7. E. MOOSER and W. B. PEARSON, *J. Electron.* (1956) 629.
8. J. B. MULLIN, R. J. HERMITAGE, C. H. HOLIDAY and B. W. STRAUGHAN, *J. Crystal Growth* 3/4 (1968) 281.
9. BDH Ltd, Poole Dorset, UK.

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Observation of shear bands in crystalline, spherulitic polypropylene under compression at low temperatures

When glassy polymers are stretched or compressed, local zones of concentrated strain (crazes or shear bands) are often obtained. Their formation depends on strain rate, temperature, and sign of the stresses (tensile or compressive). The process of craze formation which mainly occurs under tension, and their influence on crack propagation and fracture have been elaborated to a large extent in recent years [1–3]. A few reports indicated, however, that crazing can occur as well in crystalline polymers [4–7]. This was shown, in particular, for crystalline polypropylene by Olf and Peterlin [8]. Crazes form at low temperatures, in the range between −210 and 0° C.

Shear band formation is commonly associated only with glassy polymers [9–11]. The shear bands are formed by highly localized shearing of the randomly oriented material. This plastic deformation yields high molecular orientation of the material in the shear bands. They possess a thickness of less than 1 μm perpendicular to the direction of the applied shear stress, which has to be induced by compression. They can grow laterally as long as the local stress concentration at the sharp tip of the shear band is sufficient for propagation. When a certain degree of local deformation is exceeded, coarse shear bands can induce final fracture of the material [12].

In contrast to investigations on crazes in crystalline polymers, there are no studies which deal with the formation of shear bands in such materials. There are only some papers which treat the mode of deformation of oriented polymers in compression at low temperatures [13, 14].

In an attempt to check this effect with an unoriented crystalline polymer, spherulitic isotactic polypropylene was studied in the temperature range −196 to −50° C. At these temperatures the testing material is below its glass transition temperature. Shear band formation is expected to be easy, if this process is analogous to the well known shear band formation of some amorphous polymers under compression below their glass transition temperatures.

The experiments described here were made with polypropylene specimens having the following dimensions: 10 mm × 10 mm × 20 mm. The notched specimens were loaded under compression at −196° C and at −50° C with a strain rate of $\epsilon = 4 \times 10^{-4}$ sec^{-1}. Before notching, the test pieces were subjected to different heat-treatments which are described elsewhere [15]. Thus different spherulite diameters could be produced. Two types of polypropylene with various atactic content were used: PP 1120LX, ~5% atactic and PP 1320, ~20% atactic, both obtained from the BASF. AG, Ludwigshafen, Germany.

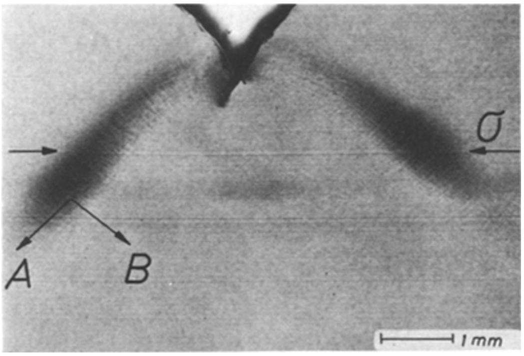

Figure 1 Two sets of shear bands (A, B) formed under compression in the vicinity of a notch in crystalline, isotactic polypropylene. Scratches produced after the test indicate the compression axis.

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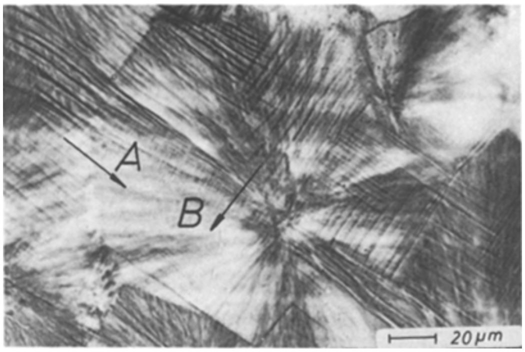

Figure 2 Polarized micrograph of a thin section taken from the deformation zone of the bulk specimen. Two band packets (A, B) can be observed.

