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Scattering and birefringence properties of polymeric films modified with nanoparticles of different nature

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Abstract. Scattering properties of directed polyvinyl alcohol films modified with titanium dioxide or silver nanoparticles and illuminated by a 0.63 μm linear polarized He-Ne laser radiation were investigated. Ability of the investigated nanomaterials to depolarize and scatter incident radiation and to form an illumination background close to diffuse scattering was studied.

Keywords: reflection, transmission, polarization, TiO_2, Ag nanoparticle, polyvinyl alcohol film.

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1. Introduction

Influence of addition of various type nanoparticles on properties of polymers is intensively investigated last decade, since introduction to the polymeric matrix even a small amount of nanoparticles can strongly change mechanical, thermal, optic and other properties of material [1]. It is interesting how addition of TiO_2 or silver nanoparticles changes scattering and polarizing properties of oriented birefringent polyvinyl alcohol (PVA) films.

In addition, there is information on modification of a polymeric film by silver nanoparticles with the purpose to manufacture a linear film polarizer with high climatic stability [2, 3], since the polarizer made of ordinary film is characterized by poor photo- and thermo-stability.

PVA films modified by TiO_2 and Ag nanoparticles may be applied as linear film polarizers, compensative retarder films and diffusely scattering elements for creation and control of illumination background of liquid crystal displays (LCD) operating at twilight illumination just in sunlight as well as in devices of latent pattern identification.

The goal of this work was to investigate ability of a polymeric PVA film modified with titanium dioxide or silver nanoparticles to scatter incident linear polarized radiation of He-Ne laser and form an illumination background close to diffuse scattering with the minimal power losses, as well as the investigation of the influence of treatment technology (unidirectional tension and cross-linked of polymer matrix by oxidation during UV irradiation) on scattering and polarizing properties of modified PVA films.

2. Experimental procedure

For manufacturing the polymeric matrix, the 10 % solution of PVA "Mowiol 28-99" of Hoechst Akiengesllschaft (Germany) was used. In the course of preparation of the PVA films modified with TiO_2 or Agnanoparticles in a water solution of PVA, loaded were dosed amounts of the modifier Iriodin 119 (pearl pigment of "Merck & Co., Inc." – mica particles look like a flakes with deposited TiO_2 nanoparticles) or 2 % solution of silver nitrate. Then the mixtures were dispersed in an ultrasonic dispersant for 30 min up to a homogeneous consistence. The compositions were spread on a degreased surface of smooth glasses by the greasing type spinning nozzle equipment. Liquid films were dried in the drying chamber at the temperature of 35±5 °C in solvent atmosphere within 1 day up to the residual humidity 7 to 10 %. As a result, the modified PVA films with the mass content of pearl pigment from 0.1 up to 1.0 % (mass content of TiO_2 nanoparticles from 0.04 up to 0.25 %, respectively) or 0.6 % of silver particles were obtained. The PVA films with different nanoparticles content were directed by strain with axial ratio 5.

Scattering properties of the PVA films modified with TiO_2 or Ag nanoparticles and polarization characteristics of the reflected and transmitted radiation were investigated with laser goniophotometricStokes polarimeter [5]. 0.63 µm wavelength He-Ne laser radiation with 5 mm beam diameter was directed at theangle of –5° to the film surface normal. Incidence of radiation close to normal is often realized in practical use of LCD. The radiation scattered by films within the range of angles from 5° up to 80° was recorded. Characteristics of the radiation transmitted by a film at the transmitting angle of 175° to the surface normal were recorded, too. The solid angle of the registration system that received scattered radiation was $7.2\cdot10^{-3}$ sr that conformed to the angular resolution in the plane of incidence of ~5°. The scattering plane was situated horizontally and coincided with the plane of incidence. The incident radiation was co- or cross-polarized relatively to the plane of incidence.

The polarization characteristics of radiation, namely: the degree of polarization (P), principle angle of polarization (φ), and polarization ellipticity (e), were determined on the basis of measurements of Stokes vector elements (I, P_1, P_2, P_3) for the radiation reflected by the investigated films [6].

