$$p_{aa}(\mathbf{r}) = p^0_{aa}(\mathbf{r}) - \alpha(r)p^0_{aa}(\mathbf{r}) + \alpha(r)p^0_{ac}(\mathbf{r}) .$$

Combining these with equation (*A*1), and observing that $p^0_{ca} = 1 - p^0_{cc}$, and $p^0_{ac} = 1 - p^0_{aa}$, one finds

$$\Gamma(\mathbf{r}) = \Gamma^0(\mathbf{r})\{1 - 2\alpha(r)\} . \qquad (A2)$$

As the changes, Δk, of the number of intersections with lamellar interfaces are assumed to be distributed at random over the vectors, the lengths of the vectors for which $|\Delta k| = 1$ must show a Poisson distribution:

$$f_1(r) = (1/d)\exp(-r/d) . \qquad (A3)$$

Here, d is the 'distortion length', mentioned before. The distribution of the vectors for which $|\Delta k| = n$ can be obtained by n successive convolutions of equation (*A*3), which leads to:

$$f_n(r) = [r^{n-1}/\{(n-1)!d^n\}]\exp(-r/d) . \qquad (A4)$$

At a given value of r, the integral

$$\int_0^r f_n(\varrho)\mathrm{d}\varrho$$

gives the fraction of the vectors for which $|\Delta k| = n$ or more. The fraction F_n, for which k has changed by no more or less than n times, can therefore be found from

$$F_n(r) = \int_0^r \{f_n(\varrho) - f_{n+1}(\varrho)\}\mathrm{d}\varrho ,$$

which, combined with equation (*A*4) leads to

$$F_n(r) = \frac{1}{n!}\left(\frac{r}{d}\right)^n \exp(-r/d) . \qquad (A5)$$

The definition of α given before requires that

$$\alpha(r) = \sum_{n=1,3,5\ldots}^{\infty} F_n(r) ,$$

which, with the aid of equations (*A*2) and (*A*5), yields

$$\Gamma(\mathbf{r}) = \Gamma^0(\mathbf{r})\left\{1 - 2\exp(-r/d)\sum_{n=1,3,5\ldots}^{\infty}\frac{1}{n!}\left(\frac{r}{d}\right)^n\right\} .$$

By developing $\exp(-r/d)$ into a series, and multiplying this with the summation, one can verify that this is equivalent to equation (6).

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Small-Angle X-ray Diffraction Studies and Morphology of Microporous Materials and Their 'Hard' Elastic Precursors

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Changes in small-angle X-ray diffraction when microporous materials, formed from hard elastic precursors, are immersed in liquids has established that the interlamellar fibrils are crystalline. It is concluded that the stabilization of the extended void structure is due to crystallization of the fibrils.

The superstructure of hard elastic materials such as polypropylene fibers and films has been shown to consist of well oriented lamellae. The small-angle pattern of the 'as-extruded' materials has the character of a narrow fan on the meridian, indicating the existence of a distribution of long spacings and thus lamellar thicknesses along the extrusion direction and of very large lateral lamellar dimensions. With increasing annealing temperature, the meridional fan increases in intensity, it becomes shorter and eventually the lamellar thickness (long spacing) becomes so uniform that in addition to the basic spacing the second-order scattering is visible. This is easily observed when annealing in the temperature range 130–150 °C. The details of the preparation of these materials, their diffraction pattern as function of extrusion and annealing conditions have been published elsewhere (Noether & Whitney, 1973; Park & Noether, 1975).

A characteristic feature of these highly crystalline, highly oriented materials is the fact that they can be extended 50–100%, this extension being practically completely and immediately reversible. Small-angle and wide-angle X-ray diffraction (SAXR and WAXR) and electron-microscopy data show that these fibers or films, on extension beyond 20–25%, rupture in the interlamellar regions to form elongated voidy regions parallel to the lateral lamellae direction. The void size in the stretch direction is proportional to

the degree of extension. In the case of the annealed fibers, the SAXR pattern reveals that the change in superstructure developed during extension is completely reversible. The sharpness of the diffraction pattern during extension indicates a very uniform deformation behaviour during this process. This behaviour is confirmed by electron-microscopic examination of an annealed sample at 0 and 80% extension (Noether & Whitney, 1973; Park & Noether, 1975). In the case of the unannealed material, which has a distribution of lamellar thicknesses, the extension process is not completely reversible, for on return to zero stress, some void scattering remains; probably some lamellae are being deformed beyond their elastic limits.

