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Notes

Optical Properties of Oriented Polymer/Dye Polarizers. 2. Ultimate Properties

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Introduction

Polymeric sheet polarizers are widely used in applications such as liquid crystalline displays.^{1–4} These polarizers are manufactured from oriented sheets of semicrystalline polymers containing dichroic dyes.^{5–8} Orientation of the host polymer is introduced by solid-state drawing at temperatures close to, but below, the melting temperature of the polymer. During drawing, the dichroic dyes orient, and consequently, anisotropic absorption of light in the visible wavelength range is generated. This results in the typical characteristics of a polarizer, i.e., two crossed polarizers hardly transmit light whereas two parallel polarizers are highly transparent. In part 1 of this series, a theoretical model was presented to describe the optical performance of oriented polymer/dye polarizers.⁹ The model was used to describe the optical performance of polymeric sheet polarizers in terms of their polarizing efficiencies (PE) and single piece transmittances (T_{sp}).^{6,9} In this study, this model is used to estimate the ultimate optical properties of oriented polymer/dye polarizers with respect to polarizing efficiency and single piece transmittance. Moreover, the theoretical predictions are compared with experimental data on polymer/dye polarizers based on drawn poly(vinyl alcohol) and polypropylene.

Theoretical Section

In this section, the theoretical model is briefly discussed. A more detailed description of the model can be found elsewhere.⁹ In the model, it is assumed that upon (uniaxial) solid-state drawing the orientation of both the host polymer and the dichroic dye can be described using the pseudo-affine deformation scheme (eq 1).^{10,11} In eq 1, λ represents the draw ratio and θ

$$\langle \cos^2 \theta \rangle_{\text{polymer}} = \frac{\lambda^3}{\lambda^3 - 1} - \frac{\lambda^3}{\sqrt{(\lambda^3 - 1)^2}} \arctan \sqrt{(\lambda^3 - 1)} = \langle \cos^2 \theta \rangle_{\text{dye}} \quad (1)$$

the angle between a statistical chain segment and the direction of uniaxial deformation. Furthermore, it is assumed that the drawn guest–host system consists of

an aggregate of optically anisotropic elements which orient according to eq 1.¹² Each element is considered transversally isotropic and the properties of an optically anisotropic element are described with an extinction coefficient parallel (ϵ_{\parallel}) and perpendicular (ϵ_{\perp}) to the axis of the optical element. The macroscopic extinction coefficients parallel (E_{\parallel}) and perpendicular (E_{\perp}) to the orientation direction of the guest–host system are calculated using a transformation of coordinate systems from the microscopic frame to the laboratory frame, followed by an averaging procedure (eqs 2 and 3):¹²

$$E_{\parallel} = \langle \sin^2 \theta \rangle \epsilon_{\perp} + \langle \cos^2 \theta \rangle \epsilon_{\parallel} \quad (2)$$

$$E_{\perp} = \frac{1}{2} (\langle \cos^2 \theta \rangle + 1) \epsilon_{\perp} + \frac{1}{2} \langle \sin^2 \theta \rangle \epsilon_{\parallel} \quad (3)$$

Combining eqs 2 and 3 with eq 1 directly results in relationships between the macroscopic draw ratio (λ) and the macroscopic extinction coefficients. The absorbances parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the direction of draw are calculated using the Lambert–Beer law (eqs 4 and 5).¹³ In eqs 4 and 5, c and d are

$$A_{\parallel} = E_{\parallel} cd \quad (4)$$

$$A_{\perp} = E_{\perp} cd \quad (5)$$

respectively the concentration of the dichroic dye (mol/L) and the film thickness (cm). From the absorbances, the transmissions parallel (T_{\parallel}) and perpendicular (T_{\perp}) to the orientation direction are calculated ($T = 10^{-A}$). Subsequently, the polarizing efficiency and single piece transmittance are calculated using eqs 6 and 7.⁶

$$PE = (T_{\perp} - T_{\parallel}) / (T_{\perp} + T_{\parallel}) \quad (6)$$

$$T_{sp} = \frac{1}{2} (T_{\parallel} + T_{\perp}) \quad (7)$$

Experimental Section

The isotactic polypropylene (i-PP) used in this study was Stamyilan 14M10 (DSM, Geleen, The Netherlands; MFI = 2.0 dg/min). The dichroic dye was a triazo dye (BASF/Germany) with a melting temperature of 124 °C, and the chemical structure is shown in Figure 1. A mixture of polypropylene