The bidirectional reflectance R(α, β), transmittance T(α,β) and polarizance q(α, β) (characterizing the degree of polarization of reflected light when unpolarized light is incident) of the investigated films were determined by expressions:

$$R(\alpha,\beta)=\frac{I_r}{I_0} \tag{1}$$

$$T(\alpha,\beta)=\frac{I_t}{I_0} \tag{2}$$

$$q=\frac{R_{\max}-R_{\min}}{R_{\max}+R_{\min}} \tag{3}$$

where I_r, I_t, and I_0 are the intensities of reflected, transmitted and incident laser radiation; α and β are the incidence and scattering angles; R_{max} and R_{min} are the bidirectional reflectance of the film illuminated with radiation linearly co- and cross-polarized as to the film strain direction, respectively.

3. Results and discussion

Investigations have shown that the bidirectional reflectance of modified PVA films with TiO_2 content of 0.04 and 0.13 % as well as its changes with increasing the scattering angle is practically equal. With growth of the scattering angle β from 5 to 20°, the bidirectional reflectance of the investigated films is decreased and practically does not depend on the TiO_2 content. In further increasing of the scattering angle the bidirectional reflectance R(α, β) of the investigated films decreases essentially slower (see Fig. 1a), which indicates the noticeable diffuse component in the reflected flux. Usually, it is caused by scattering on a surface roughness and material volume heterogeneity.

Within the whole range of scattering angles from 5° to 80°, the bidirectional reflectance of modified PVA film with TiO_2 content of 0.25 % varies more smoothly than R(α, β) of PVA films with lower mass content of TiO_2 nanoparticles, which indicates more diffuse character of reflection (see Fig. 1b). For all the scattering angles, the bidirectional reflectance of modified PVA film with TiO_2 content of 0.25 % is equal for co- and cross-polarized radiation and is significantly higher (nearly two orders) than the bidirectional reflectance of PVA films with the lowest TiO_2content.

PVA films modified by Ag nanoparticles reflect the incident radiation more specular than the films modified with TiO_2 nanoparticles (see Fig. 1). The bidirectional specular reflectance of the directed but uncross-linked PVA film modified with Ag nanoparticles is ~0.07. With increasing the scattering angle up to 15°, the bidirectional reflectance of the investigated film sharply decreases indicating the specular reflection and does not depend on the azimuth of polarization of the incident radiation (see Fig. 1c). With further increasing the scattering angle, the bidirectional reflectance of the investigated film decreases much more slowly and rather steadily. Hence, reflection from the investigated film diffuses for the scattering angles over 15°. In addition, in the diffusely reflected flux a difference in the Fresnel reflection coefficients of the investigated material is appeared. Therefore, the bidirectional reflectance R(α, β) of the investigated films illuminated by cross-polarized radiation is systematically rather higher than in the case of illumination by co-polarized laser radiation (see Fig. 1c).

For the scattering angles within the range from 20 up to 80°, the difference in the bidirectional reflectance of a modified PVA film directed and cross-linked by oxidation with dichromate during UV irradiation reaches one order for orthogonal linearly polarized components of the incident radiation. Therefore, one may conclude that this film in this range of scattering angles is a reflective linear polarizer with the polarizance $q \sim 0.8$ (see Fig. 2) and with angular distribution of the reflected radiation close to the diffuse one (see Fig. 1d). The bidirectional reflectance of a modified PVA film directed and cross-linked by oxidation is nearly two orders higher than R(a, β) of the only directed PVA film.

It is interesting to know changes of the polarization characteristics of radiation reflected by this type of scatterers since LCD image visualization is based on polarization effects. Our measurements show that with increasing the scattering angle the trend of changing the degrees of polarization for radiation reflected by modified films with the TiO_2 content 0.04 and 0.13 % are equal, but differ from corresponding dependence for a PVA film with the TiO_2 content 0.25 % (see Figs 3a,b). Thus, the degree of polarization for radiation reflected by films containing 0.04 and 0.13 % of TiO_2

