

Birefringence of Etired Poly (Vinyl Alcohol) (PVA) Foils

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Thin foils of poly (vinyl alcohol) (PVA) with different thickness were prepared and dried without modifying their separation surfaces. The induced by stretching under heating birefringence of PVA films was measured under with a Babinet Compensator. An increase of birefringence versus the stretching degree of the PVA foils was evidenced for all studied samples. The dependence of the birefringence on the films thickness was evidenced in this paper.

Keywords: birefringence, Babinet Compensator, stretching degree

Poly (vinyl alcohol) (PVA) [1] is an important material due to its large-scale applications, such as biomaterials, biosensors, electrochemical sensors, membranes with selective permittivity [2,3], viscous medium for controlling the crystallization process of salts, for controlled drug delivery or catalytic systems, etc.

PVA is a white and granular polymer. PVA is soluble in hot water but it is insoluble in cold water and common organic solvents. Poly (vinyl alcohol) often is prepared in a water solution. The viscosity of PVA water solutions varies with concentration and temperature [4]. The films cast from water solutions are transparent having high tensile strength and tear resistance. The PVA films provide a unique combination of properties. The films have water solubility, resistance to oils, grease or solvents and impermeability to most gases.

This polymer is used for biomedical applications in drug delivery, tissue replacement [5], for improving and correction of human organs functionality, immunological kits [6], and for cancer therapy due to their high embolism effect [7].

PVA is an optical polymer widely used as material for various optical devices, for example, lenses, or optical disks, due to their ease of processing, high transparency, and low cost [8].

The PVA films are polarizing material for the LCD (Liquid Crystal Display). An evaluation of optical characteristics by the observation of birefringence is important, since it is directly related to display qualities such as angle of visibility, contrast, and color tone reproducibility [9].

The birefringence of polymers derives from the asymmetry of their molecular structures. Most polymers have intrinsic optical anisotropy caused by different orientation of the chain units [10] derived from asymmetry of their chemical structures. A polymer material becomes macroscopically isotropic when its chains are randomly oriented. A polymer material becomes birefringent when its 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.

The main refractive indices (extraordinary, n_e and ordinary, n_o) of the polymer foils measured in linearly polarized light with its electric field intensity oriented in parallel and perpendicular on the stretching direction are usually different.

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

$$\Delta n(\lambda) = n(\lambda) - n_o(\lambda) \quad (1)$$

where:

$n(\lambda)$ is the refractive index of the film for radiation having the electric field direction parallel to the stretching direction ;

$n_o(\lambda)$ - the refractive index of the film for radiation having the electric field direction perpendicular to the stretching direction [11].

The birefringence of the stretched polymer foils could be considered a measure of the order degree of the polymer chains in the sample.

Experimental part

The polymer foils were prepared using PVA with the number of molecular weight

$M_n = 65\ 000-87\ 000$, 20% solution in distilled and deionized water (Loba Feinchemie-Austria). A viscous and transparent solution of PVA has been obtained after the mixture was stirred for 5 h at a temperature for about 80-90° C. Then the solution was cast on a glass slide (220x240mm²) by means of doctor blade with a slit of 0.6 mm. The films were dried at low pressure 1-2 mm Hg for 48 h.

The thickness of the foils was measured with a micrometer.

The device devoted to birefringence measurement with a Babinet Compensator is given in figure 1.

Initially, the Babinet Compensator must be standardized in a monochromatic radiation (the yellow radiation of a Na lamp was used in our experiment). The differences thickness of the two prisms of the compensator for which the monochromatic radiation keeps its polarization state are evaluated and correlated with the interference order of the radiations in the standardization operation. The standardization graph at $\lambda = 5893\text{\AA}$ is given in figure 2.

In figure 2, k is the order of interference (order of channel in the visual field of the compensator). For equal thicknesses of the two prisms, zero order is obtained.

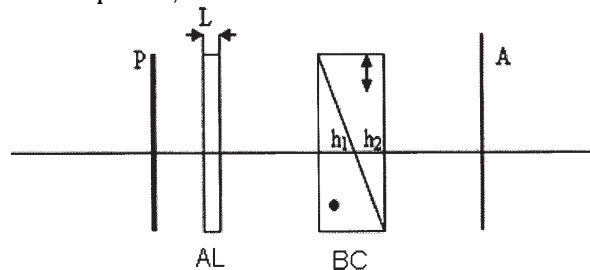


Fig. 1. Device for determining the birefringence by a Babinet Compensator

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Two identical polarizers, P and A are used in this device. Light does not pass through the crossed polarizers. When the anisotropic film is introduced between the crossed polarizers, the radiations which change their polarization state can pass through the device. If a Babinet Compensator is introduced into device, after the thin film, in a convenient position, it will compensate the pathway introduced by the film and the illumination in the median plane will be null.

There are more positions of the Babinet Compensator for which the pathway is a multiple of the wavelength of the radiation, when a monochromatic radiation is used. These positions satisfy relation:

$$\frac{2\pi}{\lambda} (n_e - n_o)(h_1 - h_2) = 2k\pi, \quad k = 0, 1, 2, \dots \quad (2)$$

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

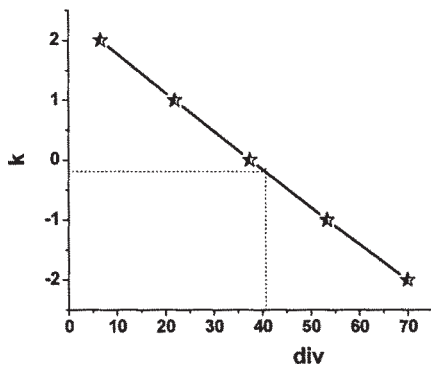


Fig. 2. The standardization graph at $\lambda=5893\text{\AA}$ for Babinet Compensator

Results and discussion

The degree of stretching was evaluated by the ratio of the semi axes of an ellipse in which a circle drawn on the polymer foil degenerates. The stretching degree has been calculated with the formula:

$$\gamma = \frac{a}{b} \quad (3)$$

where:

a is the length of the large semiaxis;

b - the length of the small semiaxis of the ellipse which results, after stretching, from a control circle drawn upon the film.