A crude model, a three-dimensional leafspring, has been proposed which roughly represents the extension–relaxation behaviour. A more sophisticated model has also been proposed, based on the reduction of surface energy in the interlamellar regions, as well as some entropic effects connected with the collapse of the interlamellar fibrils (Sprague, 1973; Göritz & Müller, 1974, 1975).

Stable microporous materials can be prepared from these elastic fibers or films by a variety of process conditions, by stabilizing the *extended* hard elastic structure. The electron micrograph (Fig. 1) shows that the material consists of ridges of very uniform lamellar regions, connected by fibrillar voidy structures. Additional details of this structure have been elucidated by WAXR and SAXR studies. WAXR shows that we still have a highly oriented structure; the degree of orientation has not changed noticeably compared to that of the original 'hard' elastic material. The SAXR pattern shows a strong equatorial streak, probably due to the interlamellar fibrillar structures or voids. It also has a diffraction spot on the meridian which could correlate with the thickness of the lamellae in the ridges, or some repeat distance in the fibrils.

Using liquids with different electron densities, we have shown that the equatorial streak is in fact caused by the fibrillar structures in the interlamellar regions (Fig. 2). Moreover, when cyclohexanol is used (Fig. 2*e*) as the liquid to fill the voids (they are all accessible) only the lamellar scattering on the meridian remains, the equatorial streak in the SAXR pattern having completely disappeared. Since the electron density of cyclohexanol is equal to that of crystalline polypropylene this shows that the fibrils are crystalline.

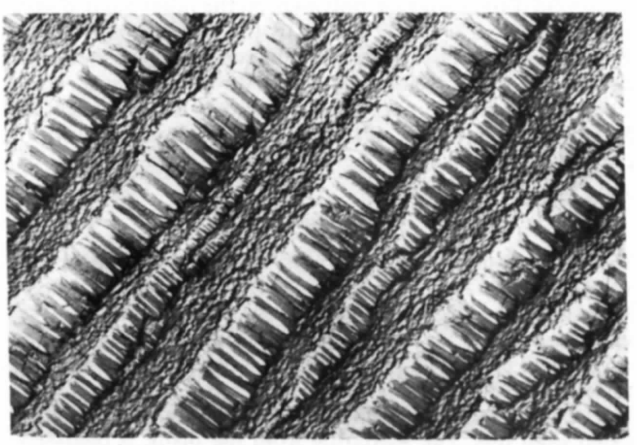

Fig. 1. Electron micrograph of Celgard®.

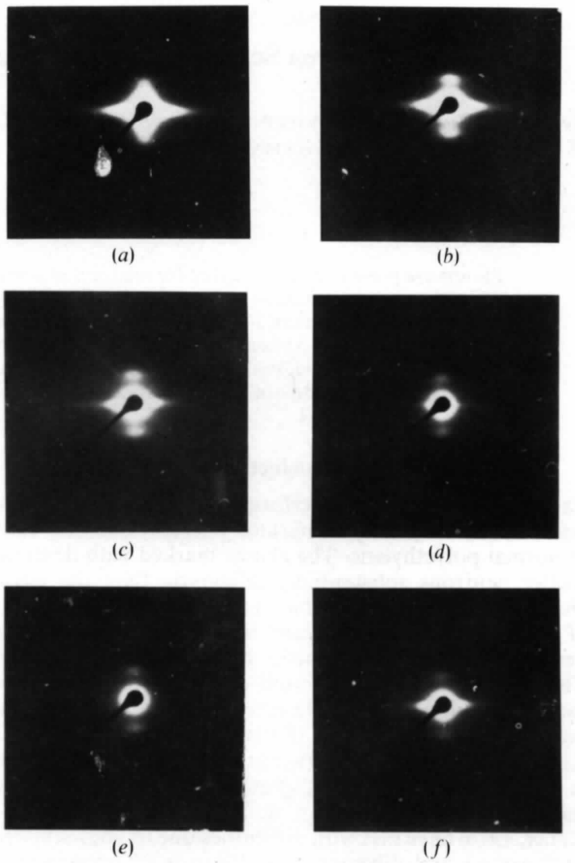

Fig. 2. SAXR Pattern of Celgard® with solvents of various electron densities. Solvents: (*a*) air, (*b*) heptane, (*c*) methanol, (*d*) decalin, (*e*) cyclohexanol, (*f*) methylsalicylate.

It is well known that crystalline fibers of polypropylene are stable at room temperature. It is concluded therefore that the reversibility of the extension of the 'hard' elastic material is destroyed during the stabilization process by the crystallization of the interlamellar fibrils.

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