The main features of our observations were two discrete sets of shear bands having formed under compression at very low temperatures (Fig. 1). Angles between the compression axis and the bands of 35° to 42° were measured. They are similar to those which were observed in glassy polymers [16] or amorphous metals [17]. Higher magnifications of the bands obtained with the aid of thin sections under polarized light showed that the bands had propagated along spherulite boundaries as well as through the crystalline arrangements inside the spherulites (Fig. 2). This indicates that sliding can take place in various planes of individual crystal lamellae. The occurrence of these processes has also been directly observed by Argon [18] in crystals of spherulitic HDPE. In many cases, one set of shear bands had locally caused intersections of individual shear bands running nearly perpendicular to this zone. The thickness of these intersections of individual bands with each other or with perpendicular oriented spherulite boundaries was determined to be nearly 1 μm (Fig. 3a and b).

An additional important observation was the interaction of these zones of inhomogeneous deformation with the final fracture of the specimen under compression. In comparison to a macroscopically brittle fracture produced by tensile stresses at these temperatures [15], the fracture surface induced in the shear band package under shear stress conditions was relatively smooth (Fig. 4). Higher magnifications of the fracture surface obtained in the SEM indicated, however, that high amounts of plastic deformation must have occurred during fracture inside the bands. In some cases one could observe drawn fibrils which appeared to have melted at their ends.

In addition, individual traces bridged by those fibrils were found on the fracture surface. They lay perpendicular to the sliding direction of the specimens and were due to the second set of shear

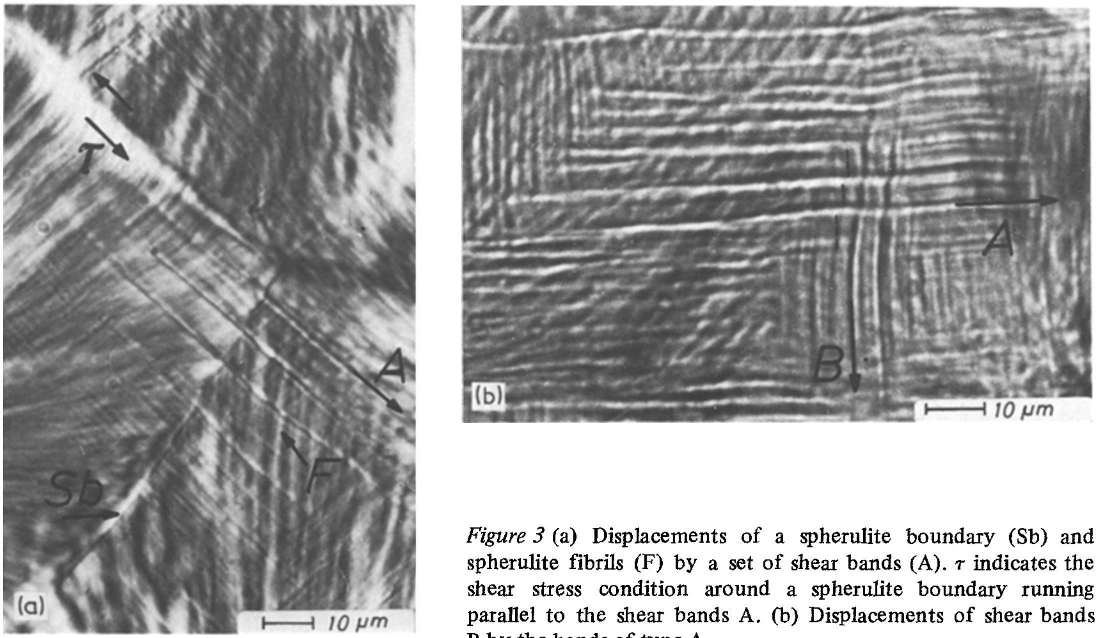

Figure 3 (a) Displacements of a spherulite boundary (Sb) and spherulite fibrils (F) by a set of shear bands (A). τ indicates the shear stress condition around a spherulite boundary running parallel to the shear bands A. (b) Displacements of shear bands B by the bands of type A.

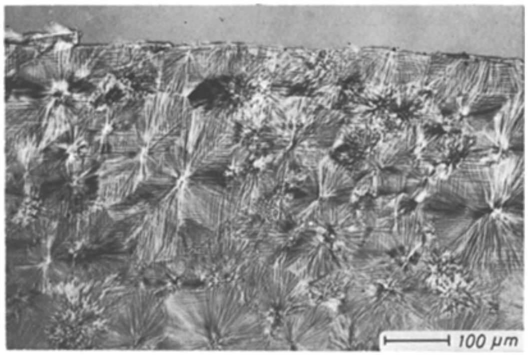

Figure 4 Fracture profile along shear bands of type A.

