Research Article

Optical Properties of Polyvinyl Alcohol Films Modified with Silver Nanoparticles

Vladimir Agabekov,¹ Nadezhda Ivanova,¹ Viacheslav Dlugunovich,² and Igor Vostchula²

¹ Institute of Chemistry of New Materials, The National Academy of Sciences of Belarus, F. Skarina Street 36, 220141 Minsk, Belarus

² B. I. Stepanov Institute of Physics, The National Academy of Sciences of Belarus, Nezalezhnastsi Ave. 68, 220072 Minsk, Belarus

Correspondence should be addressed to Vladimir Agabekov, agabekov@ichnm.basnet.by

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Polyvinyl alcohol (PVA) films modified with Ag nanoparticles and orientated by single-axial tension do not possess dichroism at light passing as well as the film that is cross-linked under the action of bichromates and UV light. These films are double-ray refracting and behave themselves as phase plates that transform linearly polarized incident radiation to elliptically polarized one. The film of latter type has optical properties of reflective diffuse polarizer with polarizing ability ~ 0.8 in the range of observation angles from 20° to 80° .

1. Introduction

The influence of the addition of nanoparticles of various types on the properties of polymers is intensively investigated lately since introduction of even a small amount of nanoparticles to the polymeric matrix can strongly change mechanical, thermal, optic, and other properties of a material [1]. It is known that for manufacturing of polymer films with high light and thermal stability they are modified with silver nanoparticles [2, 3], and to improve moisture resistance of polymer matrices they are treated with strong oxidants that are cross-linked PVA molecules under the influence of ultraviolet irradiation [4].

PVA films modified with Ag nanoparticles may be used as linear film polarizers, compensative retarder films and diffusely scattering elements for creation and control of illumination background of liquid crystal displays (LCD) operating in twilight illumination and also in sunlight as well as in the devices of latent pattern identification.

We have developed polaroid films of transmissive, reflective [5, 6], and transreflective types, including those with extended temperature range of operation [7] for the near-IR [8] and UV [9] regions, as well as a new generation of circular and reflective linear polarizers with improved optical characteristics.

The purpose of this work is to examine the ability of PVA films modified with silver nanoparticles, to scatter incident linear polarized He-Ne laser light, as well as to determine the effect of processing conditions (uniaxial tension, cross-linking of the polymer matrix during irradiation by UV radiation in presence of bi-chromates) on scattering and polarizing properties of modified PVA films.

2. Experimental Procedure

The solution of PVA “Mowiol 28–99” of Hoechst Akiengesellschaft (Germany) (10 wt%) with characteristics presented in Table 1 was used to obtain PVA films.

Dosed amounts of modifier, solution AgNO_3 (2 wt%) and glycerin (2.3–2.8 wt%) as plasticizer and weak reducer that were dispersed by ultrasound from 30 min to a homogeneous consistence, were incorporated into a cooled solution of PVA to modify PVA films with Ag nanoparticles. After that watering solutions were applied on a degreased surface using a filler of a smearing type. Liquid films were dried in the drying chamber at $35 \pm 5^\circ\text{C}$ in solvent atmosphere during 1 day up to residual humidity 7–10%. Oxidation-reduction reaction of Ag^+ and glycerin with the formation of silver nanoparticles in colloid stage occurs inside the films at drying, and these nanoparticles give orange-brown color to

TABLE 1: Characteristics of polyvinyl alcohol.

PVA	Molecular weight	Polymerization degree	Content of acetate groups, %	Solubility, %	Transparency, %
Mowiol 28–99	145000	3300	0.6	99.9	94.6

FIGURE 1: Atomic force microscope surface images and profile of PVA films modified with Ag nanoparticles: (a) nonoriented film; (b) oriented and cross-linked PVA film.

the films. 60 nm thick modified films containing 0.6 wt % of silver nanoparticles, that had maximal optical density at the wave length 410–420 nm and particle size 10–20 nm (according to [10]), were chosen for studies. It has been pointed out in article [11] that the adsorption spectrum of silver nanoparticles in colloidal solution having one narrow and permitted (like in our case) peak, that is localized at $\lambda = 410$ nm, indicates the monodispersity and uniformity of separate silver nanoparticles of a spherical shape. The surface roughness of investigated films ranged from 10 to 20 nm (Figure 1(a)). The roughness of films surface considerable decreased to 3–10 nm after single-axial orientation with axial ratio 4 and cross-linking under the action of oxidizer-ammonium bichromate with following UV radiation (Figure 1(b)). The degree of cross-linking of PVA molecules in the film was controlled by UV spectra of reflectance (Fourier UV-spectrophotometer “Nicolet”-Protégé-460)—the disappearance of intensive strip 3340 cm^{-1} that is related to valent fluctuations of OH group.

