velocities in brittle materials [5]. Approximately half-way along the final crack there is a transition (Fig. 1c) from a serrated to a smooth crack (Fig. 1d), and this transition point is the limit of slow crack growth on loading. The velocity of the crack, calculated from the size of the serrations, is 6×10^{-3} m min^{-1} when the cross-head speed on the Instron is 5×10^{-5} m min^{-1}.

This slow surface crack growth occurs simultaneously with the formation of median vents [6]. The median vent is an internal penny-shaped crack lying in the same plane as the surface crack but separate from it. On unloading or at high applied loads the penny-shaped median vent runs to the surface joining the surface corner crack and forming a semi-circular crack. The smooth crack extending beyond the transition point (Fig. 1c and d) is due to the median vent breaking through to the surface. Similar experiments with cone indenters showed no sign of slow crack growth, which suggests that surface cracks associated with such indents are only formed by median vents running to the surface at high loads or on unloading, and that the slow crack growth reported here is due to stress concentration around the corners of the Vickers indenter.

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Molecular mechanisms in annealing of oriented polypropylene

Deformation mechanisms in oriented crystalline polymers have been studied using a combination of low-angle X-rays (LAXP) and wide-angle X-rays (WAXP) [1–3]. In the present note, similar techniques have been applied to the study of mechanisms by which these materials change lamellar orientation on annealing after deformation.

The various deformation mechanisms in oriented crystalline polymers have been examined in some detail [1–3]. The mechanisms are those involving shear processes (intermolecular, interlamellar and interfibrillar), normal processes (interlamellar separation or fibrillar separation) and twinning processes within the lamellae. In oriented polypropylene, both X-ray diffraction and yield behaviour studies have shown the predominance of the intermolecular shear process in room temperature deformation [3]. This has been demonstrated for a range of orientations of approximately $20° < \theta_0 < 70°$ (where θ_0 is the angle between the molecular axis and the tensile axis).

Commercially obtained polypropylene sheet was hot drawn in air at 150° C to a total residual strain of ~ 600%. Tensile specimens of the standard "dumb-bell" shape were cut from this material at an angle $\theta_0 = 31°$ which was within the range of intermolecular shear on tensile deformation. These were ground and polished to approximately 0.5 mm thickness. The specimens were mounted in a small tensile jig suitable for *in situ* low- and wide-angle X-ray studies [3]. The jig was constructed so that it could be removed, with the specimen under load, and the specimen annealed in an oil bath. Thus the specimen was constrained by fixed grips.

A specimen was deformed in tension to a strain of 64% and annealed in a series of steps as follows:

Time at temperature (h)	Annealing temperature (° C)
1	100
1	100
1	130
1	140

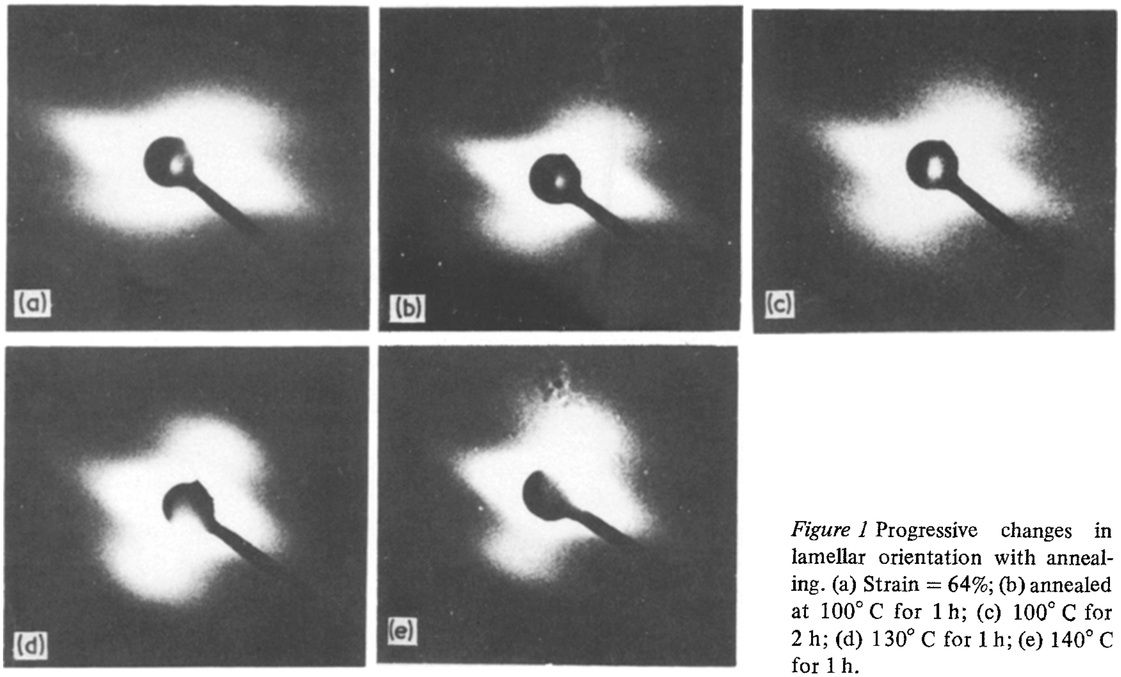

Figure 1 Progressive changes in lamellar orientation with annealing. (a) Strain = 64%; (b) annealed at 100° C for 1 h; (c) 100° C for 2 h; (d) 130° C for 1 h; (e) 140° C for 1 h.

