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Studies on the Biaxial Stretching of Polypropylene Film. VII. Refractive Index of Film Measured with Abbé Refractometer

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Synopsis

The refractive index of a film measured with an Abbé refractometer differs often depending on which surface of the film faces the refracting prism of the refractometer. This phenomenon was elucidated by using well-characterized films especially prepared for the purpose. The experimental results led to the conclusion that the measurement with an Abbé refractometer gives the refractive index of the film surface facing the refracting prism independently of the refractive index distribution within the film. The importance of this conclusion is stressed in relation to the structural studies of polymer films, especially of biaxially stretched films.

INTRODUCTION

The physical and mechanical properties of polymer films are closely related to the molecular orientation in the films. Therefore, the measurement of the molecular orientation is very important for the characterization of a film. For this purpose the refractive index is one of the most useful parameters.

One of the authors found that an Abbé refractometer can be applied to the measurement of the refractive index of a solid such as an anisotropic film.[1] The application makes it possible to measure easily and accurately the refractive indices not only parallel to the film surface, but also normal to the film surface.[1-3] The latter refractive index is necessary to characterize the film structure, especially of biaxially stretched film, and has been used extensively in our studies.[4-7] However, it has been observed recently that two different readings of the refractive index are often obtained depending on which surface of the film faces the refracting prism of an Abbé refractometer.[7,8] The observation is incompatible with the principle of the Abbé refractometer if the film were optically homogeneous. A brief explanation of this phenomenon had been given already,[7] but a more extensive investigation is made to elucidate the phenomenon in this paper.

EXPERIMENTAL

Sample Films

The sample films used in this study were commercial films supplied by Chisso Corp. and another company. Their characteristics are listed in Table I.

TABLE I
Characteristics of Sample Films

Sample film[a]	$\bar{M}_v$[b]	Tacticity[c], %	Thickness, μ
C_1	3.0×10^5	95	100
B_1	3.1×10^5	97	400

[a] Symbol C denotes a sample supplied by Chisso Corp.; B is a commercial film from another company. Subscript indicates lot number.
[b] Evaluated by the equation of Kinsinger and Hughes.[9]
[c] Determined by extraction with boiling *n*-heptane.

Preparation of Films

Several kinds of melt-pressed film were prepared as follows. Pieces of C_1, each 10 × 10 cm, and aluminum foils of 15 μ in thickness, each 8 × 8 cm, were piled up alternately as shown in Figure 1. The pile was melt pressed between two stainless steel plates at 230°C for 5 min at a pressure of 10 kg/cm² and quenched in ice water. The thickness of the plate was varied in order to change the cooling rate. The conditions for preparing the films are summarized in Table II.

TABLE II
Conditions for Preparing the Films

Film	Number of C_1 pieces in pile	Temp. of melt pressing, °C	Thickness of metal plates, mm
1	8	230	0.1 and 3
2	2	230	0.5
3	4	230	0.5
4	6	230	0.5
5	8	230	0.5

A specimen about 1 × 1 cm was cut of the melt-pressed film and the pieces were peeled off one by one. The inserted aluminum foils acted as separators, and peeling was easily achieved. Reference films were prepared by piling up C_1 pieces without the insertion of aluminum foils.

Refractive Index

The refractive indices were measured by using a Bausch and Lomb Abbé refractometer model 32. All measurements were made with transmitted light, and the eyepiece of the refractometer was always equipped with a polarizer to discriminate the critical lines for the refractive indices along

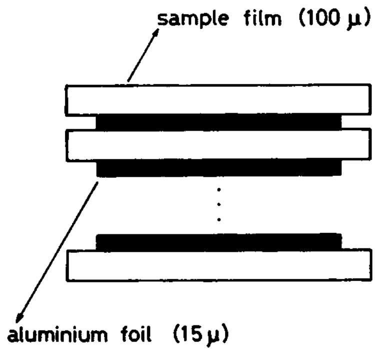

Fig. 1. Side view of pile composed of film pieces and aluminum foils piled up alternately.

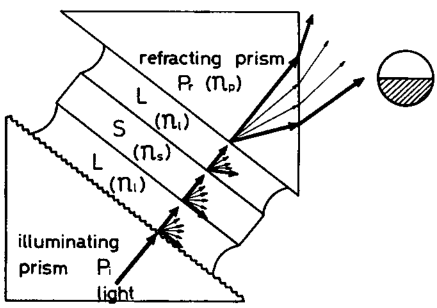

Fig. 2. Schema of Abbé refractometer: P_i, illuminating prism; L, contacting liquid; S, sample; Pr, refracting prims; n_p, n_l, and n_s represent the refractive indices of P_r, L, and S, respectively. Arrows indicate path of light beam.

mutually perpendicular principal axes. In order to minimize the surface reflection and to avoid the total reflection at the surface of the specimen, benzyl alcohol or α-bromonaphthalene was employed as contacting liquid.