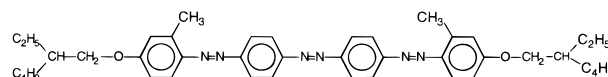


Figure 1. Chemical structure of triazo dye.

containing 0.25% (w/w) triazo dye was fed into a twin-screw extruder. A film was extruded; tapes were cut from these films (30 × 15 × 0.33 mm) and subsequently drawn on thermostatically controlled hot-shoes. The tapes were pre-drawn (λ_1) at 135 °C and subsequently post-drawn at 150 °C (λ_2). The draw ratio was determined by measuring the displacement of ink marks.

The drawn tapes were coated with a thin layer of mineral oil (Aldrich) to reduce the surface scattering of the films. Subsequently, the films were sandwiched between two glass slides.⁸

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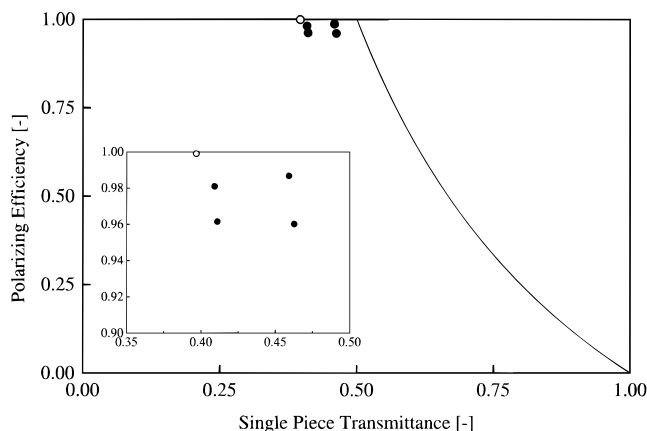


Figure 2. Polarizing efficiency as a function of single piece transmittance: (—) theory, infinite draw ratio ($\lambda = \infty$) and infinite anisotropy of the dye ($\epsilon_{\parallel}/\epsilon_{\perp} = \infty$); (●) i-PP/triazo dye (460 nm); (○) PVAL/iodine (460 nm).

The optical anisotropy of the oriented i-PP/dye tapes was analyzed with a double-beam UV-Vis spectrometer in the wavelength range 400–600 nm (Perkin-Elmer Lambda 900). A special procedure was used to determine the optical performance of the drawn tapes.^{6,14} This specific procedure has several advantages: (i) the polarizing efficiency and single piece transmittance can be determined without the use of an auxiliary polarizer, and (ii) the measurements are corrected for instrument polarization and reflections at the air/glass interfaces. Basically four transmittances were measured as a function of wavelength: no polarizer in the measuring beam, only glass slides (T_0); coated polarizer in the measuring beam positioned horizontally (T_h); respectively vertically (T_v); and finally, two crossed polarizers in the measuring beam (T_{hv}). The two principal transmittances (T_{\parallel} and T_{\perp}), necessary for the calculation of the polarizing efficiency and single piece transmittance (eqs 6 and 7) can be derived using eqs 8 and 9:¹⁵

$$T_{\parallel} = \frac{T_h + T_v}{2T_{hv}} \left[1 - \sqrt{1 - \frac{4T_0 T_{hv}}{(T_h + T_v)^2}} \right] \quad (8)$$

$$T_{\perp} = \frac{T_h + T_v}{2T_{hv}} \left[1 + \sqrt{1 - \frac{4T_0 T_{hv}}{(T_h + T_v)^2}} \right] \quad (9)$$

Results

In Figure 2, the ultimate properties of oriented polymer/dye polarizers are plotted in terms of their polarizing efficiency and single piece transmittance. The ultimate properties are calculated for an infinite draw ratio ($\lambda = \infty$) and infinite anisotropy of the dichroic dye ($\epsilon_{\parallel}/\epsilon_{\perp} = \infty$). The drawn curve is obtained by systematically varying the dye concentration (c) and/or the film thickness (d), assuming, to a first approximation, Lambert-Beers law to hold at high absorbances in the theoretical model.¹⁶

In Figure 2, the theoretical predictions are compared with experimental data on a commercial poly(vinyl alcohol)/iodine polarizer. The polarizing efficiency of the poly(vinyl alcohol) polarizer reaches almost full contrast ($PE \approx 1$); i.e., no light passes two crossed polarizers. However, the single piece transmittance of the poly(vinyl alcohol) polarizer is rather low in comparison to the theoretical limit ($T_{sp} < 0.40$). Experimental data on i-PP/dye polarizers are also shown in Figure 2. The polarizing efficiency of these polarizer is less than the commercial poly(vinyl alcohol) polarizers. However, despite the scatter in experimental data, the single piece

transmittance of these polarizers is systematically enhanced compared to their poly(vinyl alcohol) counterparts.

