Determination of the refractive index and birefringence for biaxially stretched poly(ethylene terephthalate) at microwave frequencies

Shigeyoshi Osaki and Kimiyoshi Uranishi
Research and Development, Kanzaki Paper Manufacturing Company Ltd, 4-3-1, Jokoji, Amagasaki, Hyogo 660, Japan
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Refractive index and birefringence were determined without contact for biaxially stretched poly(ethylene terephthalate) (PET) films at a microwave frequency. The following relationship was obtained between the birefringences Δn_{MW} at a frequency of 4.0 GHz and Δn_{OPT} at a visible wavelength of 589 nm for many kinds of biaxially stretched PET films: $\Delta n_{MW} = 1.3933\ \Delta n_{OPT}$. The correlation coefficient between Δn_{MW} and Δn_{OPT} was 0.969, indicating a very good correlation. On the other hand, the observed relation between the refractive indices n_{MW} at 4.0 GHz and n_{OPT} at 589 nm could be expressed as $n_{MW} = -0.5567 + 1.4243\ n_{OPT}$. The n_{MW} was larger than the n_{OPT} in all the directions of the sheet plane. This difference may arise from difference in contribution of ε' associated with the local motion (β-relaxation) of PET molecules.

(Keywords: refractive index; birefringence; dielectric anisotropy; poly(ethylene terephthalate); microwave frequency)

INTRODUCTION

Measurements of optical anisotropy provide direct information on the orientation of polymer molecules in the crystalline and amorphous regions. If polymer materials are transparent, refractive index and birefringence measurements are quite suitable[1–3]. However, this has not been the case for opaque or coloured polymer materials at visible wavelengths because of poor transmission of visible rays through the sample. Recently, we developed a new type of analyser by using microwaves, and reported successful results for the molecular or fibre orientation and dielectric anisotropies of polymer films, paper sheets, and non-woven fabrics[4–11]. We also tried to determine the microwave refractive index for paper sheets[9] as well as opaque samples.

The present paper describes determination of refractive index and birefringence for biaxially stretched poly(ethylene terephthalate) (PET) films at a microwave frequency of 4.0 GHz. The results are compared with those at a visible wavelength.

EXPERIMENTAL

Refractive index and birefringence at 4.0 GHz were determined by means of a microwave molecular orientation analyser model No. MOA-2001A, which consists of a pair of rectangular waveguides with a narrow gap in the cavity resonator system[4–11]. The sample sheet was set in the gap, and polarized microwaves were irradiated vertically to it. This sample sheet was rotated to different fixed angles around the central axis normal to the sheet plane. At each rotating angle the refractive index was evaluated from the resonance frequency measured in the resonator system. Here, the resonance frequency is defined by the frequency at the maximum of the transmitted microwave intensity in the resonance curve.

The birefringence was determined as a difference between the refractive indices observed in two directions which were perpendicular to each other. The experimental procedure was as follows.

The test specimen, cut to a fixed size of 100 × 100 mm, was inserted in the cavity resonator. The refractive index was determined from the resonance frequency in the resonance curve. The time necessary for determining the refractive index was about 15 s at a fixed angle or in a fixed direction. The frequency ranged from 3.9 to 4.3 GHz. The electromagnetic mode used was a transverse electric wave (TE) of a type of TE_{10L}.

The dielectric constant ε' for the dielectric sheet may be written[7,9]

$$\varepsilon' = 1 + A(c/t)[(f_1 - f_2)/f_2] \qquad (1)$$

Here, t is the thickness of the sample, c a parameter related to the depth of the rectangular waveguide, A a constant associated with the instrument, and f_1 and f_2 the resonance frequencies with the subscripts 1 and 2 indicating the values before and after insertion of the sample.

The refractive index n for the sheet material can be derived from the Maxwell equation[12]. When ε'' of the dielectric material is very small and the magnetic permeability is assumed to be unity the following equation is obtained:

$$n = (\varepsilon')^{1/2} \qquad (2)$$

The refractive index was also measured at a visible wavelength of 589 nm, using an Abbe refractometer.

The samples used in the present study were biaxially stretched PET films with crystallinities of 30–40%, which were evaluated from the empirical formula between ε'' and the crystallinity given in ref. (7).

