CHANGE WITH EXTENSION OF MOLECULAR ORIENTATION
OF HARD ELASTIC POLYPROPYLENE

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Change with extension of the molecular orientation of hard elastic polypropylene has been studied by use of x-ray diffraction, birefringence and polarized dye-fluorescent intensity distribution method. The degree of orientation of the c-axis oriented crystals decreases slightly with extension, which is inferred to be not due to the bending of crystals but due to the rotation because the sharpness of the crystalline diffraction remains unchanged under high extension, though the width becomes slightly larger. Birefringence decreases remarkably after yielding point because the negative contribution of the form birefringence due to the void formation. The change of the polarized dye-fluorescent intensity distribution showed that the molecular orientation decreases with extension, suggesting that dye-dichroism in this case was related to the crystalline orientation but not to the amorphous orientation.

Introduction

The mechanism of elongation of hard elastic polypropylene (PP) has been studied by many authors with the most important result that the elongation is related to the separation of stacked lamellae to form voids between their interfaces. We also evidenced the origination of voids by gas permeability measurements. In addition to this essential void formation, there are some interesting structural changes which can be observed during elongation, for example bending of crystal lamellae and disorientation of the crystals. In the present work, the change in the molecular orientation with extension of the material was studied by use of X-ray diffraction, birefringence and polarized dye-fluorescence intensity distribution methods.

Experimental

Sample: A film 10 μm thick and 25 mm wide was spun from molten isotactic PP (Sho-Allomer: Mf=7–8) by use of an extruder equipped with T-die. The film had a high degree of crystal orientation but its elasticity was not high. In order to improve the elasticity, it was annealed at 140°C for 1 hour in an air-circular pyrostat, during which time the length of the film was kept constant so that thermal shrinkage would not occur. This annealing caused the film to become highly elastic, as shown in the stress-strain curve set forth in Fig. 1. Fig. 1 shows that almost all strain is recovered even after 100% extension. X-ray diffraction photograph of the film is given in Fig. 2.a, indicating that the degree of orientation of the crystalline region is high. The density of the film was 0.908 g/cm³, and the crystallinity X, calculated by eq. (1) was 0.66.

\[
\frac{1}{\rho_s} = \frac{x}{\rho_c} + (1 - x) / \rho_a
\]

Fig. 1 Stress-strain curve of hard elastic PP at room temperature.
Strain rate: 50%/min.
where $\rho_s$, $\rho_c$ and $\rho_a$ were densities of the sample, crystalline and amorphous regions, respectively. In calculating the crystallinity, 0.936 g/cm$^3$ and 0.858 g/cm$^3$ were taken for the values of $\rho_c$ and $\rho_a$.

X-ray measurements and Determination of degree of crystal orientation: Ni-filtered CuKα radiation was used in Rigakudenki D3 type apparatus. The conditions for x-ray measurements were as follows; for the incident beam, a long pin-hole slit, 1 mm wide and 10 cm long, was mounted in the Rigakudenki fiber-specimen holder 1.5 cm before the sample; for the scattered beam, a pin-hole slit of 2 mm diameter was placed 15 cm from the sample and the scintillation counter was placed just behind the slit. A platelet sample 0.1 mm thick was prepared by stacking the sample films. In the measurement of the width of the diffraction profile, silicon powder was used to compensate the width due to the apparatus. Eq. (2) was used in the compensation of the diffraction width.

$$W_{\text{obs}}^2 = W_{\text{sample}}^2 + W_{\text{silicon}}^2 \quad (2)$$

where $W_{\text{obs}}$, $W_{\text{sample}}$ and $W_{\text{silicon}}$ were width observed, that inherent to the sample and that observed for silicon. In calculation of the degree of crystal orientation, Wilchinsky's equation$^9$), eq. (3), was used, and then the orientation function, defined by eq. (4) was calculated.

$$\cos^2 \varepsilon = 1 - \frac{1 - 2 \sin^2 \theta_{(110)} \cos^2 \theta_{(040)} - (1 - 2 \sin^2 \theta_{(040)} \cos^2 \theta_{(110)})}{\sin^2 \theta_{(040)} - \sin^2 \theta_{(110)}} \quad (3)$$

$$f = (3\langle \cos^2 \varepsilon \rangle - 1)/2 \quad (4)$$

where $\varepsilon$ was the angle between the chain axis and the fiber axis, $\theta_{(040)}$ and $\theta_{(110)}$ were angles between the (040) and (110) normals and the b-axis, and $\theta_{(040)} = 0^\circ$ and $\theta_{(110)} = 72.5^\circ$ in this case.

Polarized dye-fluorescence measurement: The sample was dyed with a disperse dye, WhiteX SNK, at 80°C for 6 hours before extension. The conditions were as follows; 4 ml dye and 0.5 ml dyeing assistant were dissolved into 100 ml water, and 1 g sample was dyed in the 1000 ml solution. After dyeing the sample was washed in an aqueous solution of Noygen 120 at 80°C for 100 min. In the measurement of polarized dye-fluorescent intensity, Nihonbunko polarizing fluorophotometer FOM-1 was used.

