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The iodization time influence on spectral and polarization characteristics of polyvinyl alcohol polarizers

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Studies performed to optimize the polarization ability of polyvinyl alcohol systems have revealed the effect of iodine concentration on spectral and polarization characteristics of thinfilm polarizers. The time of treating the polyvinyl alcohol film in the potassium iodide solution has been determined, which is optimal in view of obtaining optically transparent polarizers with the polarization degree of about 95–99%.

Keywords: polyvinyl alcohol, polarizers, polarization degree, iodization, potassium iodide.

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It is known (and widely used in optoelectronics) that a polarized light wave may be regarded as a tool for controlling optical components. As an example, uptodate liquid-crystal display elements may be considered [1–3]. The liquid-crystal cell operating principle is based on anisotropic optical and electrical properties of liquid crystals. Depending on the assembling method and moleculesóriention in the cell irradiated with polarized light, the cell can either transmit or absorb the electromagnetic radiation, i. e. the display visualizes either a bright or dark pixel. Hence, the key role in creating an efficiently operating optical component is played by a polarizer generating radiation with a certain direction of the vector of the electromagnetic waveś electrical component. Tendencies towards miniaturization of technological components impose certain requirements on the polarizer parameters. Polarizers should be thin, mechanically strong and flexible; they should also possess high optical transparency and polarizing ability.

Among polarizers with the specified properties there are film polarizers made from polyvinyl alcohol (PVA). PVA is a water-soluble polymer widely used in the food industry, medicine, packaging materials, and also as a base for creating films and various membranes [4–8]. The operating principle of PVA polarizers is based on dichroism of dye molecules introduced into the PVA matrix. As the dichroic molecules, organic dyes, nanoparticles, and iodine are used. The choice of dye affects the operating spectral range. To create visible-spectrum (400–700 nm) polarizers, iodine molecules are introduced into the PVA matrix. Among the main disadvantages of the created iodinepolyvinylalcohol polarizers there are their thermal instability and hydrophilicity. However, in a number of practical applications these disadvantages are alleviated by the polarizerśhigh optical characteristics and relative ease of fabrication.

As a PVA solvent for casting the films, water is typically used; however, heat— and moistureresistant films may be obtained by using as solvent the tungsten-phosphoric acid (TPA). As a result of casting and heating the films, dichroic polarization films of PVA–polyene/TPA get formed [9]. At present, development of synthesis of new Schiff-base dichroic dyes (azomethines) [10] is in progress; those dyes enable obtaining polarizers having a higher heat resistance but operating in a narrow visible spectrum range (400–550 nm).

Here we continued investigation of thinfilm light polarizers fabricated using a conventional technique developed earlier at the S.I. Vavilov State Optical Institute [11,12]. Our team has previously studied the influence exerted on polarization properties of thinfilm polarizers in the process of sensibilizing the PVA matrix bulk with graphene oxide and in structuring the film surface with carbon nanotubes [13,14]. Graphene oxide was shown to positively affect polarization and optical properties of the polarizers. This study was devoted to optimizing the manufacturing process and addresses the issue of the iodization time effect on polarization properties of the iodine-polyvinyl-alcohol polarizers in the visible spectrum range.

Polarizing films were cast from the 8% aqueous solution of PVA 40/2 (the highest grade); this meets actual GOST 10779–78. The procedure for fabricating iodine-polyvinyl-alcohol polarizers consists of several stages. The first stage is obtaining aqueous solution of polyvinyl alcohol in which PVA molecules form „head-to-tail"chains: $(CH_2{-}CH{-}OH){-}(CH_2{-}CH{-}OH)$ [15]. Transparent films are cast from the PVA aqueous solution and then dried at