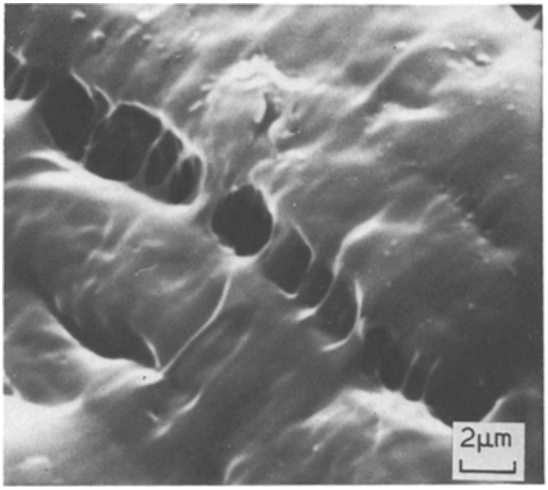

Figure 6 Craze-like fibrillation inside normally deformed shear bands of type B.

bands (Fig. 5), which must have formed first. After intersection by the bands which have been initiated from the notch, they leave a craze-like pattern on the final fracture surface (Fig. 6). This pattern is formed by an opening of the shear bands during the sliding process of the specimen pieces at the onset of fracture. Thus these sites of intersection act preferentially as sites of crack nucleation, as is demonstrated schematically in Fig. 7a. Indeed, in some regions of the fracture surface, former shear bands which had just developed into cracks can be observed (Fig. 7b). These can provide fracture perpendicular to the initially activated fracture plane, and so a splintering of the specimen may be expected by this mechanism.

As a third consequence of the experiments, it can be established that there is also a modification between shear bands and spherulite boundaries. If a spherulite boundary is oriented nearly parallel to the second set of shear bands, this boundary is preferred for the shearing process. At these sites of intersection a jumping from one fracture shear band to another often occurs, providing sharp steps on the shear fracture surfaces (Fig. 8a). This effect is combined with a hindrance of sliding of the individual counterparts which leads to a further site of crack initiation and final fracture (Fig. 8b). Similar observation has also been made recently during a study of the intersection of shear bands in polystyrene [19].

Finally, taking a look at the band initiation

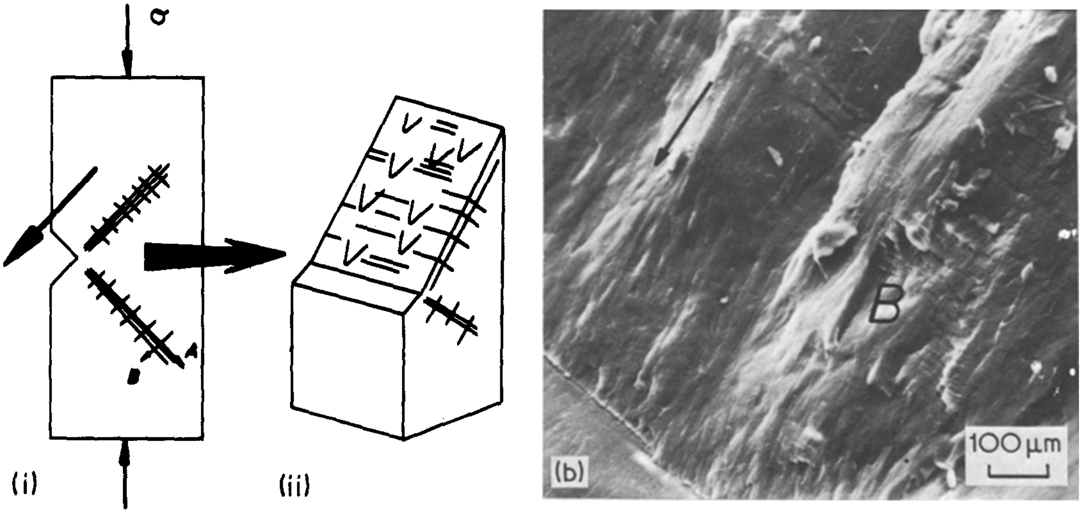

Figure 5 (a) Schematic representation of shear fracture. (b) SEM micrograph of a shear fracture surface. The arrow indicates the sliding direction of the counterpart. The parallel traces (B) are due to the second set of shear bands.

