12. *Idem, Phil. Mag.* **22** (1970) 893.
13. H. E. CLINE and T. R. ANTHONY, *Acta Met.* **19** (1971) 175.
14. *Idem, J. Appl. Phys.* **43** (1972) 10.

*Received 11 May
and accepted 28 May 1976*

R. D. DOHERTY*
T. R. STRUTT
*School of Engineering and Applied Sciences,
University of Sussex,
Brighton, UK*

*On leave of absence at the Departamento de Materiais, Centro Tecnico Aeroespacial, Sao Jose dos Campos, S.P. Brazil.

†Present address: British Steel Corporation, Sheffield, UK.

Crystallite orientation in heat shrinkable polytetrafluoroethylene tubing

Polytetrafluoretylene (PTFE) tubing has found extensive use as a heat shrinkable protective coating. The molecular structure of PTFE has been established by Bunn and Howells [1], and deformation mechanisms in biaxially oriented PTFE have been studied by Young [2]. We report an X-ray analysis of PTFE tubing* and discuss the behaviour of this biaxially oriented material upon thermal contraction.

Fig. 1 shows wide-angle X-ray diffraction (WAXD) photographs of PTFE tubing taken before and after heat shrinking at 365° C for 10 sec. The sharper diffraction ring corresponds to a Bragg d spacing of 4.9 Å; the d spacing does not change significantly on heating. Evidence of preferred orientation is seen in the ring; further, upon heat shrinking the position of the maximum intensity shifts 90° in the azimuthal direction. Samples having orientation maxima between these two azimuthal positions were sought with no success. During heating, the tubing underwent a large differential shrinkage amounting to 35% radially but only 5% longitudinally.

To better determine the degree of crystallite order in the axial and transverse directions of the tubing, diffraction intensity was measured along chi on an automated four-circle Picker Corporation diffractometer (Fig. 2). The orientation function $f(\chi)$ was calculated from the intensity distribution with the peak maxima assigned to 90° χ [3]. The value of $f(\chi)$ decreased on heating from 0.85 to 0.68, indicating not only a 90° change in preferred orientation direction upon heating, but also that the material loses about one-third of its molecular order. This calculation is

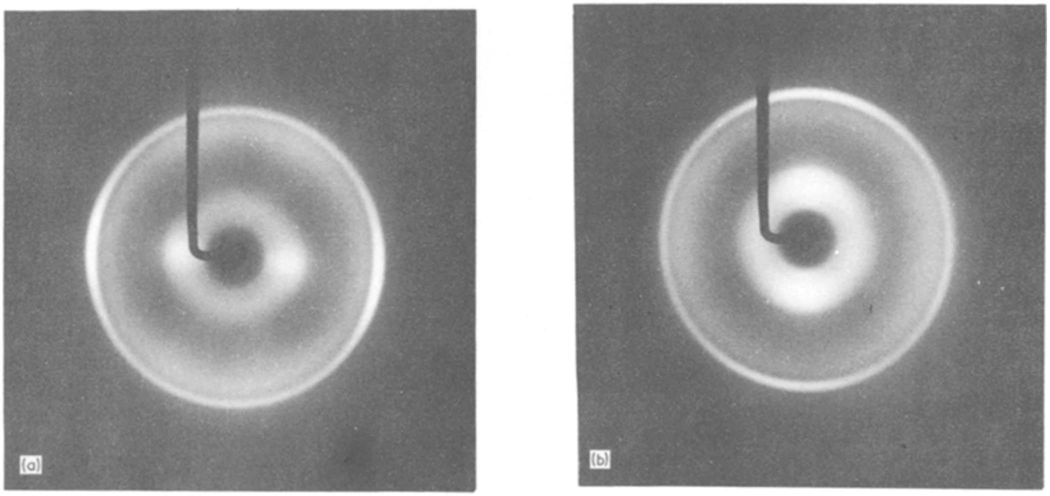

Figure 1 Wide-angle X-ray diffraction photographs of PTFE tubing: (a) before, (b) after heat shrinking at 365° C. Tube axis direction horizontal. Co$K\alpha$ radiation, exposure time 1 h.

* Kindly supplied by Alpha Wire Company, Elizabeth, New Jersey.

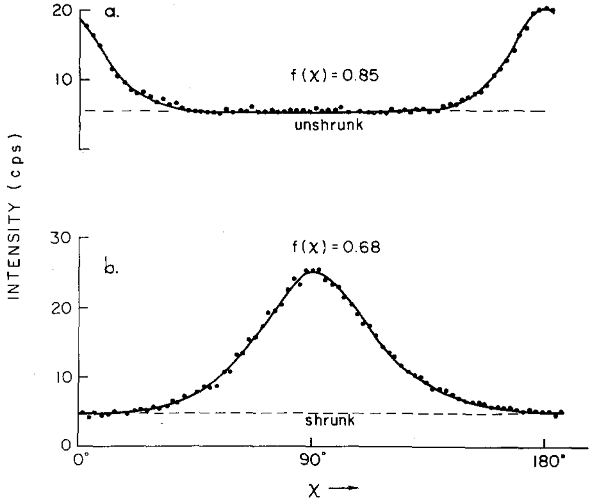

Figure 2 Azimuthal step scans of PTFE X-ray diffraction intensity at 18.2° 2θ using Cu$K\alpha$ radiation; (a) unshrunk tubing, (b) heat shrunk tubing.

supported qualitatively by conoscopic observations [4] of the PTFE tubing under a polarizing microscope. Before heating, a biaxial interference figure with strong polarization colors was seen, whereas observation of the tubing after shrinking revealed a very weak biaxial figure indicating a reduction in differential order.

Iwato and co-workers [5] recently found similar WAXD behaviour during stretching and contraction of axially oriented polypropylene film. In addition, a correlated change in the small-angle X-ray scattering (SAXS) was also noticed. These authors concluded that reversible rotation of lamellar crystallites could explain the observed behaviour. We therefore made SAXS photographs of the PTFE tubing both before and after shrinking to determine if the WAXD changes were due to motions of lamellae as these workers had proposed. The SAXS photographs of the tubing were featureless in the 50 to 150 Å region after 48 h exposures on a rotating anode X-ray generator, suggesting little or no lamellar structure exists in the tubing.

References

1. C. W. BUNN and E. R. HOWELLS, *Nature* **174** (1954) 549.
2. R. J. YOUNG, *Polymer* **16** (1975) 450.
3. L. E. ALEXANDER, "X-ray Diffraction Methods in Polymer Science" (Interscience, New York, 1969) p. 241.
4. N. H. HARTSHORNE and A. STUART, "Crystals and the Polarizing Microscope", 4th Edn. (Edward Arnold, London, 1970) p. 323.
5. N. IWATO, H. TANAKA and J. OKAJIMA, *J. Appl. Polymer Sci.* **19** (1975) 303.

Received 11 May
and accepted 28 May 1976

STEPHEN P. PETRIE
JAMES R. KNOX
Institute of Materials Science,
University of Connecticut
Storrs, Connecticut, USA