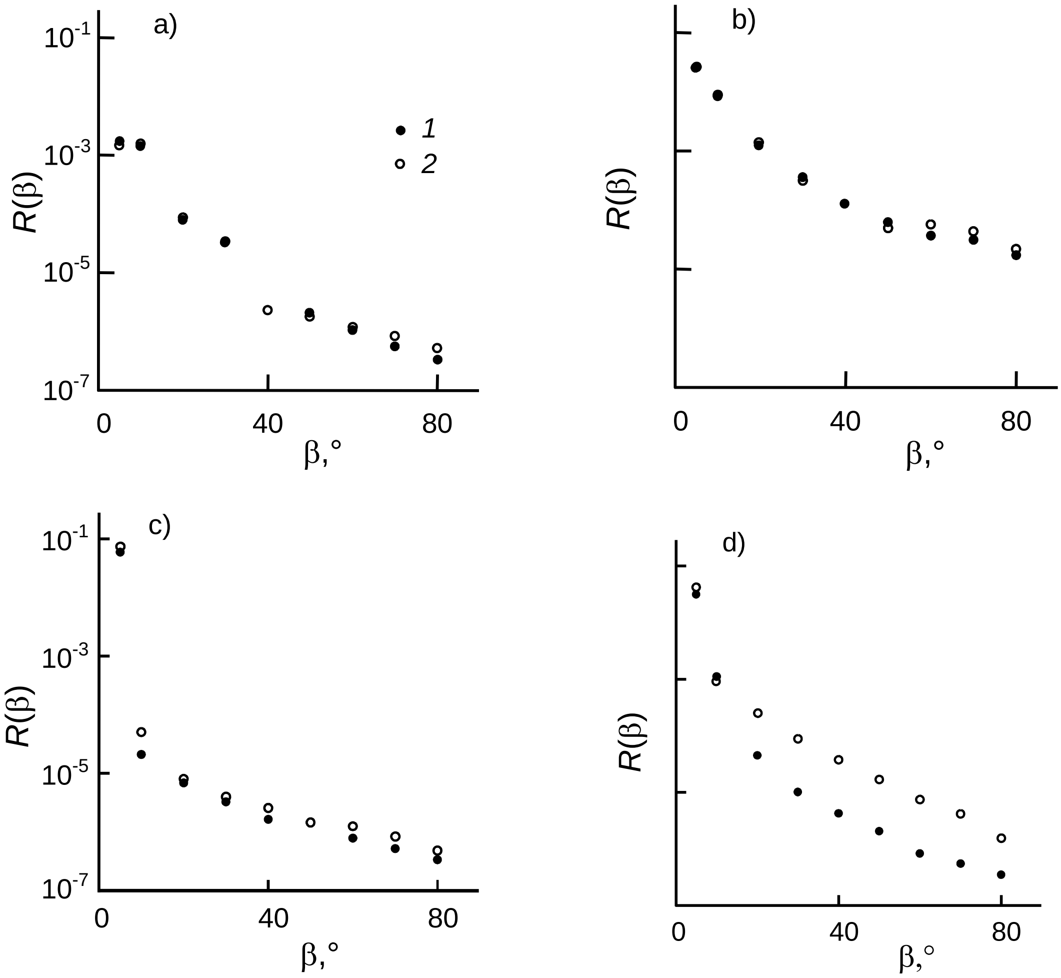

Fig. 1. Bidirectional reflectance of the PVA films modified with TiO_2 and Ag nanoparticles for various scattering angles. The mass concentration of TiO_2 nanoparticles is 0.04 % (*a*) and 0.25 % (*b*). The only oriented PVA film with the concentration of Ag nanoparticles 0.6 % (*c*). Oriented and cross-linked by oxidation with dichromate during UV irradiation of PVA film with the concentration of Ag nanoparticles 0.6 % (*d*). Incident radiation is co-polarized (*1*) and cross-polarized (*2*).

nanoparticles illuminated by co-polarized radiation is continuously decreased from 1.0 to 0.6 with the increasing the scattering angles from 5° up to 80° (see Fig. 3a). Here, the polarized part of the reflected radiation maintains polarization state of the incident radiation. The residual part of the reflected radiation represents completely unpolarized radiation. This is verified by measurements of the principle angle of the polarization and ellipticity of the reflected radiation. The ellipticity of radiation reflected by all the investigated samples is close to zero, and changes of the principle angle of polarization in comparison with incident radiation are insignificant. During illumination of these films by cross-polarized radiation, the degree of polarization of the reflected radiation continuously decreased from 0.95 to 0.85 with increasing the scattering angle (see Fig. 1a).

