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The UV-treatment influence on optical and surface properties of polyvinyl alcohol films, sensitized with a shungite

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The spectral characteristic changes and modification possibility of polyvinyl alcohol films, sensitized with a shungite, under the UV-treatment have been demonstrated at the present publication.

Keywords: polyvinyl alcohol, shungite, surface average roughness, optical transmittance coefficient, UV-radiation.

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The examination of polymers and methods for modification of their bulk and surface properties (especially in light of their polarization characteristics) is of the utmost interest in contemporary science. This is attributable to the fact that polymer materials have a wide range of application in laser and display engineering, biomedical materials science, mechanical and aeronautical engineering, manufacture of paint coatings, etc. Water-soluble polyvinyl alcohol (PVA) is one of the promising polymer compounds. A number of research groups [1–5] are currently engaged in in-depth examination of its properties, including those achieved by doping the PVA matrix.

Polyvinyl alcohol has the capacity to form films: durable and flexible thin films are produced based on it. Thin polarization filters [6,7], which are used in modern liquid-crystal display elements, are fabricated by coloring PVA films with dyes or iodine and subjecting them to subsequent stretching.

The effect of UV irradiation on thin PVA films sensitized with atoms of metals or other substances has been examined in several studies for the purpose of production of novel biomedical materials [8] and films that block UV radiation [9]; the potential for development of biocomposite PVA-based films has also been appraised [10].

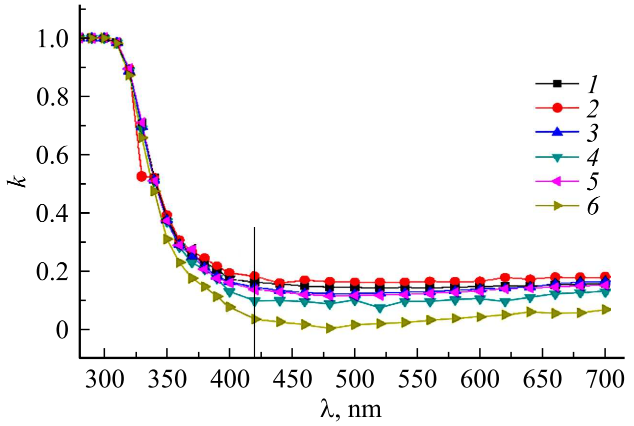
At the same time, the interaction of UV radiation with polymer chains induces degradation of polymer composites, which has a negative effect on their mechanical strength and leads to a considerable suppression of transmittance in the visible spectral range [11]. Thus, the search for sensitizers suppressing the negative influence of short-wave radiation on the polymer PVA matrix is a topical issue [12].

In the present study, the effect of UV radiation with wavelengths of 126 and 173 nm on thin PVA films sensitized with shungite nanoparticles is examined with a view to, on the one hand, enhance the optical transmittance and, on the other hand, analyze the potential fabrication of a new relief for orienting the liquid-crystal mesophase that is used in display, laser, and modulation engineering.

Shungite was used as a sensitizer. It is a naturally occurring material, a multilevel fractal structure composed of graphene fragments (~ 1 nm) and secondary and tertiary levels of turbostratic stacks ($\sim 1.5-2.5$ nm) and globular compositions of stacks ~ 6 nm in size; i.e., the structure of shungite may be presented as a multilevel fractal network of reduced graphene oxide sheets [13]. The properties of shungite and the domains of its practical application are being studied extensively throughout the world [14,15]. The efficiency of shungite-filled polymer composites and their high performance have been proven in [16]. It has also been demonstrated that shungite has certain nonlinear optical properties and allows one to reinforce the refractive parameters of organic matrices, which may become widely used in scientific research and in practice [17,18].

Thin films made of a 8% PVA solution with 0.1 wt.% of shungite introduced into the bulk of it were examined in the present study. Their spectral characteristics within the wavelength interval of 250–1200 nm were studied using an SF-26 spectrophotometer, and the films themselves were examined with a Solver Next AFM (OOO „NT-MDT,“ Moscow, Zelenograd) atomic force probe microscope. The surface roughness of films irradiated with argon ($\lambda = 126$ nm; the energy density was 200 and 400 mJ/cm^2) and xenon lamps ($\lambda = 173$ nm; the energy density was 200 and 400 mJ/cm^2) was determined.