Birefringence measurement: A Nihonkogaku polarized microscope equipped with a Berek compensator was used for 550 nm ray. The thickness of sample (ca. 10 μm before extension) was measured with a thickness gauge with an accuracy of ±0.1 μm. The decrease in the thickness with extension was very small, which was one of the important character of this sort of hard elastic material.

Results and Discussion

Crystal orientation

X-ray diffraction photographs taken under given extensions are shown in Fig. 2. They indicate that slight disorientation of the c-axis oriented crystals is caused by extension, as has been reported by Noether and Whitney$^3$). At the same time some change in the orientation is observed for the a*-axis oriented crystals. In Fig. 3 the orientation functions for the c-axis and a*-axis oriented crystals are plotted as a function of extension.
This slight disorientation of the c-axis crystal might be related to the bending of lamellae\(^5\). Thus we have calculated the effect of the bending on the x-ray diffraction profile, under an assumption that a lamella bends uniformly with a given curvature. The result shows that the diffraction pattern loses the character of crystal diffraction even under very small curvature when the lamellar width is several hundred angstroms, as is the present case; the analysis of the (110) diffraction profile of the sample have shown that the width of lamella in the direction normal to the plane is larger than 200 Å. These calculations and the experimental results lead us to assume that the slight disorientation of the c-axis oriented crystals is not due to the bending of lamella but must be due to the small rotation of crystals, which is caused by the force (pressure) working in the direction normal to the extension. The force works against the volume increase of the extended sample. It should be noted that crystal lamellae suffer from not only this small rotation leading to the disorientation but also from the lattice disorder. Fig. 4 shows the width of the (110) diffraction profile as a function of extension. It may be noted that the width increasing with extension is recovered after unloading, which suggests that the increase in the width is related to the lattice disorder induced by extension but not to the decrease in the crystal size. The disorder parameter defined by Hosemann\(^10\) in eq. (5), is calculated from the width under assumption that the width of the diffraction profile is caused only by the lattice disorder. The results are shown in Fig. 5.

\[ \delta \beta_{110} = \frac{1 - \exp(-2\pi^2 g^2 h^2)}{2 d_{110}} \]

where \( g \) is the disorder parameter, \( h \) is the order of the diffraction and in this case \( h=1 \), and \( d_{110} \) is the (110) spacing.

**Birefringence**

In Fig. 6 the birefringence of the sample is shown as a function of extension. This figure shows that the birefringence remains almost constant before yielding point and then abruptly decreases to become negative, and then increases passing a minimum value at about 70% extension. Recently Samuels\(^6\) studied in detail this problem and indicated that this change in the birefringence could be explained by the effect of form birefringence due to the voids formed between lamellae. In Fig. 7 the birefringence of the sample, measured in liquid paraffine, is shown as a function of extension. In this case the effect of form
Fig. 6 Change of birefringence of hard elastic PP with extension.

Fig. 7 Change of birefringence of hard elastic PP with extension measured in liquid paraffine. Birefringence diminishes because paraffine fills up the voids and makes the density difference between void and polymer very small. Fig. 8 shows the difference of the values of birefringence shown in Fig. 6 and 7. This gives the contribution of the form birefringence approximately. This figure shows that the form birefringence increases with extension and then decreases passing a maximum at about 60% extension. Form birefringence may be proportional to the number of voids in unit volume of the sample and to the birefringence inherent to a void which depends on the anisotropy of the size. The number increases with extension after yielding but reaches a predetermined value because the voids must be formed only between lamellar interfaces. On the other hand, the anisotropy of void size must be larger in the earlier extension because the thickness, the length in the direction of extension, of voids increases with extension of the sample, while the width of voids cannot increase beyond the width of a lamella.

**Dye-fluorescence intensity distribution**

Fig. 9 shows the change with extension in the angular distribution of polarized fluorescent intensity of dye sorbed in the hard elastic sample. Before stretching, there are two components with
different types orientation: one is of fiber orientation and the other is of perpendicular orientation. The perpendicular component, the fraction of which is much less than that of normal fiber orientation, smears into another component with increasing extension. It has been long believed that dye-dichroism measured in polymer matrix reflects the degree of orientation of the amorphous chains\textsuperscript{11).} However, the pattern obtained here seems to suggest that in this case the dye-dichroism measures the crystalline orientation rather than that of the amorphous. This is because (1) the appearance of the perpendicular component is easily explained by assuming that dyes are sorbed on the side surfaces of the a\textsuperscript{\textdegree}-axis oriented crystals, and (2) the change of the pattern shown in Fig. 9, as a whole, indicates some decrease in the orientation which is very similar to the change in the crystalline orientation studied above. The amorphous chains doubtlessly increases the orientation with extension in this case, and therefore the pattern should become sharper with extension if dyes are sorbed selectively on the amorphous chains. Then we recall Yoshioka et al.'s report\textsuperscript{12)\textdegree} that the molecular orientation of a disperse dye in drawn PP seemed to reflect well the crystalline orientation rather than the amorphous orientation.

\textbf{Reference}