Scattering properties of PVA films modified with Ag nanoparticles and polarization characteristics of reflected and transmitted radiation were investigated using laser goniphotometric Stokes polarimeter [12]. Radiation of He-Ne laser with $0.63\text{ }\mu\text{m}$ wavelength and 5 mm beam diameter was directed at an angle of $\sim 5^\circ$ to the film surface normal. Analogous lightning conditions are often realized in practical use of LCD. Radiation reflected by films was recorded at the observation angles (β) ranging from 5° to 80° and characteristics of radiation transmitted by a film were recorded at registration angle 175° to the surface normal. Solid

angle, where the radiation was registered, was $7.2 \cdot 10^{-3}$ sr, which conformed to angular resolution in the plane of incidence. The registration plane was situated horizontally and coincided with the incident plane. Incident radiation was polarized in the registration plane or cross-polarized.

Polarization characteristics of radiation as a degree of polarization (P), azimuth of polarization (φ), and polarization ellipticity (e) were determined on the basis of measured of Stokes parameters (I, P_1, P_2, P_3) of radiation reflected by investigated films [13]

$$\begin{aligned}
 P &= \frac{\sqrt{P_1^2 + P_2^2 + P_3^2}}{I}, \\
 e &= \frac{\sqrt{P_1^2 + P_2^2 + P_3^2} - \sqrt{P_1^2 + P_2^2}}{P_3}, \\
 \varphi &= \frac{1}{2} \arctan \frac{P_2}{P_1},
 \end{aligned} \tag{1}$$

where I is the total intensity of radiation reflected within the solid angle of the registration system, P_1 is the parameter that characterizes the advantage of horizontal polarization, P_2 is the parameter that characterizes the advantage of linear polarization with 45° azimuth, and P_3 is the parameter that characterizes the advantage of right-circular polarization. All Stokes parameters (I, P_1, P_2, P_3) have units of intensity and completely characterize the polarization state of radiant flux.

FIGURE 2: The dependence of bidirectional reflectance coefficient of PVA films modified by Ag nanoparticles on the angle of reflection: (a) only oriented film; (b) oriented and cross-linked film. Incident radiation is polarized: (1) in plane of incidence, (2) perpendicular to the plane of incidence.

Bidirectional reflectance $R(\alpha, \beta)$, transmittance $T(\alpha, \beta)$, and polarizing efficiency $q(\alpha, \beta)$ of investigated films were determined by the following equations:

$$\begin{aligned} R(\alpha, \beta) &= \frac{I_r}{I_0}, \\ T(\alpha, \beta) &= \frac{I_t}{I_0}, \\ q(\alpha, \beta) &= \frac{R_{\max} - R_{\min}}{R_{\max} + R_{\min}}, \end{aligned} \quad (2)$$

where I_r , I_t , and I_0 are the intensities of reflected, transmitted, and incident radiation, respectively; α and β are the incident and registration angles; $R_{\max}$ and $R_{\min}$ are bidirectional reflectances of film illuminated with radiation linearly co- and cross-polarized to the film strain direction, respectively. Relative standard deviation of the measurement of bidirectional reflectance, transmittance, and degree of polarization did not exceed 0.05.

3. Results and Discussion

PVA films modified with Ag nanoparticles specularly reflect incident radiation (Figure 2).

Bidirectional specular reflectance coefficient of modified and oriented film in the direction of specular reflection is ~ 0.07 . With the increase of observation angle up to 15° R values sharply decrease and do not depend on the azimuth of polarization of the incident radiation (Figure 2(a)). During further increase of β , the values of bidirectional reflectance coefficients (R) of investigated film decrease substantially

slower and monotonously. Hence, reflection from the investigated film is diffuse at registration angle more than 15° . Besides that, difference in Fresnel reflectance of investigated material manifests its effect in diffusely reflected flux [14]. This shows that, at sounding with radiation that is polarized orthogonally to the plane of incidence, $R(\alpha, \beta)$ values of investigated samples are systematically higher than in case of illumination by copolarized laser radiation (Figure 2(a)).

For PVA film modified with Ag nanoparticles, oriented and cross-linked with oxidizers under UV radiation, the difference in reflectance coefficients for orthogonally linear polarized components of sounding radiation at observation angles increasing from 20° to 80° reaches one order of magnitude. This means that the given film is a reflecting linear polarizer with polarizing ability $q \approx 0.8$ in the range of observation angles from 20° to 80° (Figure 3) and angular distribution of reflected radiation close to a diffuse one (Figure 2(b)). At the same time its bidirectional reflection coefficients is on nearly two orders of magnitude higher than $R(\alpha, \beta)$ of just oriented PVA film (Figures 2(a) and 2(b), curve 1).