The dependence of the induced birefringence on the degree of stretching for different thicknesses of the PVA foils is given in figure 3. From this figure it results the tendency of the birefringence to decrease with the increasing of the foils thickness.

For a given thickness, the birefringence tends to increase linearly with the degree of stretching, for the degrees of stretching smaller than 2.5. For the degrees of stretching bigger than 2.5, the slopes of the lines in figure 3 are smaller, proving saturation in the alignment of the polymer chains, for high degrees of stretching.

For the thicknesses higher than 2mm the process of the internal alignment of the polymer chains is more complex and the dependences for the degrees of stretching higher than 2.00 are not linear.

The variation of the birefringence computed for the foils of extreme thickness was estimated. The birefringence

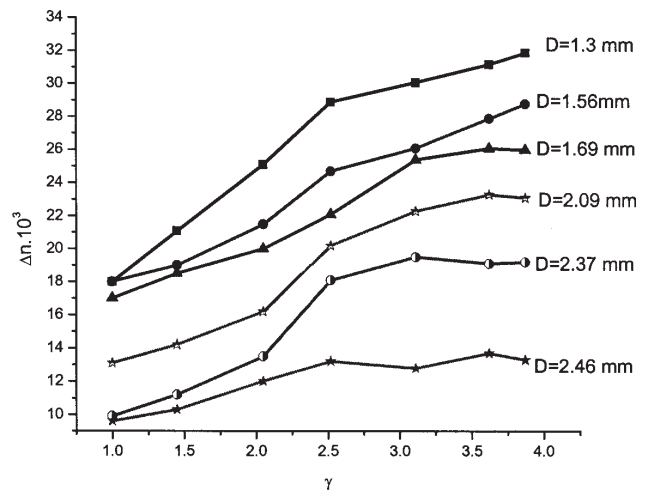


Fig. 3. Birefringence, $\Delta n(\lambda)$ versus stretching degree, for different thickness

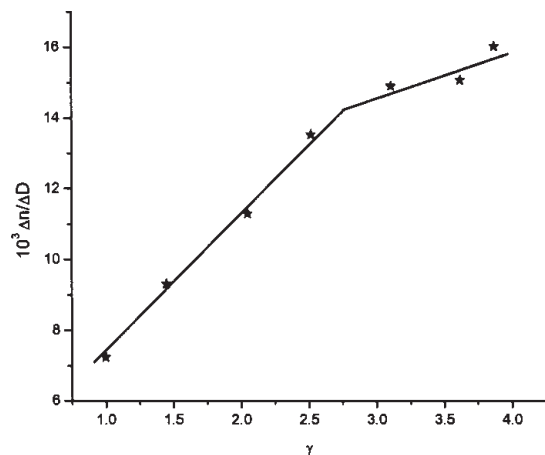


Fig. 4. Ratio $\Delta n/\Delta D$ versus stretching degree for PVA

reported to the unity thickness was estimated and correlated with the degree of stretching (fig. 4).

The graph from figure 4 illustrates the changes in the slopes of the linear dependence of the ratio $\Delta n/\Delta D$ versus the degree of the stretching.

The dependence of the birefringence, $\Delta n(\lambda)$ on the thickness *D* of the PVA foils, for different stretching degrees, γ , is given in figure 5. For the small degrees of stretching ($\gamma < 2.00$) the decrease of the birefringence is

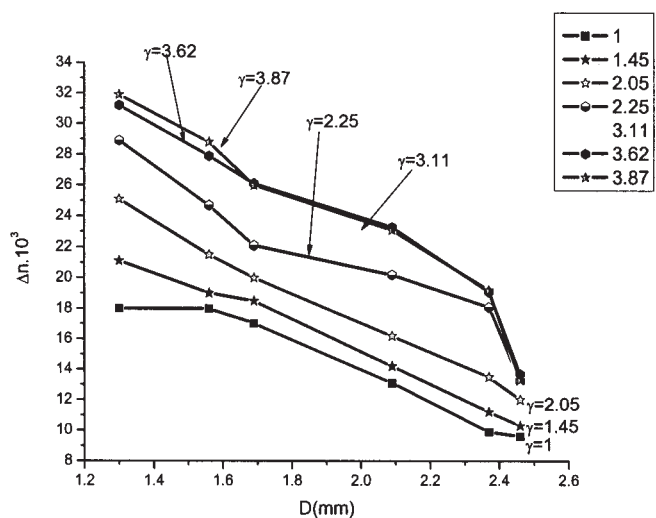


Fig.5. Birefringence, $\Delta n(\lambda)$ versus thickness, for different stretching degree

quite linear with the increase of the foil thickness. Translations between the polymer chains are possible for big thickness in the case of high degree of stretching.

The slopes of the lines in the plane $\Delta n(\lambda)$ versus D change their slopes. The irregular decrease of the birefringence with the thickness could be explained by the impossibility to determine a good alignment of the polymer chains in the case of foils with a large thickness.

Conclusions

An increase of birefringence by increasing the stretching degree of the polymeric foils was remarked, for the same film thickness.

A saturation of the birefringence at stretching degree over the value 2.5 was observed for all thickness of the studied foils.

For the same stretching degree the birefringence decreases with the foils thickness.

The results obtained in this paper demonstrate that the optical anisotropy is caused by orientation of the chain units in the thickness film, when it is stretched.

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