RESULTS AND DISCUSSION

According to the principle of the Abbé refractometer, the smallest refractive index of the substances existing between the illuminating prism (P_i) and the refracting prism (P_r) should be obtained if the substances are optically homogeneous (Fig. 2). In order to confirm this principle, the following experiment was performed by using two glass prisms of 2 mm in thickness. These prisms had refractive indices of 1.5161 and 1.6196, respectively, and are designated hereafter as P_1 and P_2. P_1 and P_2 were placed on P_r, as shown in Figure 3. α-Bromonaphthalene was employed for the contacting liquid, whose refractive index (1.6588) is higher than that of P_1 or P_2. The angle of incidence of the light beam was 90°, as shown by arrows in the figure.

In the case of Figure 3a, only the refractive index of P_1 is read, whereas in the case of 3b, two refractive indices, or P_1 and P_2, are read. In the case of 3c, where the side planes of P_2 are covered with black vinyl tape to shut

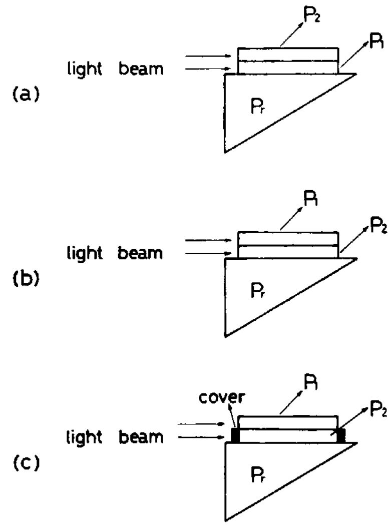

Fig. 3. Positions of glass prisms with different refractive indices on the refracting prism of an Abbé refractometer. Refractive indices of P_1 and P_2 are 1.5161 and 1.6196, respectively; (a) prism of smaller refractive index faces P_r; (b) prism of larger refractive index faces P_r; (c) side planes of P_2 are covered with black vinyl tapes to cut off incident light beam upon them.

out the incident light beam from P_2, only the refractive index of P_1 is read. It is evident from the observation in 3a and 3c that only the refractive index of P_1, which is smaller than that of P_2, is always read irrespective of whether P_1 faces P_r or not; and this is taken as evidence for the validity of the principle of the Abbé refractometer. As for the observation in Figure 3b, two refractive index values are measured because the light beam propagating within P_1 parallel to its surface can enter P_2 because the refractive index of P_1 is smaller than that of P_2. In the case of 3a, only one value is read because the light beam propagating within P_2 parallel to its surface cannot enter P_1 owing to the total reflection.

Sample B_1 as received is a typical example for the different refractive index readings depending on which film surface faces P_r. The refractive indices of the sample are summarized in Table III. Here, n_{pp}, n_{ps} and n_{ss} are the refractive indices along the machine direction, transverse direction, and normal to the film surface, respectively. The mean value of the three refractive indices, n_{iso}, is defined as follows:

$$n_{iso} = (1/3)(n_{pp} + n_{ps} + n_{ss}).$$

TABLE III
Refractive Indices of Sample B_1

Surface which faces P_r	n_{pp}	n_{ps}	n_{ss}	n_{iso}
(1) Upper surface	1.5020	1.5013	1.5015	1.5016
(2) Back surface	1.4944	1.4943	1.4939	1.4942

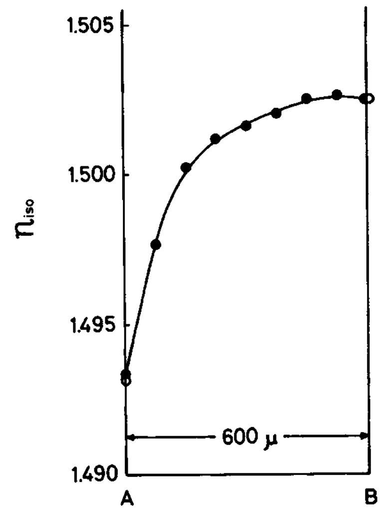

Fig. 4. Distribution of n_{iso} across the section of a film quenched at unequal cooling rates on both surfaces (film 1 in Table II). Surface A was in contact with a stainless steel plate 0.1 mm in thickness, and B was in contact with a stainless steel plate 3 mm in thickness: (●) refractive indices of peeled-off film pieces; (O) refractive indices of reference film.