Discussion

The maximum attainable draw ratio of poly(vinyl alcohol) films is rather low ($\lambda < 5$) due to intermolecular interactions (hydrogen bonds) which restrict the unfolding of lamellas upon solid-state drawing.^{17–19} In polyolefins, such as isotactic polypropylene, strong intermolecular interactions are absent and high draw ratios (> 10) can be obtained. The experimental results depicted in Figure 2 indicate that this enhanced drawability results in efficient orientation of the guest molecules. The polypropylene/dichroic dye polarizers possess an improved balance between polarizing efficiency and single piece transmittance in comparison to the conventional poly(vinyl alcohol)/iodine polarizers. The dye molecule used in this study is a linear triazo dye possessing a high aspect ratio (Figure 1). The combination of this highly anisotropic dichroic dye and the highly drawable i-pp results in polarizers with an optical performance close to the theoretical limit set at infinite draw ratio and infinite dye anisotropy. Moreover, these polarizers have some additional advantages in comparison to poly(vinyl alcohol)-based systems with respect to temperature and/or humidity resistance.²⁰ This improved resistance to rough environments is a potential advantage in, for instance, automotive (i.e., dashboard) applications of liquid crystalline displays.

A few critical remarks with respect to the results in this study are appropriate. The polarizing efficiency and single piece transmittance of the polarizers were measured at the absorption maximum of the dye. A single dye was used, and consequently, the polarizers are effective only in a rather narrow region of the visible wavelength range. Moreover, producing so-called neutral grey polypropylene-based polarizers, which cover the entire visible wavelength range, is problematic because of the poor compatibility of most dichroic dyes with apolar host polymers.

Conclusions

A theoretical model was used to predict the ultimate optical properties of oriented polymer/dye polarizers with respect to polarizing efficiency and single piece transmittance. In the calculations, it is assumed that both the host polymer and the dichroic dye are perfectly oriented. The theoretical predictions are compared with experimental data on commercial poly(vinyl alcohol)-based polarizers and with polarizers based on polypropylene/dye systems. It is shown that the enhanced drawability of the latter system results in polarizers with an improved performance with respect to polarizing efficiency and single piece transmittance. Moreover, the performance of these polarizers closely approaches the theoretical ultimate properties.

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- (15) For the exact derivation of eqs 8 and 9, the reader is referred to page 10-78 in ref 6.
- (16) Application of the Lambert-Beers law will result in errors at high absorbances, in the order of $A = 2$. Therefore, the error in the predictions of the PE and single piece transmittance (T_{sp}) will be mainly due to errors in the parallel absorbance ($A_{||}$) which can attain high values at high draw ratios combined with high dichroic ratios and high dye concentrations. From eqs 6 and 7, it follows that

$$\left| \frac{\delta PE}{PE} \right| = \frac{2 \times 10^{(A_{||} + A_{\perp})} \ln 10}{10^{2A_{||}} - 10^{2A_{\perp}}} |\delta A_{||}| \approx 2 \ln 10 \frac{A_{||}}{10^{A_{||}}} \left| \frac{\delta A_{||}}{A_{||}} \right| \quad (10)$$

$$\left| \frac{\delta T_{sp}}{T_{sp}} \right| = \frac{\ln 10 A_{||} 10^{A_{\perp}}}{10^{A_{||}}} \left| \frac{\delta A_{||}}{A_{||}} \right| \approx \ln 10 \frac{A_{||}}{10^{0.9A_{||}}} \left| \frac{\delta A_{||}}{A_{||}} \right| \quad (11)$$

- assuming that $A_{\perp} \approx 0.1A_{||}$. So, for example, at an absorbance of $A_{||} = 2$, the relative error in the polarizing efficiency is already 10 times smaller than the relative error in the parallel absorbance. The same holds for the single-piece transmittance. In other words, at high absorbances, the PE and T_{sp} are mainly determined by the low perpendicular absorbance A_{\perp} for which the Lambert-Beer law does apply.
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