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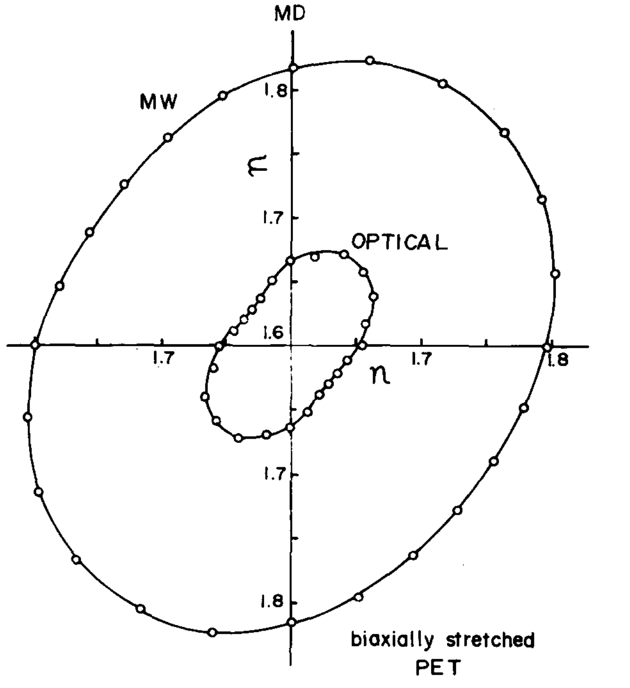

Figure 1 Angular dependence of n at a microwave frequency of 4.0 GHz (MW) and a visible wavelength of 589 nm (optical) for a biaxially stretched PET film with a thickness of 100 μm

RESULTS

Figure 1 shows the angular dependence of n determined at a wavelength of 7.5 cm (4 GHz) and a wavelength of 589 nm for a biaxially stretched PET film with a thickness of 100 μm. The refractive indices at the microwave frequency are larger than those at the visible wavelength in all the directions of the sheet plane. This difference may arise from different contributions of ε' associated with the local motion (β-relaxation) of PET molecules[13]. In other words, the larger n (hence larger ε') of the PET film at the microwave frequency may be ascribed to the polarization of β-relaxation.

It can be seen in *Figure 1* that the direction of the maximum n at the microwave frequency substantially coincides with that at the visible wavelength. Both deviate from the machine direction MD by about 35°.

The relationship between the refractive index n_{MW} at the microwave frequency and the refractive index n_{OPT} at the visible wavelength for the biaxially stretched PET film is shown in *Figure 2*. The observed relation can be expressed as

$$n_{MW} = -0.4426 + 1.3561 n_{OPT} \quad (3)$$

The correlation coefficient between n_{MW} and n_{OPT} was 0.981.

In *Figure 3*, the birefringence Δn_{MW} determined at 4.0 GHz for many kinds of biaxially stretched PET films are plotted against the birefringence Δn_{OPT} at 589 nm. The birefringence Δn for each sample was determined from a difference in n between the transverse direction TD and the machine direction MD perpendicular to the TD.The indicated straight line gives

$$\Delta n_{MW} = 1.3933 \, \Delta n_{OPT} \quad (4)$$

The correlation coefficient between Δn_{MW} and Δn_{OPT} was 0.969, indicating a very good correlation.

For the above-mentioned PET films the following empirical equation was obtained.

$$n_{MW} = -0.5567 + 1.4243 n_{OPT} \quad (5)$$

Although this relation differs slightly from equation (3), both give n_{MW} values which agree within about 0.1% throughout the range of n_{OPT} studied.

Figure 4 shows Δn_{MW} at a wavelength of 7.5 cm as a function of the distance from the left rim of a biaxially

