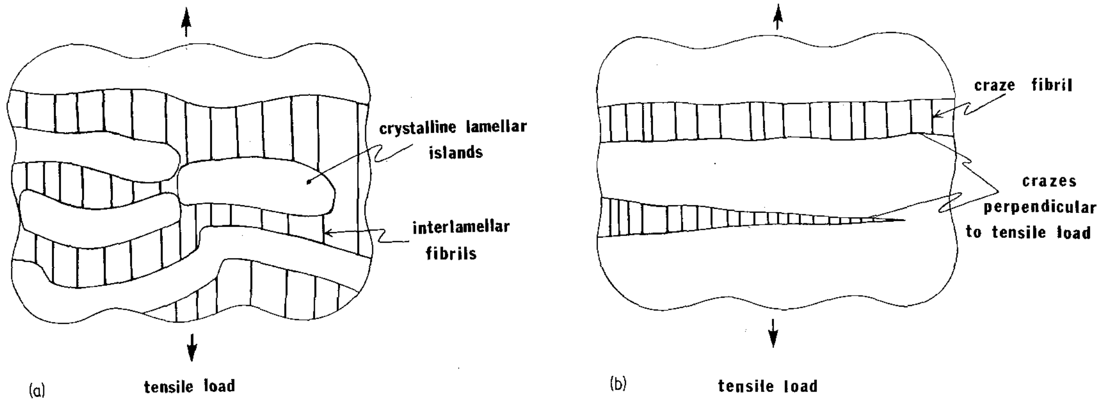

Figure 1 (a) Structure of strained "hard elastic" fibre of a crystalline polymer showing separated lamellae and interlamellar fibrils. (b) Structure of a strained glassy polymer showing crazes. In both cases, the arrow indicates the straining direction.

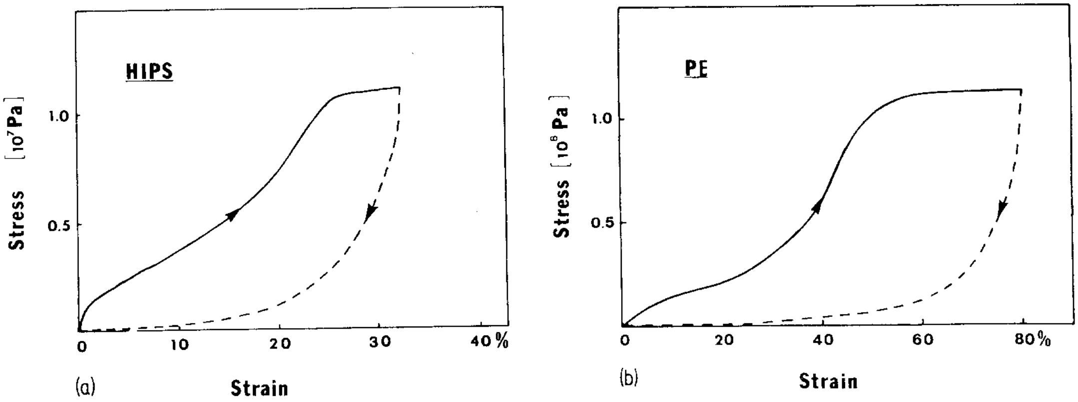

Figure 2 Stress–strain curves for loading and unloading at room temperature of: (a) a pre-crazed HIPS specimen, (b) a "hard elastic" PE fibre (courtesy Miles, Petermann and Gleiter).

and (2) stress–relaxation tests were performed at various temperatures, in the range 17 to 70° C, in air and in silicone oil, in order to determine if the nature of any observed elasticity could be the same as that of the traditional "hard elastic" crystalline polymers.

Fig. 2a shows the stress–strain curve for a crazed HIPS specimen strained at 0.0002 $\sec^{-1}$ to about 35% at room temperature. Upon unloading this strain is completely recoverable. Thus, it has been observed that highly crazed HIPS does exhibit the "hard elastic" behaviour as was predicted. The loading and unloading stress–strain curve has the same characteristics as that of a "hard elastic" fibre of polyethylene (PE) shown in Fig. 2b for comparison. Upon loading there is an initial S-shaped region followed by a plateau region. In addition, as in the case of PE, the specimen cross-sectional area remained constant during straining and the stress level of the plateau elastic" behaviour. The specimen was then immersed in silicone oil; this resulted in a displacement of the time-independent stress to a lower value. For comparison, Fig. 3b shows the result of a similar experiment performed on a "hard elastic" fibre of PE. The results are essentially the same. In addition, the time-independent stress for a HIPS specimen allowed to stress-relax in air was found to have a negative temperature coefficient in the range 17 to 70° C. This indicates that the region was found to increase with increasing strain-rate. Kambour [7] has reported a similar stress–strain curve for a single craze in polycarbonate.

