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Measurement System for Very Small Photoelastic Constant of Polymer Films

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Summary: We produced a new system for measuring the small photoelastic constant of a polymer thin film with a small birefringence. Using our mesurement system, we evaluated the photoelastic constant of a polymer film in real time by quantitative analysis. Photoelastic constants of 11.30×10^{-12} Pa^{-1} for a cellulose triacetate film and 78.38×10^{-12} Pa^{-1} for a polycarbonate film were obtained. Furthermore, we obtained a small photoelastic constant of 0.12×10^{-12} Pa^{-1} for a cycloolefin film for liquid crystal displays, using our new measurement system. This value is very small. We emphasize that, if a small change in retardation and stress cannot be detected simultaneously using our system, then we cannot obtain such a small photoelastic constant.

Keywords: films; liquid crystal display; optics; photoelastic constant

Introduction

In general, the birefringence and photoelastic constants of polymer films are very large compared with those of inorganic materials. However, currently, a large number of optical polymer films with small birefringence and photoelastic constant used for liquid crystal displays (LCDs) are commercially available.[1] When an optical film used in the LCD is distorted by applying a force or increasing temperature, the retardation of the optical film is induced. As a result, an irregular color due to the induced retardation is observed in the LCD.[1] To realize distinct picture quality in LCDs, a practical, useful application of an optical polymer film with a very small photoelastic constant is required. Thus, we must design the molecule of a polymer with a very small photoelastic constant. To realize this, we need information on photoelasticity, as a physical constant of the polymer. Therefore, precise photoelasticity measurement is required.

Mathematical Representation of Photoelasticity of Polymer Film

Photoelasticity is a phenomenon in which the change in an optical parameter (refractive index) is caused by elastic deformation. Photoelastic constants contain two kinds: one is piezooptical constant and the other is elastooptical constant. Equation 1 is the optical indicatrix of the crystal using orthogonal coordinates, O-x_1-x_2-x_3[2,3], as shown in the right figure of Figure 1.

$$\frac{\chi_1^2}{n_1^2} + \frac{\chi_2^2}{n_2^2} + \frac{\chi_3^2}{n_3^2} = 1 \tag{1}$$

Here, n_i is the refractive index of x_i axis ($i =$ 1, 2, 3). In the case of a uniaxial crystal, $n_1 = n_2 = n_o$ and $n_3 = n_e$. Here, n_o is the refractive index for an ordinary ray, and n_e is the refractive index for an extraordinary

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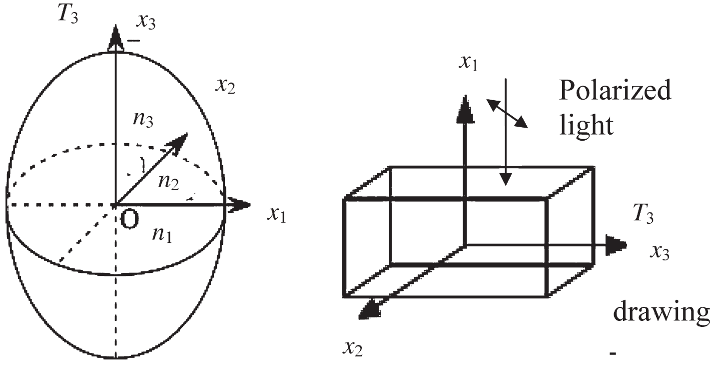


Optical indicatrix

Polymer film

Figure 1.
Optical system.

ray. Under the application of a small stress T_3 parallel to the x_3-axis (principal axis), we derive Eq. (2) from Eq. (1). [2,3]

$$n_1 = n_o - \delta n_1 \qquad (2)$$

$$\delta n_1 = 1/2\, n_o^3 \pi_{31} T_3 \qquad (3)$$

Here, π_{31} is the piezooptical constant. The second term δn_1 in Eq. (2), which is induced by applying T_3, represents photoelasticity.

