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Polarized coloration of stretched poly(vinyl alcohol) films by heat treatment

Y. YAMAMOTO, S. TAGAWA
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
E-mail: y-yama@sanken.osaka-u.ac.jp

A commercial polarizer consisting of stretched poly(vinyl alcohol) (PVA) films contains iodine aligned along the oriented polymer molecules. The present study is the first attempt to prepare a polarizer by the thermal degradation of the polymer itself. Since the heat treatment of PVA films results in coloration by the formation of conjugated double bonds on the polymer backbone [1–5], the stretching of the films is expected to be effective for the polarized coloration. The color of the heated films through a polarizer changed between pale brown and black by rotating the polarizer. Absorption spectra of the colored films were measured with the polarizer placed in front of the samples. Dependence of absorption intensity on the direction of the stretching of the films and on the angle of the polarizer is described.

PVA (Wako Chemicals; completely hydrolyzed; average degree of polymerization, 400–600) was dissolved in distilled water without further purification. Self-supported PVA films were prepared from the aqueous solution (3 wt%) by the solution casting method. The weight of the 40 mm square film was 96 mg, corresponding to a thickness of 60 μm by taking the density of the film as unity. The film was stretched in warm steam for the width of the film to be reduced approximately to one-half its initial width. Two rectangular samples, approximately 30 mm long and 6 mm wide, were prepared to be vertically and horizontally stretched. The film was sealed under vacuum in a Pyrex glass tube having a branch. While the sample was heated in an electric furnace, the branch was cooled with liquid nitrogen to trap volatile products, largely consisting of water; the coloration was enhanced by removing the decomposition products. Absorption spectra of the films were measured by using Shimadzu UV-3100PC scanning spectrophotometer. The polarizer of Shimadzu Simple Polarimeter (LP-1) was used to examine the polarization of the thermal coloration.

The stretched films were colored upon heating at 160 °C for 2 h. Color change observed through the polarizer demonstrates that the heat treatment results in a polarized coloration. In order to reveal the polarization, the absorption spectra of the films were measured with the polarizer placed in front of the samples. Fig. 1 shows the absorption spectra of the polarizer alone and the vertically stretched film with the polarizer placed in front of it. The wavelength range of the spectra was limited to be above 400 nm because of poor transmission of the polarizer in the UV range. The absorption spectra of the polarizer (curves a and b) were measured at the angles giving the minimum and maximum absorption intensities. The change in absorption intensity of the polarizer with its angle is due to the effect of the diffraction grating of the spectrophotometer; the analyzing light is polarized by the diffraction grating to some extent. The minimum and maximum absorption intensities were attained at right angles of the polarizer to each other. The angles giving the minimum and maximum absorption intensities are named vertical and horizontal angles, respectively. The absorption spectra of the vertically stretched film (curves c and d) were measured through the polarizer at the vertical and horizontal angles after the heat treatment. These are the superposition of the absorption spectra of the colored film and the polarizer. However, it is clear that the net absorption intensity of the vertically stretched film is larger at the horizontal angle than at the vertical angle of the polarizer, since the difference in absorption intensity is much larger for the films (difference between curves c and d) than for the polarizer (difference between curves a and b).

Fig. 2 shows the difference spectra between the vertically and horizontally stretched films and the polarizer at the vertical and horizontal angles. The spectra show the net absorption of the polarized light by the colored films. The absorption spectrum of the vertically stretched film with the polarizer at the vertical angle (curve a) is quite similar to that of the horizontally stretched film with the polarizer at

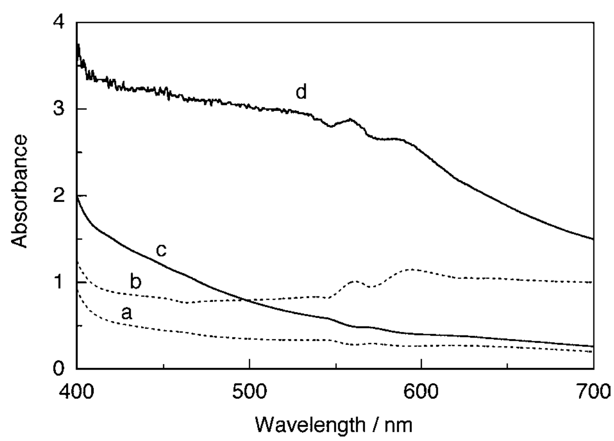

Figure 1 Absorption spectra of the polarizer alone (dotted lines) at the (a) vertical and (b) horizontal orientations and of the vertically stretched PVA film with the polarizer (solid lines) at the (c) vertical and (d) horizontal orientations; the film was heated at 160 °C for 2 h.

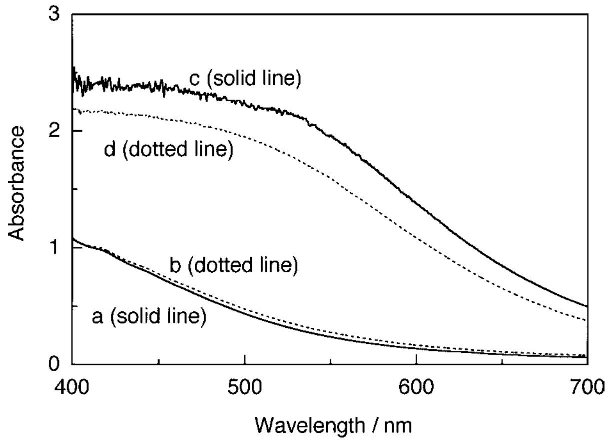

Figure 2 Difference absorption spectra of the colored PVA films and the polarizer: (a) (solid line), the vertically stretched film and the polarizer vertical, (b) (dotted line), the horizontally stretched film and the polarizer horizontal, (c) (solid line), the vertically stretched film and the polarizer horizontal, and (d) (dotted line), the horizontally stretched film and the polarizer vertical.

the horizontal angle (curve b). Similarly, the large absorption of the vertically stretched film at the horizontal angle (curve c) is close to that of the horizontally stretched film at the vertical angle (curve d). Thus, the thermal coloration of the vertically and horizontally stretched films is shown to be similar, except the directions of the polarization planes are right angles to each other. This method can be applied to other thermally colored vinyl polymers such as poly(vinyl acetate) and poly(vinyl chloride) for the preparation of polarizers.

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