Fig. 3a shows the result of the stress–relaxation test. The HIPS specimen was strained to about 40% and then allowed to stress-relax in air for about 40 min, during which time the stress decayed to a "time-independent" value which represents the true retractive stress in "hard

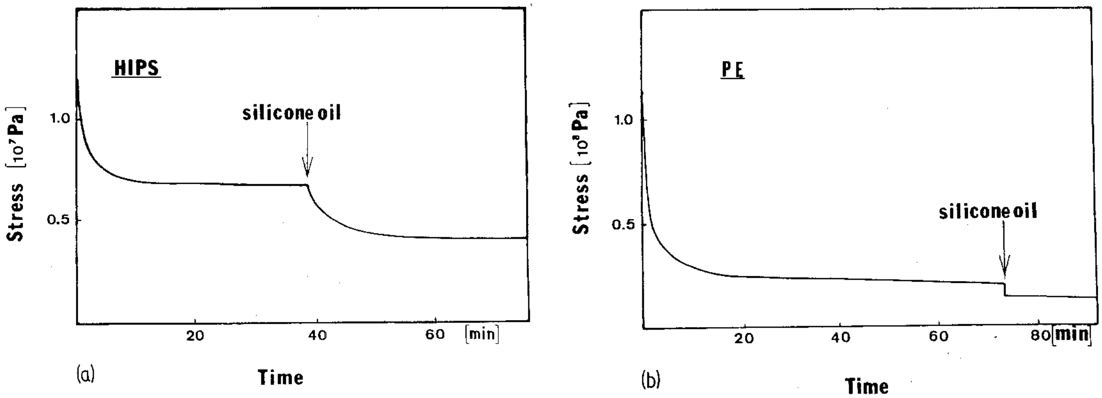

Figure 3 Stress–relaxation curves in air and silicone oil for: (a) highly-crazed HIPS strained 40%, (b) "hard elastic" PE fibre strained 50% (courtesy Miles, Petermann and Gleiter).

retractive force of the highly-crazed HIPS is controlled by energy effects rather than entropy. The environmental dependency of the time-independent stress suggests that the retractive force results from surface-energy effects, as in the case of PE, if it is assumed that the silicone oil lowers the surface energy of the fibrils.

Pre-crazed HIPS specimens could be reversibly strained to over 40% and thus exhibited "hard elastic" behaviour. The stress–strain and stress–relaxation behaviour of the highly-crazed HIPS showed the same features as those of "hard elastic" PE, verifying the prediction of the model based on the geometrical structure of the strained state, and indicating that the retractive force is generated by a surface-energy effect in the craze fibrils. Not only does this lend support to the model proposed by Miles *et al.* [4], it also demonstrates the possibility of a new type of material: a "hard elastic" glass.

References

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The toughness of fibre composites with inhomogeneous fibre packing

A recent paper by [4] refers to the possible effect of fibre bunching on the fracture toughness of glass-fibre and carbon-fibre reinforced plastics. This effect was first postulated and demonstrated for brittle fibre–ductile matrix composites [1, 2] from a consideration of the existing theory of the toughness of such composites [3]. The effect of fibre bunching in such composites is to increase the work-to-fracture in an unnotched Charpy impact test by a factor of two or three. This increased energy absorbtion is postulated to be due basically to the non-linear variation of absorbed energy with fibre volume fraction which is such that regions of low fibre-volume fraction have a disproportionately high work-to-fracture. The effect of fibre bunching is to produce such regions in the composite and their effect outweighs that of the regions of high fibre-volume fraction.

In the case of brittle fibre–brittle matrix composites the energy absorption mechanisms are different and ostensibly one would not expect fibre bunching to have the same effect. There have, however, been suggestions that fibre bunching is an effective method of increasing the toughness of such composites since the fibre bundles can be regarded as single fibres of large diameter and there are indications that the toughness of composites increases with increasing fibre diameter [1, 3]. The present author (unpublished work) has seen indications of a beneficial effect due to increasing the modulation of fibre-volume fraction in laminates of carbon-fibre reinforced plastic. Harris and Ankara [4] have looked for the effect in fibre composites and their data are summarized in Table I. They conclude that since an increase in n, the number of fibres per group, from 1 to 5 (and hence an increase of fibre-volume fraction of a factor of five) gives only a four-fold increase in work-to-fracture then the effect of fibre bunching

TABLE I Relationship between number of fibres in a group and the work of fracture of the material for a material composed of groups of fibres spaced 50 mm apart along the line of the crack path

Number of fibres in group, n	Work of fracture of the material W (J m^{-2})
1	110
2	100
3	125
4	300
5	400