The scattering angles from 5° up to 50°, the degree of polarization P of radiation reflected by the film with the TiO_2 content 0.25 % is very high. The degree of polarization of radiation reflected in these conditions is 0.9–1.0 and does not depend on the azimuth of polarization of the incident linearly polarized radiation (see Fig. 3b). This trend of changing the degree of polarization for radiation reflected by a modified PVA film indicates conservation in the reflected flux the state of linear polarization of the incident radiation. This is verified by the equality of the measured values for the principle angle of polarization of the incident and reflected radiation and by zero elliptically polarized components in the reflected radiation. When increasing the scattering angles from 50° up to 80°, a considerable decrease in the degree of polarization for the reflected radiation (down to 0.45) occurs (see Fig. 3b). But the polarized part of the reflected radiation maintains the polarization state of the incident radiation. The residual part of the reflected radiation is the completely unpolarized one.

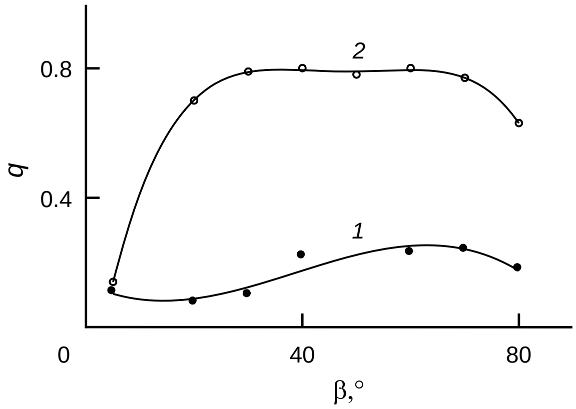

Fig. 2. Polarizance of the PVA films modified with Ag nanoparticles. Only oriented PVA film with Ag nanoparticle concentration 0.6 % (*1*). Oriented and cross-linked by oxidation with dichromate during UV irradiation of PVA film with the concentration of Ag nanoparticles 0.6 % (*2*).

Investigations of polarization characteristics for radiation reflected at the scattering angles from 5° to 40° by a PVA film modified with Ag nanoparticles have shown that the degree of polarization *P* for the radiation reflected by the investigated film both only directed and directed and cross-linked is very high, too. The degree of ion *P* for the reflected radiation lies within the range from 1.0 to 0.8 and is independent on the principle angle of polarization for the incident linearly polarized radiation (see Figs 3c,d).

Change of the degree of polarization for radiation scattered by a PVA film modified with Ag nanoparticles at the scattering angles above 40° depends on the polarization azimuth of the incident radiation. For example, the degree of polarization for radiation scattered by the investigated film illuminated with radiation cross-polarized to the plane of incidence keeps