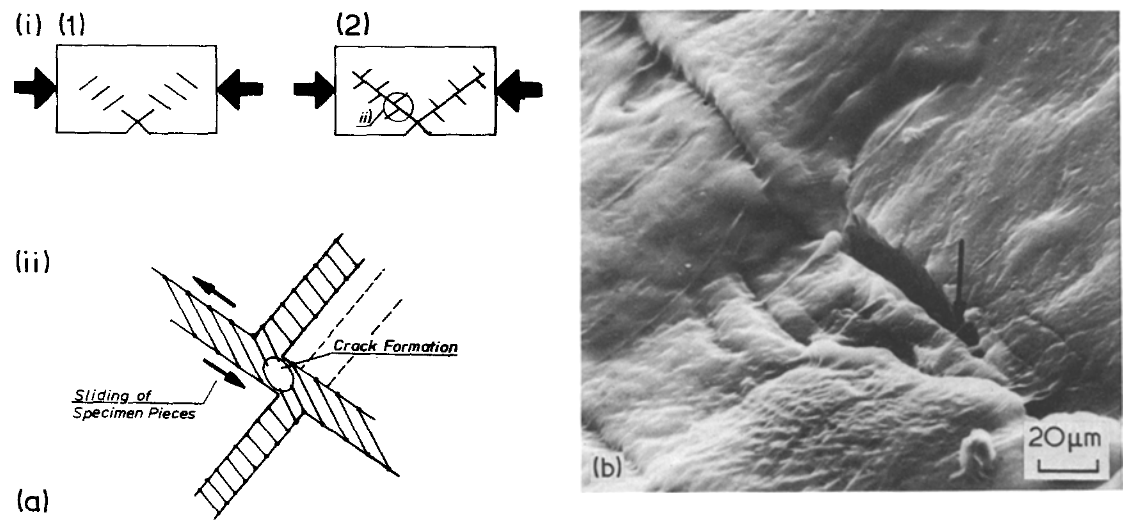

Figure 7 (a) Mechanism of crack formation at the intersections of shear bands. (i) Sequence of shear band formation; (ii) Chain scission at the intersection. (b) Crack initiation in one of the perpendicular oriented bands (arrow).

stress (Fig. 9), one can recognize higher values with both lower atactic content and bigger spherulite diameter. This effect seems to be due to the highest amount of crystallinity in the material PP at 5% with a spherulite diameter of 400 μm. On the other hand, the degradation of the spherulite boundary matter which mostly occurs in this kind of morphology, does not play a role under compressive load.

However, there seems to be a dependence of the values on the spherulite diameter, if one considers the process of step formation at spherulite boundaries during shear fracture. It is expected that with increasing spherulite size the macroscopic shear strain decreases, while the maximum stress and the band initiation stress are shifted to higher values. Further experiments to check these correlations will be carried out in the near future.

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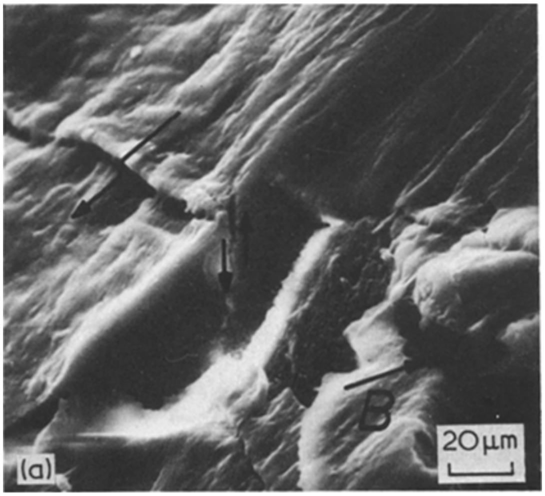
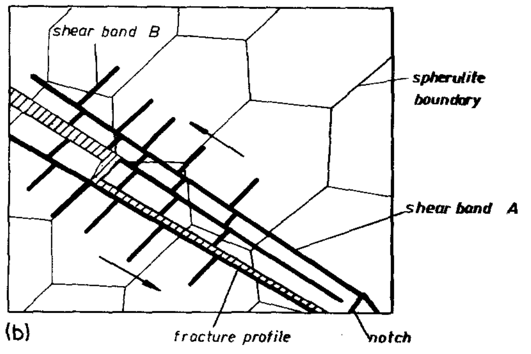


Figure 8 (a) Step along a spherulite boundary, which runs parallel to the band packet B. The black arrow, B, shows cracking perpendicular to the shear band plane. (b) Mechanism of crack formation at the intersections of spherulite boundaries and shear bands.