We emphasize that Eq. (2) sets up the following preconditions [2,3]:

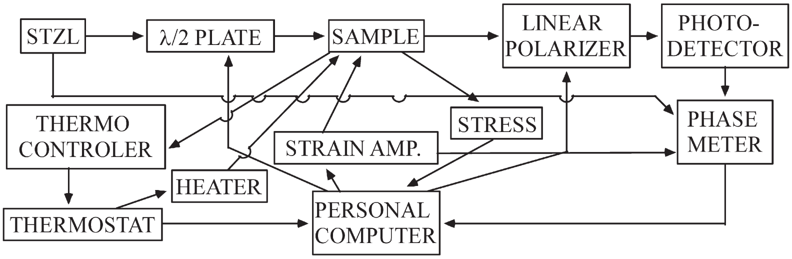
1) The azimuth of the principal axes n_1, n_2 and n_3 in an optical indicatrix does not change and rotate, under stress, for example, T_3.
2) $T_i = C_{ij} S_j$ $(i, j = 1 \sim 6)$ holds. Here, C_{ij} is the elastic modulus. S_j is the strain.

Then, the equation $p_{ij} = \pi_{ik} C_{kj}$ gives the relationship between the piezooptical and elastooptical constants, π_{ij} and p_{ij}.

In the case of a polymer film, for example, even though the system is isotopic, two independent components of π_{ij} exist. For an oriented polymer film with achiral chain molecules, the point group for representing the symmetry of the system becomes $D_{\infty v}$ as shown in the right figure of Figure 1. In this case, the drawing direction is roughly parallel to the principal axis of optical indicatrix: two independent components of piezooptical constants exist. In this study, on the basis of above principle, we evaluated the π_{31} of polymer films.

Measurement System

The system developed here, as shown in Fig. 2, is based on the simultaneous measurement of a small change in retardation and stress under the application of a small strain. In this system, we adopted the measurement method based on the heterodyne interferometry principle [4, 5], in order to improve the accuracy of the retardation measurement. The details of this technique have been reported previously.[4, 5] So, we give a brief outline as follows. A stabilized transverse Zeeman laser (STZL) emits orthogonally polarized two-frequency light of $\lambda = 632.8$nm. A half-wave plate and a linear polarizer are set on rotating stages controlled by a microcomputer. The laser beam passes through the half-wave plate, film sample, which undergoes intrinsic-birefringence-induced retardation and stress-induced retardation, and linear polarizer, which is incident to a photodetector. The optical beat signal obtained at the photodetector is synchronously detected by a phase meter. The output signals are stored in a microcomputer. In particular, we ensure that the measurement accuracy of retardation is 0.015 nm and the measurement time is 0.1 s. Then, the azimuth angle of the optical



Stabilized transverse Zeeman laser (STZL)

Figure 2.
Schematic diagram of measurement system for photoelastic constant of polymer film.

principle axis of the sample can be measured simultaneously with an accuracy of 0.1 degrees. For reference, the characteristics of our previous system [6] based on the conventional method, such as the Senarmon method [7] are as follows: The accuracy of retardation change is about 10 nm. Then, the azimuth of the optical principle axis of a sample must be aligned with the azimuth angle of the measurement system.

Basically, we obtain the photoelastic constant from the induced retardation under the application of stress to a film sample, as shown in the right figure of Figure 1. When the measurement accuracy of retardation is low, it is necessary to apply a large stress to the polymer film. As a result, a large stress-induced retardation is obtained. The retardation behavior deviates from the linear relationship between the induced refractive index and stress. This measurement violates the conditions for measuring the minute change in the optical indicatrix induced by stress. For this reason, the measurement of the photoelastic constant must also be possible, even if the azimuth of the principal indices of the optical indicatrix faces any direction due to the application of a large stress, described in the previous section. At very low strain and stress, the relationship between stress and strain is linear. However, with increasing strain and stress, the relationship becomes nonlinear. This relationship is called the stress-strain curve. Sometimes, a complicated elastic deformation is accompanied by a very partial plastic deformation. The photoelastic constant can be measured using the Senarmon method [6, 7] when the deformation mode of the polymeric film becomes complicated. In this case, the photoelastic constant obtained is not a physical constant.