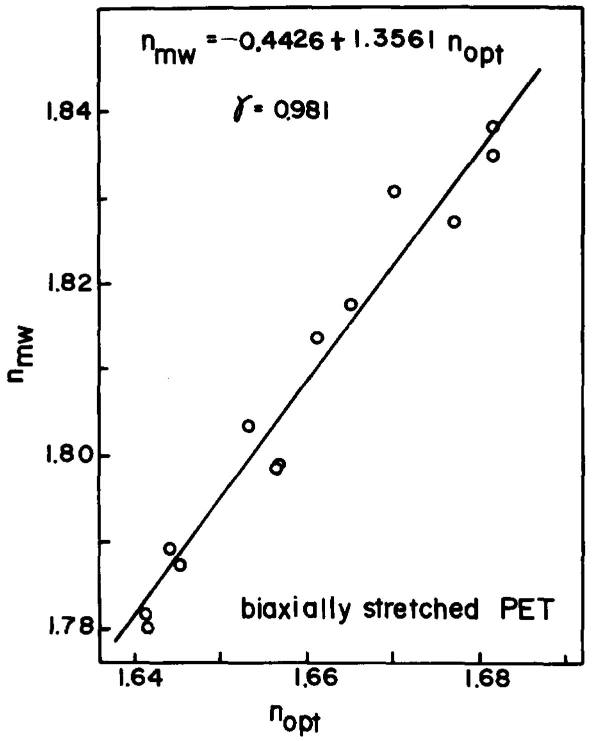

Figure 2 Refractive index n_{MW} at 4.0 GHz plotted against refractive index n_{OPT} at 589 nm for a biaxially stretched PET film with a thickness of 100 μm. The correlation coefficient between n_{MW} and n_{OPT} is 0.981

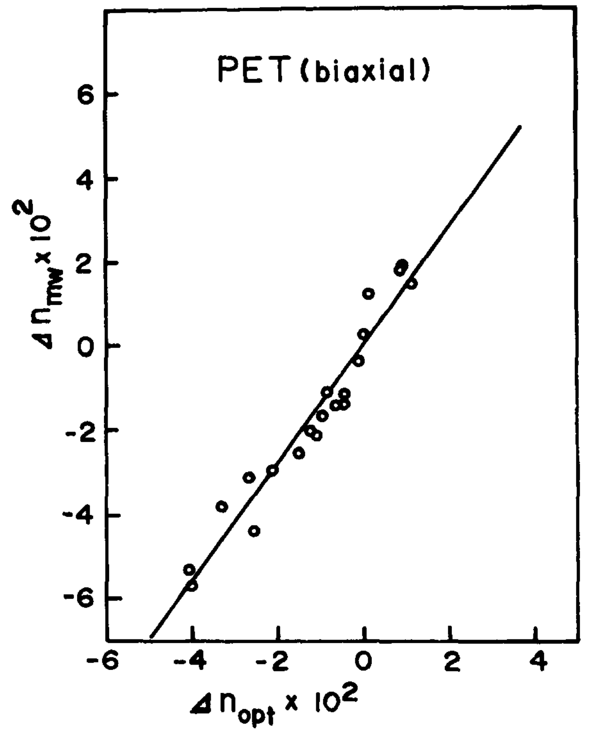

Figure 3 Birefringence Δn_{MW} at 4.0 GHz plotted against birefringence Δn_{OPT} at 589 nm for many kinds of biaxially stretched PET films

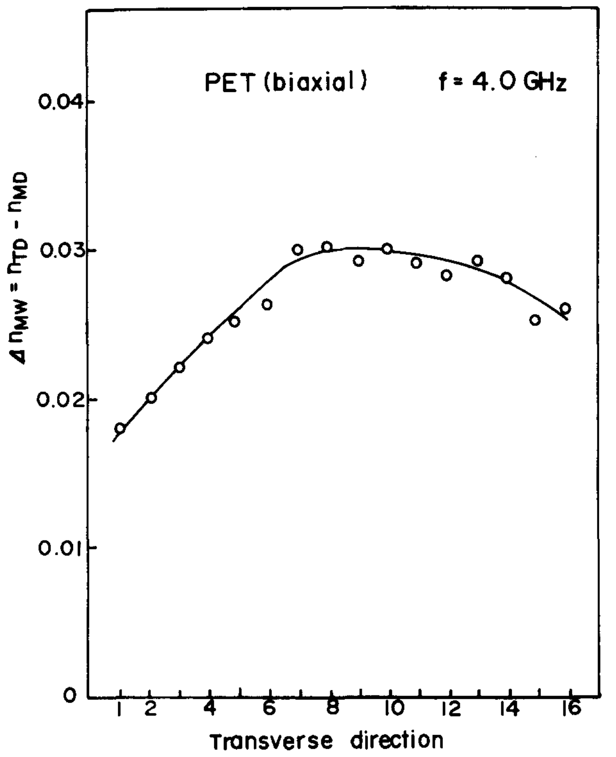

Figure 4 Birefringence Δn_{MW} ($=n_{TD}-n_{MD}$) at a frequency of 4.0 GHz between the left and right rims of a biaxially stretched PET film with a thickness of 100 μm and a 1600 mm width; n_{TD}, refractive index in the TD; n_{MD}, refractive index in the MD. The samples with a size of 100 × 100 mm are numbered from 1 to 16 from the left to right rims along the transverse direction

stretched PET film with a thickness of 100 μm and a 1600 mm width. The birefringence changes with position in the TD of the film, revealing a non-uniformity of the film in this direction. Though not shown here, Δn was essentially independent of position in the MD.