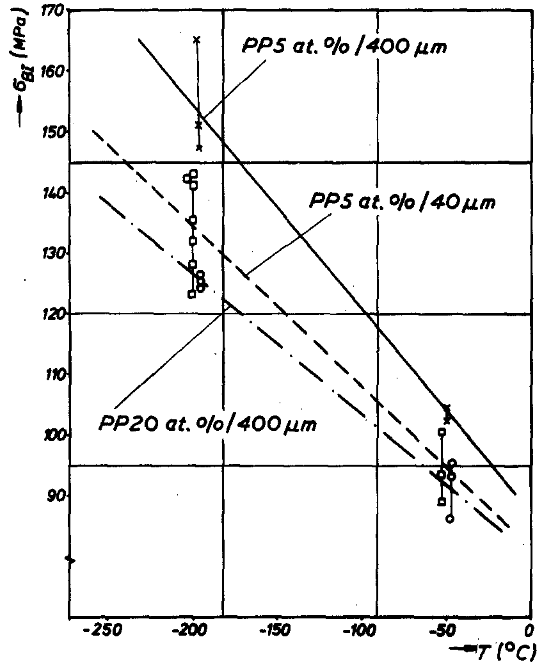


Figure 9 The influence of the atactic content and the spherulite diameter in PP on the band initiation stress σ_{BI} at various temperatures, T. With increasing temperature (−196 to −50° C) the discrete shear band deformation develops into a more homogeneous deformation along a broad shear zone.

References

1. S. RABINOWITZ and P. BEARDMORE, *CRC. Crit. Rev. Macromol. Sci.* 1 (1972) 1.
2. R. P. KAMBOUR, *J. Polymer. Sci. Macromol. Rev.* 7 (1973) 1.
3. P. BEAHAN, M. BEVIS and D. HULL, *Proc. Roy. Soc. London* 343 (1975) 525.
4. J. S. HARRIS and I. M. WARD, *J. Mater. Sci.* 5 (1970) 573.
5. G. MENGES, *Kunststoffe – Plastics* 8 (1977) 15.
6. K. FRIEDRICH, *Prog. Colloid Polymer Sci.* 66 (1979) 299.
7. H. G. OLF and A. PETERLIN, *J. Polymer. Sci. Polymer. Phys. Ed.* 12 (1974) 2209.
8. H. G. OLF and A. PETERLIN, *Macromolecules* 6 (1973) 470.
9. A. S. ARGON, *Phil. Mag.* 28 (1973) 839.
10. E. J. KRAMER, *J. Macromol. Sci.-Phys.* 1 (1974) 191.
11. J. B. C. WU and J. C. M. LI, *J. Mater. Sci.* 11 (1976) 434.
12. K. FRIEDRICH and K. SCHÄFER, *ibid* 14 (1979) 480.
13. R. A. DUCKETT and A. M. ZIHLIF, *ibid* 9 (1974) 171.
14. J. D. WILLIAMS and G. MAYER, 4th International Conference on Deformation, Yield and Fracture of Polymers, Cambridge (The Plastics and Rubber Institute, London, 1979) p. 11–1.
15. K. FRIEDRICH, *Prog. Colloid Polymer. Sci.* 64 (1978) 103.
16. E. J. KRAMER, *J. Polymer. Sci. Phys. Ed.* 13 (1975) 509.
17. U. KÖSTER, private communication.
18. A. S. ARGON, 4th International Conference on Deformation, Yield and Fracture of Polymers, Cambridge (1979), private communication.
19. K. Friedrich and K. SCHÄFER, *Prog. Colloid Polymer. Sci.* 66 (1979) 329.

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The crystal structure of the silicon cerium oxynitride, $Ce_4Si_2O_7N_2$

In an investigation on the densification of Si_3N_4 with CeO_2, Mah *et al.* [1] have reported the existence of a new quarternary compound in the system Ce–Si–O–N having a chemical formula of $Ce_4Si_2O_7N_2$, the powder diffraction pattern of which has been indexed on the basis of a monoclinic unit-cell with dimensions: $a = 10.360$ Å, $b = 10.865$ Å, $c = 3.974$ Å and $\beta = 90.33°$. However, the crystal structure proposed by these workers cannot be correlated with any known compound. While the existence of a compound with the proposed chemical composition is beyond doubt, there seems to be a discrepancy in the indexing of the powder diffraction pattern and assignment of correct unit-cell parameters for the compound.

Earlier studies on the crystal structure determination of a number of silicon–lanthanide-oxynitrides of the general formula $Ln_4Si_2O_7N_2$ (Ln = La, Nd, Sm, Gd, Dy, Ho, Er and Yb) have been carried out independently by Wills *et al.* [2]

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