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Influence of UV and Gamma radiations on the induced birefringence of stretched poly(vinyl) alcohol foils ☆

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HIGHLIGHTS

- Contact angle depends on solvent nature and on irradiation time.
- Induced birefringence increases with stretching ratio of PVA foils.
- Induced birefringence decreases due to the UV irradiation.
- Phenomena caused by Gamma radiation influence the induced birefringence.

ARTICLE INFO

ABSTRACT

The aim of our paper is to evidence the influence of Gamma and UV radiations on the induced birefringence of poly(vinyl alcohol) stretched foils. Thin foils of PVA were prepared and dried without modifying their surfaces. The polymeric foils were irradiated from 15 min to 6 h using UV and Gamma radiations. The induced by stretching under heating birefringence of PVA films was measured at λ = 589.3 nm with a Babinet Compensator. Physico-chemical processes (photo stabilization, photo degradation, oxidation) induced by irradiation of polymer matrix influence both the stretching degree and the anisotropy of etired foils. An increase of birefringence versus the stretching ratio of the PVA foils was evidenced for all studied samples. The dependence of the birefringence on the exposure time, stretching ratio and nature of radiation was also confirmed.

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1. Introduction

The deliberately exposure of a product or material to radiations is made in order to conserve, modify or improve its characteristics [1,2]. The amount of radiation energy absorbed by material depends on its mass and composition, and on the exposure time [3]. For each type of material, a certain quantity of radiation energy is required to comprehend the desired effect in the product; the exact value is determined through research [4].

Due to its transparency, easy of processing and low costs, PVA is an optical polymer widely used as material for various optical devices [5], and has a preferred role in obtaining different biomedical materials [6,7]. The PVA films are polarizing materials for the Liquid Crystal Display (LCD). The PVA foils are anisotropic layers which increase their anisotropy in the stretching process [8–10]. The intrinsic anisotropy is caused by partial orientation of the chain units [11]. A polymer material is macroscopically isotropic when its chains are randomly oriented and it becomes birefringent when the polymer chains are oriented, due to their intrinsic optical anisotropy. This type of birefringence is called orientation birefringence. When the polymer foils are stretched, a supplementary induced birefringence is added to the initial one [12].

An evaluation of optical characteristics by measuring the birefringence is important, since it is directly related to display qualities such as angle of visibility, contrast, and color tone reproducibility [13]. The PVA chemical structure is suggested in Fig. 1.

Poly(vinyl) alcohol (PVA) foils were exposed to UV and Gamma radiations (high-energy radiation). The polymer-radiation interactions can induce excitation and ionization processes [14]. The electronic excitation or removal of the valence electrons (ionization) can result in the formation of free radicals that may readily cross-link the polymer chains thereby increasing the molecular weight, hardness, and wear resistance [15]. Free radicals resulting
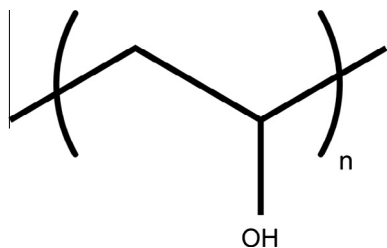
Fig. 1. Chemical structure of poly(vinyl) alcohol (PVA).

from cleavage of a chemical bond are species having an unpaired electron [16]. When oxygen is present, it reacts very rapidly with radicals produced by irradiation. The changes in chemical and physical properties of polymers [17,18] can influence the asymmetry of their molecular structures in which the birefringence of polymers derives from.

The main goal of this paper is to search the effects of Gamma and UV radiations on the induced birefringence of PVA stretched foils with comparable thickness.

The experimental results about the induced birefringence of stretched PVA films irradiated by UV and Gamma radiations can be used in fundamental research on the optical properties of PVA foils, which are important in order to obtain new retarders and polarizers [9–11].

2. Materials and methods

Poly (vinyl) alcohol (hydrolyzed 99%, with average Mw = 22,000) were obtained from Merck – Germany and used as received. 10 wt.% PVA solutions were prepared by dissolving PVA in 70 °C distilled water with stirring for 6 h. The mixed solution was outgased for 8–12 min at 10–15 torr. Then it was cast on a glass plate (220 × 240mm^2). The films were dried at low pressure (1–2 torr), for 48 h.

The UV irradiation of the PVA films was carried out by means of a middle-pressure mercury lamp, HQE-40 type, for 15, 45, 90, 180 and 360 min at a distance of 20 cm in the presence of air, at room temperature. PVA films with the same thickness were irradiated with a Gamma source ^{137}Cs, in the same experimental conditions as in the UV irradiation case.