The values in lines (1) and (2) of Table III are the respective refractive indices read when the upper and back surfaces of the films face P_r. It is noticed that the values in line (1) are larger than those in line (2). Although the results may seem to be curious, they are not unreasonable if the existence of optical inhomogeneity (due to crystallites dispersed in the amorphous part) and differences in the fine structure of the film (due to unequal rate of quenching at the surfaces) is assumed. This is because a similar optical situation of the film to that illustrated in Figures 3a and 3b then exists. (The optical inhomogeneity scatters the light beam passing through the film and gives rise to the light beam parallel to the film surface. The fine structure differences cause the refractive index differences which correspond to P_1 and P_2 in Fig. 3.)

If this were the case, the critical line due to the back surface of the film is expected to appear in the field of the refractometer, as Schael observed on laminated film,[3] when the upper surface having a larger refractive index faces P_r (see Fig. 3b). However, as the film is thought to be optically inhomogeneous, the critical line is probably too obscured to be observed owing to the scattering of the light beam while passing through the film. When the film surface is reversed, the critical line of the upper surface cannot be observed because of the total reflection, as is illustrated in Figure 3a. Thus, the refractive index of the surface layer facing P_r is measured independently of the refractive index distribution across the cross section of the film.

The interpretation is supported by the following experimental results. In Figure 4, the solid circles indicate the refractive indices, n_{iso}, of a piled

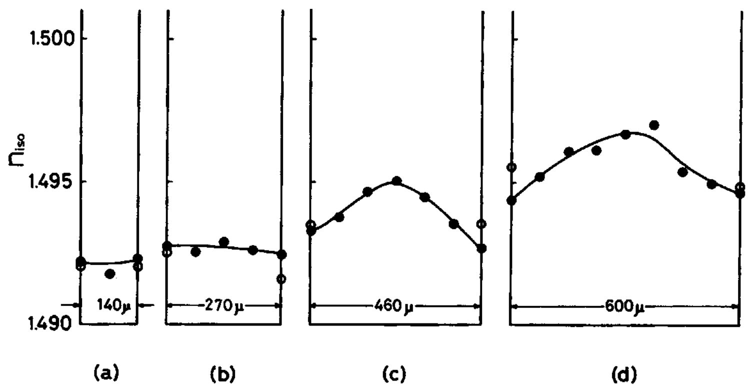

Fig. 5. Distribution of n_{iso} across cross sections of films: (●) refractive indices of the peeled-off film pieces. (O) refractive indices of the reference film; (a) film 2 in Table II; (b) film 3 in Table II; (c) film 4 in Table II; (d) film 5 in Table II.

and melt-pressed film which were read on the peeled-off pieces, while the open circles were read on the reference film. It can be seen clearly that the two values read on the pieces peeled off from both surfaces of the piled and melt-pressed film agree well with the values of the corresponding parts of the reference film. If the inserted aluminum foils acted simply as separators and had a negligible effect on the quenching process, it can be expected that nearly the same n_{iso} distribution as found within the piled film exists also within the reference film.

It is concluded that the refractive index of the film measured with an Abbé refractometer is that of the very surface facing P_r and is independent of the refractive index distribution within the film. Such a dual structure, which is often observed in commercial undrawn film, remains after biaxial stretching to a considerable extent as was already shown in Figure 6 of the preceding paper.[7]

Figure 5 gives additional support for the conclusion; here, the films were prepared by varying the number of the piled pieces of C_1, as indicated in Table II (film 2 to 5). It is clearly seen that the thinner the melt-pressed film is the less the distribution of n_{iso}. For practical purposes, a film thinner than 270 μ is structurally homogeneous under these conditions.

The conclusions made above are very important for the study of films through changes in refractive index determined with an Abbé refractometer. In order to know and study the "inner" structure of a film by this means, the film must be structurally homogeneous. Figure 5 assures us that if a film is thin enough, it is structurally homogeneous and there is no problem in using an Abbé refractometer when studying the inner structure of the film. On the other hand, it is safe and meaningful to correlate the optical observation made by an Abbé refractometer to electron microscope observations (replica) even if a film is not structurally homogeneous (see series III and V of this study). This is because both observations are related only to the structure at the film surface.

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