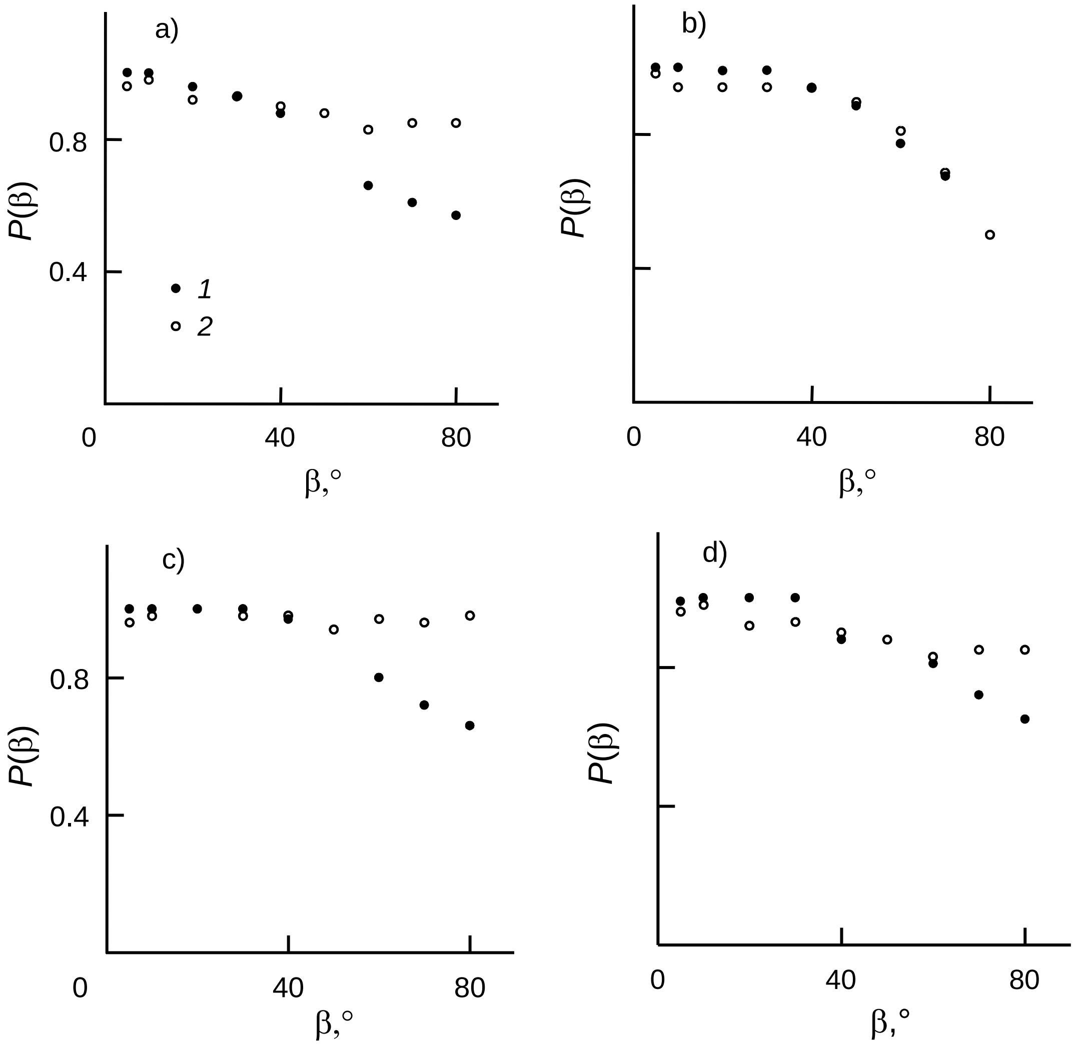

Fig. 3. Degree of polarization for radiation reflected by the PVA films modified with TiO_2 and Ag nanoparticles for various scattering angles. The mass concentration of TiO_2 nanoparticles is 0.04 % (*a*) and 0.25 % (*b*). Only oriented PVA film with the concentration of Ag nanoparticles 0.6 % (*c*). Oriented and cross-linked by oxidation with dichromate during UV irradiation of PVA film with the concentration of Ag nanoparticles 0.6 % (*d*). Incident radiation is co-polarized (*1*) and cross-polarized (*2*).

Table. Parameters of the PVA films modified by nanoparticles and polarization characteristics of the transmitted radiation at the transmitting angle of 175°.

Technological treatment	Directed PVA film modified by Ag nanoparticles	Directed and cross-linked PVA film modified with Ag nanoparticles	Directed PVA film modified with TiO_2 nanoparticles		
Modifier content, %	0.6	0.6	0.04	0.13	0.25
$T_{\|\|}$	0.73	0.44	0.76	0.64	0.47
$T_{\perp}$	0.78	0.51	0.78	–	0.49
T_{45}	0.77	0.52	0.76	0.72	0.45
$P_{\|\|}$	0.99 ± 0.01	1.00 ± 0.01	0.99 ± 001	1.00 ± 0.02	1.00 ± 004
$P_{\perp}$	0.97 ± 0.01	0.98 ± 0.01	0.98 ± 001	–	0.92 ± 001
P_{45}	0.96 ± 0.01	0.89 ± 0.01	0.95 ± 0.01	0.94 ± 0.01	1.00 ± 0.05
$e_{\|\|}$	0.01 ± 0.01	0.01 ± 0.01	–0.01 ± 0.01	–0.01 ± 0.01	–0.01 ± 0.01
$e_{\perp}$	–0.01 ± 0.01	0.03 ± 0.02	0.14 ± 0.01	–	0.01 ± 0.01
e_{45}	0.02 ± 0.02	0.81 ± 0.04	–0.56 ± 0.16	0.24 ± 0.10	0.02 ± 0.07
$\varphi_{\|\|}$, degrees	–3.8 ± 0.03	1.40 ± 0.20	–5.30 ± 1.20	0.20 ± 0.20	–6.10 ± 0.70
$\varphi_{\perp}$, degrees	88.0 ± 1.3	86.40 ± 0.20	83.40 ± 0.70	–	85.60 ± 0.20
φ_{45}, degrees	–28.9 ± 0.07	100.00 ± 1.00	85.80 ± 0.20	90.00 ± 0.40	–8.60 ± 2.80