The study of spectral characteristics is instrumental in the evaluation of band and structural parameters of a material. It is understood that the bandgap energy may be determined if the intrinsic absorption edge is known. However, the values of absorption and reflection coefficients are needed to perform accurate calculations. In the present study, we perform a qualitative analysis of absorption to identify the



Wavelength dependences of fraction k of absorbed light for 8% PVA films. *1* — Film made of non-sensitized PVA without additional treatment; *2* — non-irradiated PVA film sensitized with shungite; *3* — PVA film sensitized with shungite and subjected to irradiation with $\lambda = 173$ nm and an energy density of 200 mJ/cm^2; *4* — PVA film sensitized with shungite and subjected to irradiation with $\lambda = 173$ nm and an energy density of 400 mJ/cm^2; *5* — PVA film sensitized with shungite and subjected to irradiation with $\lambda = 126$ nm and an energy density of 400 mJ/cm^2; *6* — PVA film sensitized with shungite and subjected to irradiation with $\lambda = 126$ nm and an energy density of 200 mJ/cm^2.

influence of UV radiation on the PVA matrix sensitized with shungite:

$$k = 1 - T, \quad (1)$$

where k is the fraction of absorbed light and T is the transmittance coefficient.

Wavelength dependences of the fraction of absorbed light for non-irradiated and UV-irradiated PVA films sensitized with shungite are shown in the figure. The growth of k in the plotted wavelength dependences of absorption characterizes the bandgap energy variation. These data suggest that the absorption of all the examined samples starts increasing at a wavelength of 420 nm.

The obtained spectral data reveal a suppression of absorption (and, consequently, an enhancement of transmission) in the visible range for PVA–shungite films that were irradiated with an argon lamp ($\lambda = 126$ nm) with an energy density of 200 mJ/cm^2.

It was found in the process of calculation of roughness values that the mean roughness is 12.1 nm for a non-sensitized PVA film and 6.5 nm for a PVA film with shungite. The roughness parameter for a PVA–shungite film irradiated with an argon lamp ($\lambda = 126$ nm) with an incident radiation energy density of 200 and 400 mJ/cm^2 was estimated at 1.1 and 1.3 nm, respectively; the roughness for a PVA–shungite film subjected to UV irradiation with a wavelength of 173 nm and an energy density of 200 mJ/cm^2 decreased to 1 nm, but increased to 3.6 nm in the case of irradiation with the same xenon lamp ($\lambda = 173$ nm) with a doubled energy density (400 mJ/cm^2). Thus, the roughness of a PVA film sensitized with shungite decreased by a factor of 2 without any additional irradiation, and the roughness of sensitized PVA–shungite films subjected to UV irradiation decreased by a factor of 2–6.

The results of spectral studies and surface characteristics are correlated, since scattering gets suppressed (and, consequently, the transmittance of a material is enhanced) when the surface roughness decreases. Note that the edges of intrinsic absorption bands of all the examined samples (non-sensitized PVA and PVA with shungite before and after UV treatment) remain fixed at 420 nm. Thus, the electronic structure of PVA does not change in a substantial way after the introduction of shungite, but the surface relief is altered due to additional orienting of polymer molecules by graphene planes of shungite. If one considers the absorption of electromagnetic radiation within a material in terms of its interaction with dipole moments of the medium (shungite has an intrinsic dipole moment of ~ 2 D), the suppression of fraction k of absorbed light for the PVA sample with shungite irradiated with a wavelength of 126 nm and an energy density of 200 mJ/cm^2 is attributable to a reduction in the number of dipole moments. The energy of a radiation quantum with a wavelength of 126 nm is higher than the energy of a quantum with a wavelength of 173 nm, but the density of an incident wave is 2 times lower; this allows one to make certain assumptions regarding the optimum characteristics of incident radiation for enhancing the transmittance of a composite PVA–shungite material.

The obtained results suggest that UV irradiation may be used to modify the surface relief of PVA films sensitized with shungite for the purpose of suppressing their reflectance and enhancing the transmittance. Thus, it is distinctly possible to enhance transmission dichroism in the context of application of such films as thin-film radiation polarizers, and this system may well be recommended for use in display engineering for planar orientation of LCD dipoles.

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Conflict of interest

The authors declare that they have no conflict of interest.

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