The contact angles of the samples for different liquids were evaluated with KSV CAM 101 (Instruments Ltd., US), using the sessile drop technique. The surface polarity and the surface free of hydration of the studied films were calculated. The thickness of the foils was measured with a micrometer (accuracy ±0.5 μm). The birefringence of polymer foils was evaluated using a Babinet Compensator. The stretching temperature was 42–45 °C. The temperature was kept at this lower value in order to eliminate the effects of heat.

The birefringence of the stretched polymeric foils is the difference between the two main refractive indices being expressed by:

$$\Delta n(\lambda) = n_e(\lambda) - n_o(\lambda) \qquad (1)$$

where $n_e(\lambda)$ is the refractive index of the film for linearly polarized radiation having the electric field intensity parallel to the stretching direction, and $n_o(\lambda)$ the refractive index of the film for linearly polarized radiation having the electric field intensity perpendicular to the stretching direction [19].

The main refractive indices (extraordinary, $n_e(\lambda)$ and ordinary, $n_o(\lambda)$) of the stretched polymer foils are usually different. The birefringence of the stretched polymer foils can be considered as a measure of the order degree of the polymer chains in the sample [12]. The stretching degree was evaluated by the ratio of the semi

axes of an ellipse in which a circle drown on the polymer foil degenerates. The stretching ratio has been calculated with the formula (2):

$$\gamma = a/b \qquad (2)$$

where a is the length of the large semi-axis and b is the length of the small semi-axis of the ellipse which results, after stretching, from a control circle drawn upon the film.

The experimental design of the device devoted to birefringence measurement with a Babinet Compensator is given in Fig. 2.

Two identical polarizers, P and A are used in this device. Light does not pass through the crossed polarizers. The PVA stretched foil is an anisotropic layer (AL) introduced between the crossed polarizers, which changes the polarization state. Consequently, light passes through the analyzer (A). A Babinet Compensator (BC) is introduced into device between thin film (AL) and analyzer (A). It will compensate the pathway introduced by the film and the illumination in the median plane will be null.

BC consists in two anisotropy prisms with optical axis perpendicular one to another. For equal thicknesses of the two prisms, the pathway difference induced by BC is null for all light components. When the thickness h_1 and h_2 are different the pathway depends on the light spectral composition. There are more positions for which the pathway is a multiple of the wavelength of the radiation when the BC is illuminated by monochromatic radiation. These positions, corresponding to interference maxima satisfy relation (3):

$$2\pi/\lambda(n_e - n_o)(h_1 - h_2) = 2k\pi; \ k = 0, 1, 2, \ldots \qquad (3)$$

In visible range the pathway is null for all radiations only when light passes by equal thicknesses of the two prisms $h_1 = h_2$, at zero position of the compensator (in the mediator plane of the compensator).

Initially, the BC was standardized in a monochromatic radiation (the yellow radiation of a Na lamp was used, with $\lambda = 589.3$ nm). The differences of two prisms thickness for which the relation (3) is satisfied are evaluated and correlated with the interference order of the radiations in the standardization operation. The standardization graph at $\lambda = 589.3$ nm is given in Fig. 3, k is the order of interference (order of channel in the visual field of the compensator).

3. Results and discussion

3.1. Characterization of UV and Gamma irradiated PVA foils

The surface free energy of the PVA foils is determined from contact angle measurements, using equations of the molecular theory of wetting. The contact angles should be measured with a liquid of surface tension higher than the anticipated solid surface tension to obtain an accurate result [20]. Surface polarity was evaluated using
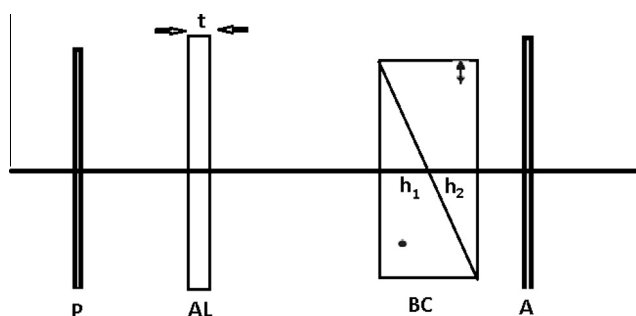

Fig. 2. Experimental set-up for determining the birefringence with a Babinet Compensator.