Next, we concretely predict of the value of induced retardation caused by the stress. For example, when we apply a force of 1 kg to a sample with a cross section of 1 mm^2 (100 μm × 1 cm), for the film with a piezo-optical constant of $100 \times 10^{-12} Pa^{-1}$, such as a polycarbonate (PC) film, a retardation of about 100 nm is induced. For an optical film with a piezooptical constant of $10 \times 10^{-12} Pa^{-1}$, a retardation of about 10 nm is induced under the application of a stress of 1 kg. The accuracy of the conventional measurement system, based on the Senarmon method [6, 7], is about 10 nm. For a film with a piezooptical constant of $100 \times 10^{-12} Pa^{-1}$, the piezooptical constant cannot be detected under the application of a force of 1g, using the Senarmon method.[6, 7] If, for films with a piezooptical constant of $10 \times 10^{-12} Pa^{-1}$, the measurements cannot be performed under the application of a force of 10 g, using the the Senarmon method [6, 7], a force of 10 kg must be applied. We emphasize here that we can measure the piezooptical constant under a very small force or strain. Therefore, in this study, our attempt is to develop a measurement system with an accuracy of 0.01 nm so that we can detect the piezooptical constant under a very small force or strain. In this case, the photoelastic constant becomes a physical constant when the minute retardation due to induced birefringence caused by the applied stress can be measured at high accuracy. To eliminate the occurrence of a complicated factor, we found that the photoelastic constant should be measured in a very low stress range.

Experimental Results

We show typical experimental results of the stress dependence of the induced birefringence of PC film in the temperature range from 20 °C to 150 °C. In Figure 3, the induced birefringence (δn_1) in Eq. (2) is plotted against the amplitude of the stress (T_3). We obtain the π_{31} from the slope of the plots, following to Eq. (3). We found that the slope in the small-stress region is different from that in the large-stress region. For reference, we show the simultaneously measured results of the stress-strain curve. We found that the relationship between stress and strain is not linear in the measurement range of stress. On the basis of the results, we conclude that, under a large stress, we cannot

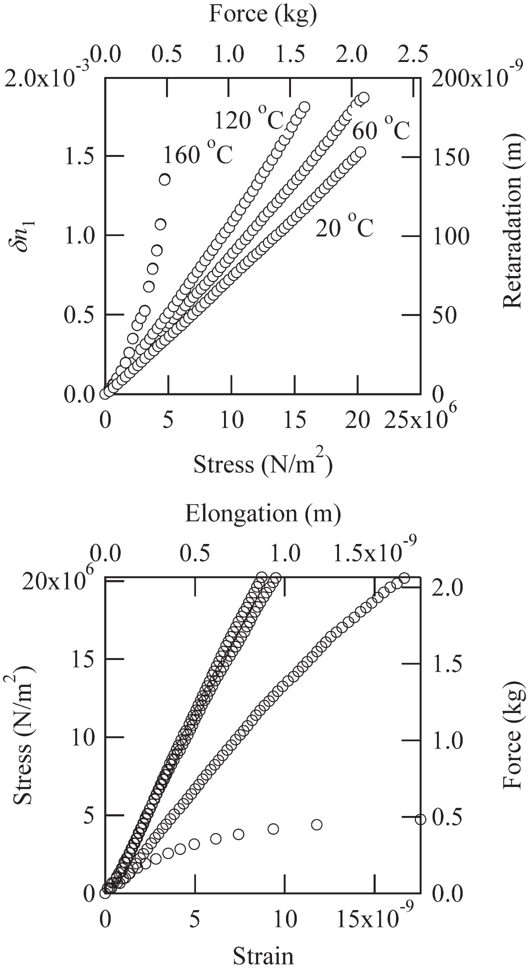


Figure 3.
Plots of induced birefringence δn_1 against stress (upper figure) and stress-strain curves (lower figure) for polycarbonate film.