After each annealing step, X-ray patterns were taken (Fig. 1) at room temperature from the same area of the specimen. By examining the specimen at room temperature, the X-ray patterns at each step were of an essentially frozen structure.

The WAXP showed no change in orientation over the entire range of annealing times and temperatures. At 100° C the LAXP showed a *progressive* change in lamellar normal orientation. The diffraction maxima showed successive shifts along layer lines towards the tensile axis, while the fibril streak and layer lines remained oriented in the same direction.

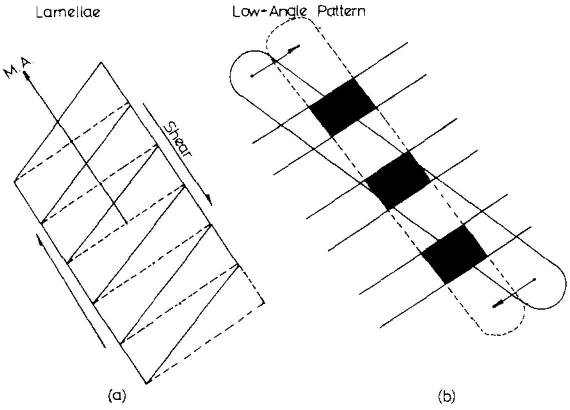

Figure 2 Schematic illustration of the real space and reciprocal space transform showing the movement of low-angle X-ray diffraction spots during annealing.

At higher temperatures (130 and 140° C), the lamellar normal has become parallel to the molecular axis and a stable structure appears to have formed. A similar effect was seen in a second specimen deformed to a strain of 100% after annealing for 1 h at 124° C.

The interpretation of the LAXP changes followed the line of reasoning described earlier [3]. In Fig. [2], a schematic illustration of the real space and reciprocal space transform is shown. The vertical axis is the tensile axis.

The periodic stacks of lamellae give rise to the two diffraction spots. The deformed lamellae in the unrelaxed state give rise to diffraction spots on the LAXP which were displaced along layer lines away from the tensile axis. Upon annealing, the diffraction spots shifted along the layer lines towards the tensile axis; The "sausage-shaped" transform of the lamellae was therefore rotating towards the tensile axis. The layer lines did not change in orientation or in separation distance with annealing, so the mechanism which accounted for the LAXP changes was some kind of shear mode parallel to the molecules.

An intermolecular shear process in a sense opposite to the initial pre-strain accounted for the

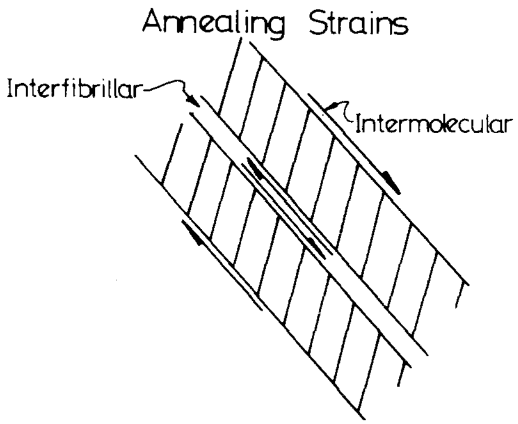

Figure 3 Combined intermolecular and interfibrillar shears.

rotation of the lamellar normal. However, under fixed grip constraints there can be no net strain and the WAXP showed no rotation of the molecular axis after annealing. The intermolecular shear must therefore be accompanied by an equal but opposite amount of interfibrillar shear (Fig. 3). The fibrils are parallel to the molecular axis, so the net rotation of the molecular axis is zero.

This behaviour, whereby intermolecular slip is in effect replaced by interfibrillar slip on annealing, may be linked to the observations of deformed polypropylene [3] and polyethylene [4] in which shear parallel to the molecular direction occurred initially by intermolecular slip but at higher strains by a mixture of intermolecular and interfibrillar slip. It may be that some intermolecular slip was replaced by interfibrillar slip before the extended X-ray observations required to deduce the above results [3, 4] were made; in any event a resistance to large shear deformation of the lamella is indicated whose origin is the same as that of the driving force for the retraction of the shear deformation of the lamella during annealing. Whether this driving force lies in the tendency of the lamella to minimize its surface energy [5] or arises from rubber-like, entropic retractive stresses in the non-crystalline regions between lamella is not yet clear.

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