DISCUSSION

The observed n_{MW} was larger than the n_{OPT} in all directions of the biaxially stretched PET films, as shown in *Figures 1* and *2*. The n_{MW} may be expressed approximately by the superposition of the refractive index n_{LM} due to the β-relaxation of PET molecules and the refractive index n_{OPT} at a visible wavelength. The dielectric β-relaxation due to the local motion in the amorphous region[7,13] contributes toward increasing the dielectric constant and refractive index at microwave frequencies. Therefore, the contribution of the amorphous region to the refractive index at a microwave frequency can be larger than that at a visible wavelength.

In the near future a quantitative comparison will be made between n_{MW} and n_{OPT} from the theoretical point of view.

In the present study, the refractive index and birefringence were determined for biaxially stretched PET films at a microwave frequency without contact. Their accuracy is somewhat less than that at a visible wavelength determined from a conventional refractometer. However, our microwave method has an advantage in that, as shown in this work, it is useful for studying the uniformity in the TD of the various films in a short time without contact. Another advantage lies in a possibility of determining various physical constants such as the crystallinity χ, the orientation function for the amorphous region f_a and the orientation function for the crystalline region f_c.

Generally, Δn_{OPT} is expressed by the sum of contributions from the crystalline and amorphous regions in the sample[14], i.e.,

$$\Delta n_{OPT} = \chi f_c \Delta n_c + (1-\chi) f_a \Delta n_a \qquad (6)$$

where Δn_c and Δn_a are, respectively, the intrinsic birefringence of crystalline and amorphous regions. This equation is valid when the difference in the refractive index between the directions parallel to and perpendicular to the macromolecular chain axis is very small in comparison with the average refractive index. However, equation (6) is not applicable to the biaxially stretched PET films because of the plane orientation of benzene ring and because of the relatively large difference in the refractive index between the directions parallel to and perpendicular to the chain axis. Therefore, for the samples to which equation (6) is applicable, the physical constants such as χ, f_a and f_c may be obtained by the following procedure. For example, Δn_{OPT} can be estimated from the observed Δn_{MW} by use of an empirical formula such as equation (4). The values of χ and f_a can also be determined by the microwave method, as shown in a previous paper[7]. With Δn_c and Δn_a determined by other methods[14], f_c may be also evaluated from equation (6).

Finally, from the empirical relations between n_{MW} and n_{OPT} and between Δn_{MW} and Δn_{OPT} it may be possible to estimate the refractive index and the birefringence, respectively, at the visible wavelength even for the opaque or coloured films.

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REFERENCES

1 Jungnickel, B. J. *Angew. Makromol. Chem.* 1984, **125**, 121
2 Ward, I. M. 'Structure and Properties of Oriented Polymers', Applied Science , London (1975)
3 Ward, I. M. 'Developments in Oriented Polymers—1', Applied Science, London (1982)
4 Osaki, S. *Bull. Jpn. Soc. Print. Sci. Technol.* 1985, **23**, 19
5 Osaki, S. *Tappi* 1987, **70**, 105
6 Osaki, S. *Polym. J.* 1987, **19**, 821
7 Osaki, S. *J. Appl. Phys.* 1988, **64**, 4181
8 Yamamoto, K., Osaki, S., Yamashita, S. and Yamada, Y. *Cell. Molec. Biol.* 1988, **34**, 571
9 Osaki, S. *J. Appl. Polym. Sci.* 1989, **37**, 527
10 Osaki, S. *Tappi* 1989, **72**, 171
11 Osaki, S submitted to *Sen-i Gakkaishi*
12 Altschler, H. M. 'Handbook of Microwave Measurements' (Eds M. Suche and J. Fox), Wiley, New York (1963)
13 Ishida, Y., Kajiyama, K., Ito, H. and Takayanagi, M. *Kolloid-Z, Z. Polym.* 1962, **184**, 97
14 Hoshino, S., Power, J., Legrand, D. G., Kawai, H. and Stein, R. *J. Polym. Sci.* 1962, **58**, 185