When comparing polarization characteristics of radiation, scattered by modified films, it can be seen that at observation angles from 5° to 40° the degree of polarization P of reflected radiation is equally high and is $0.8 \div 1.0$ for both the simply oriented film (Figure 4(a)) and the cross-linked film (Figure 4(b)) and does not depend on the azimuth of linearly polarized radiation.

The change of the degree of polarization of radiation scattered by modified PVA films at the reflected angles exceeding 40° depends on polarization azimuth of sounding radiation. Thus, if the film was illuminated with radiation

FIGURE 3: Polarizing efficiency of PVA films modified with Ag nanoparticles: (1) only oriented film; (2) oriented and cross-linked film.

that is polarized perpendicular to the plane of incidence, the degree of polarization of radiation scattered by it remains high—no, less than 0.8 at the increase of the reflected angle up to 80° (Figures 4(a) and 4(b)). High values of the degree of polarization of radiation, scattered by films over the whole range of observation angles (from 5° up to 80°), testify the preservation of polarization state of sounding radiation, which is polarized perpendicular to the plane of incidence. This is verified by the results of measurement of azimuth of polarization and ellipticity of radiation scattered by modified PVA films at mentioned sounding conditions. Indeed, the azimuths of polarization of scattered and sounding radiations coincide, and there is no elliptically polarized component in the scattered flux.

The degree of polarization of radiation scattered by investigated films illuminated with co-polarized radiation is monotonously decreased to 0.6 with the increase of reflected angle up to 80° (Figures 4(a) and 4(b)).

The results of measurement of bidirectional transmittance coefficients of investigated PVA films illuminated with radiation at $\alpha = 5^\circ$ linearly polarized in the plane of incidence ($T_{||}$) as well as in a plane that is orthogonal to it ($T_{\perp}$) and also with azimuth 45° (T_{45}) in relation to the direction of film stretching and polarization characteristics of transmitted radiation (degree of polarization, ellipticity, and azimuth of polarization) at registration angle of 175° are presented in Table 2.

It follows from the presented data that bidirectional transmittance coefficients of investigated modified PVA films are practically the same for orthogonally linear polarized radiation components. This indicates that there is no amplitude anisotropy for transmitted radiation in investigated films, and they are not linear polarizers. At the same time, investigated films possess phase anisotropy that occurs because of orientation of films by stretching and behaving themselves as phase plates.

The radiation that is linearly polarized at the angle of 45° to the film orientation direction is transformed in elliptically polarized radiation when transmitted through oriented

(a)

(b)

FIGURE 4: The dependence of the degree of polarization of radiation reflected by modified PVA films on reflection angle: (a) only oriented film; (b) oriented and cross-linked film; radiation is co-polarized (1) and cross-polarized (2).

modified PVA films. This phase anisotropy can be used for compensation of undesirable phase delay in radiation components that appear during passing of radiation through different elements of LCD.

4. Conclusions

PVA film modified with Ag nanoparticles (0.6 wt%) that is oriented and cross-linked under the action of oxidizers

TABLE 2: Optical parameters of modified PVA films and polarization characteristics of transmitted radiation at registration angle of 175° .

Type of treatment characteristics	Oriented PVA film	Oriented and cross-linked PVA film
$T_{\parallel}$	0.73	0.44
$T_{\perp}$	0.78	0.51
T_{45}	0.77	0.52
$P_{\parallel}$	0.99 ± 0.01	1.00 ± 0.01
$P_{\perp}$	0.97 ± 0.01	0.98 ± 0.01
P_{45}	0.96 ± 0.01	0.89 ± 0.01
$e_{\parallel}$	0.01 ± 0.01	0.01 ± 0.01
$e_{\perp}$	-0.01 ± 0.01	0.03 ± 0.02
e_{45}	0.02 ± 0.02	0.81 ± 0.04
$\varphi_{\parallel}$, degrees	-3.8 ± 0.03	1.4 ± 0.2
$\varphi_{\perp}$, degrees	88.0 ± 1.3	86.4 ± 0.2
φ_{45} , degrees	-28.9 ± 0.07	100.0 ± 1.0

and UV-radiation, can be used as reflective diffuse linear polarizer with polarizing ability ~ 0.8 in the range of observation angles from 20° to 80° .

It has been established that investigated films do not possess amplitude anisotropy (dichroism) when transmitting the light, but do possess phase anisotropy (birefringence) which depends on nanoparticles concentration and film thickness and they behave themselves as uniaxial phase plates that transform linearly polarized incident radiation into elliptically polarized radiation.

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