high and does not possess values less than 0.8 during increasing the scattering angle up to 80° (see Figs 3c,d). Such a high degree of polarization of radiation scattered in all the range of the scattering angles from 5 up to 80° indicates conservation in the reflected flux the state of linearly polarization of cross-polarized incident radiation. This is verified by the results of measurements for the azimuth of polarization and ellipticity of radiation scattered by the modified PVA films in these conditions. The principle angle of polarization for the scattered and incident radiation is the same, and there is no elliptically polarized component in the scattered flux. The degree of polarization for radiation scattered by the investigated films illuminated with co-polarized radiation is continuously decreased 1.0-0.9 to 0.6 with increasing the scattering angle from 40° up to 80° (see Figs 3c,d).

The results of measuring the bidirectional transmittance in the investigated PVA films modified with different TiO_2 and Ag content and illuminated with radiation linear co- ($T_{||}$) and cross-polarized ($T_{\perp}$) as well as polarized at the angle of 45° to the film orientation direction (T_{45}) and polarization characteristics of the transmitted radiation (the degree of polarization, the principle angle and ellipticity of polarization) at the transmittance angle 175° are presented in Table.

It is seen that the bidirectional transmittance of the investigated PVA films modified by TiO_2 or Ag nanoparticles is equal for the incident radiation co- or cross-polarized to the film orientation direction. This indicates that in the investigated films there is no amplitude anisotropy for transmitted radiation, and they are not linear polarizers. At the same time, these films have the phase anisotropy and are the uniaxial retardation plates. The phase anisotropy occurrence is caused by the polymer films stretch. The radiation linear polarized at the angle of 45° to the film orientation direction, when passing the modified PVA films, is transformed into elliptically polarized transmitted radiation. Ellipticity of the transmitted radiation depends on the nanoparticle concentration, methods of technological processing the films and their thickness. This phase anisotropy can be used for compensation of the undesirable phase delay between the components of the radiation appeared during light passing through the different elements of the LCD.

4. Conclusions

It has been shown that the bidirectional reflectance at the wavelength of 0.63 μm of the PVA film with the mass concentration of TiO2 nanoparticles 0.25 % is nearly two orders higher than the bidirectional reflectance of the PVA films with a lower content of TiO_2. At the same time, the scattering angle of this film is increased up to 50-60°.

Within the range of scattering angles from 20° to 80°, the bidirectional reflectance of the oriented and cross-linked by UV irradiation PVA film with the mass concentration of Ag nanoparticles 0.6 % for the incident radiation co- and cross-polarized to the film orientation differs by one order. In this range of scattering angles, this film may be used as a reflective linear polarizer with the polarizance close to 0.8 and with the practically diffuse angular distribution of the reflected radiation. In addition, the bidirectional reflectance of this film is near two orders higher than that for only oriented film. The only oriented PVA film modified with Ag nanoparticles is not amplitude anisotropic.

It has been shown that for transmitted light all the investigated films are not amplitude anisotropic. In this case, oriented PVA films modified with TiO_2 or Ag nanoparticles have phase anisotropy and can be used as uniaxial retarders.

The incident linear polarized light with the principle angle of polarization changing in the range 0 to 90° as to the film orientation direction, when passing the modified PVA films, is transformed into the elliptically polarized one.

The ellipticity of transmitted radiation depends on the nanoparticle concentration, methods of technological processing the films and their thickness.

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