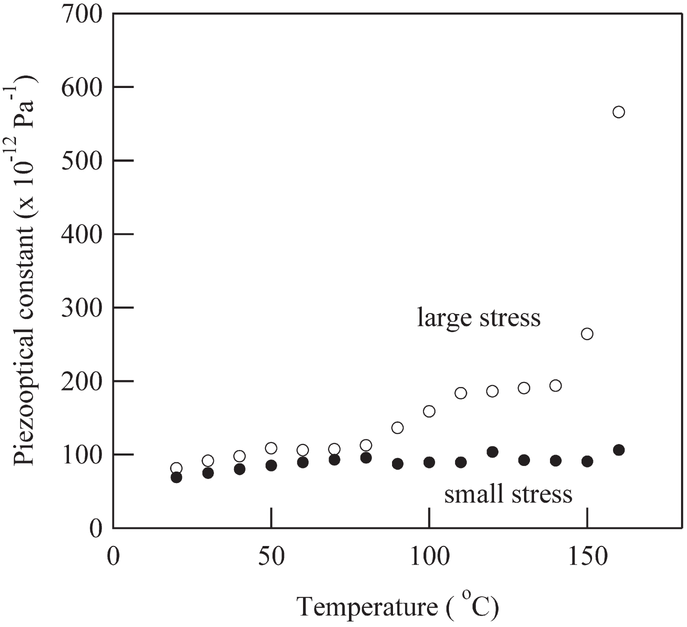


Figure 4.
Temperature dependence of piezooptical constant π_{31} of polycarbonate film.

evaluate π_{31} as a physical constant. Figure 4 shows the temperature dependence of π_{31} of PC film measured using our experimental system. These experimental results indicate that, in a conventional method such as the Senarmon method [6, 7], which must apply a large force to measure the π_{31} of a polymer film, π_{31} measured is not obtained as a physical constant. π_{31} obtained from a large stress is not generally accepted because the measurement conditions under a large stress satisfy the necessary conditions of photoelastic measurement. In the other words, π_{31} obtained from a small stress is very different from that obtained from a large stress. Examples of measurements for cellulose triacetate and PC films are shown in Table I. Furthermore, we obtained a small piezooptical constant of $0.12 \times 10^{-12} \text{Pa}^{-1}$ for a cycloolefin film used for LCDs, using our new measurement system. This value is very small. If a small change in retardation and stress under the application of a small strain had not been detectable simultaneously using our system, we would not have obtained such a small piezooptical constant. We emphasize here that it is impossible to measure such a small piezooptical constant of polymer films using the conventional measuring system on the basis of the Senarmon method.[6, 7]

Table I.
Piezooptical constants (small stress).

Sample	Width (mm)	Thickness (mm)	Piezooptical constant $\pi_{31}(\times 10^{-12}\ \text{Pa}^{-1})$	
			Average	Error range
Polycarbonate film	6.22	0.127	78.38	±1.92
Cellulose triacetate film	6.10	0.080	11.30	±0.21
Cycloolefin film	6.12	0.078	0.12	±0.11

Summary

We developed a new system for measuring the small piezooptical constant of a polymer thin film. It was possible to measure the birefringence and principal axis direction of a polymer film within 0.1 s. We obtained a small piezooptical constant of $0.12 \times 10^{-12} \mathrm{Pa}^{-1}$ for a cycloolefin film used for LCDs, using our new measurement system. This value was very small. If a small retardation had not been detectable using our system, we would not have obtained such a small piezooptical constant. The piezooptical constant obtained here is a measurable physical constant because the minute retardation due to induced birefringence caused by the applied stress was measured at high accuracy.

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