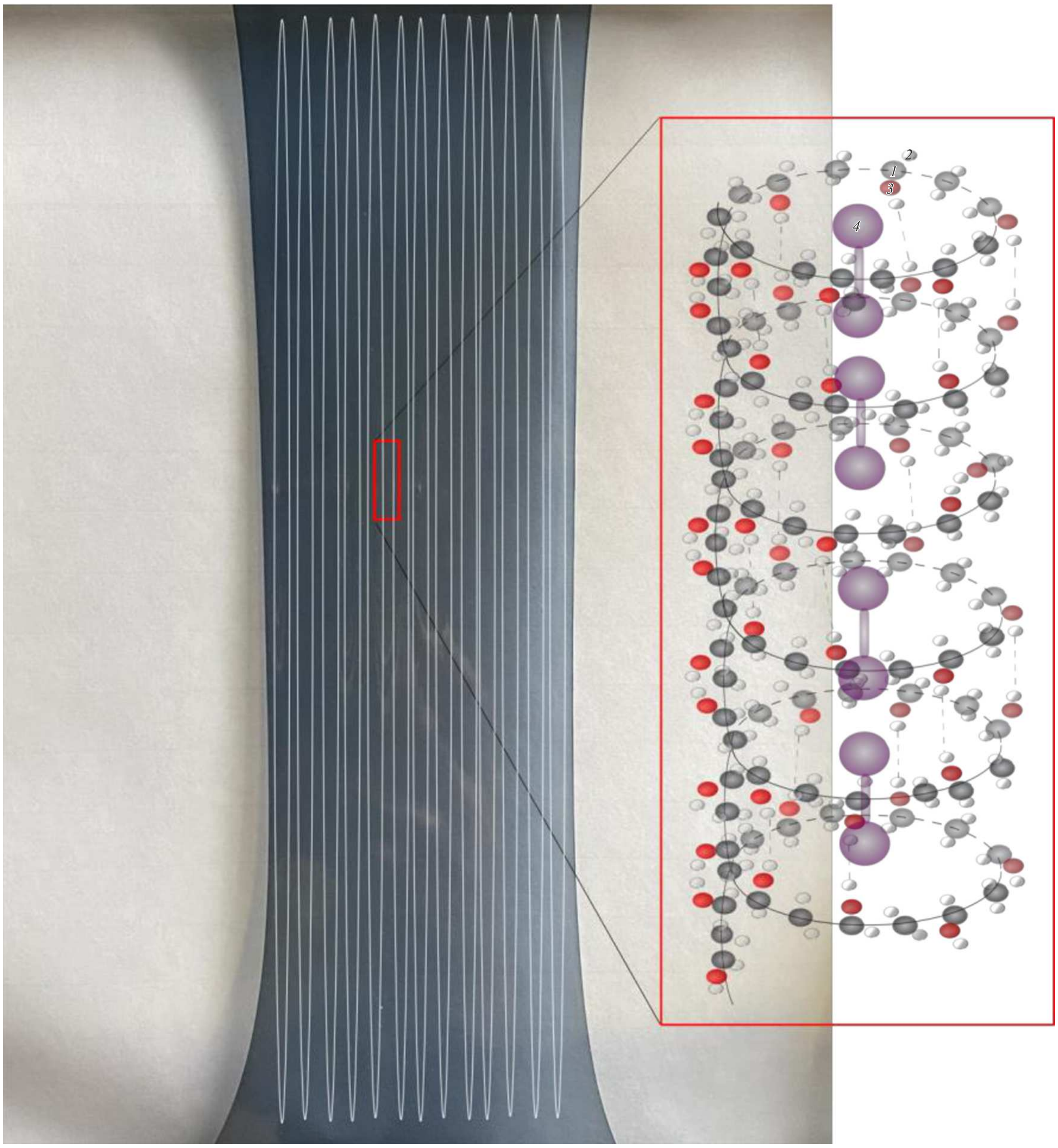

Figure 1. Iodine-polyvinyl alcohol polarizer. White color indicates orientation of polymer chains after stretching the film by 3.5 times with respect to the initial length. *1* — C atom, *2* — H atom, *3* — O atom, *4* — I atom.

room temperature (20–24°C) and air humidity of 40–60%. Being removed from glass substrates, the obtained films undergo additional plasticization in water vapor for 24 hours. Plastic transparent PVA films are treated for a few minutes in the boric acid solution (H_3BO_3). The boric acid molecule binds the PVA chain hydroxyl groups, which leads to formation of polymer helices. Films treated with boric acid are colored in the potassium iodide (I_2–KI) solution. Iodine molecules from the I_2–KI solution get inside the PVA helices. Orientation of PVA molecule helices containing I_2 molecules is performed by mechanically stretching the colored films with a special stretcher. Depending on the stretching degree, formation of a uniaxial molecular structure may occur. Typically, the film is stretched 3–4 times relative to its initial length. As a result, the polarizing film structure contains, besides molecules of water, boric acid and other components, identically arranged polymer helices I–PVA (Fig. 1).

As noted above, iodine plays the role of a dichroic agent absorbing optical radiation. The main absorption centers are ions I^-, I_3^- and I_5^- having peaks at 226, 288–350 and 650 nm, respectively [16]. Notice that, in the case of polarizers operating in the visible spectral range, the presence of ions I_5^- reduces significantly their optical transmission and restricts the possibilities of application. Therefore, the goal of this work was to study the effect

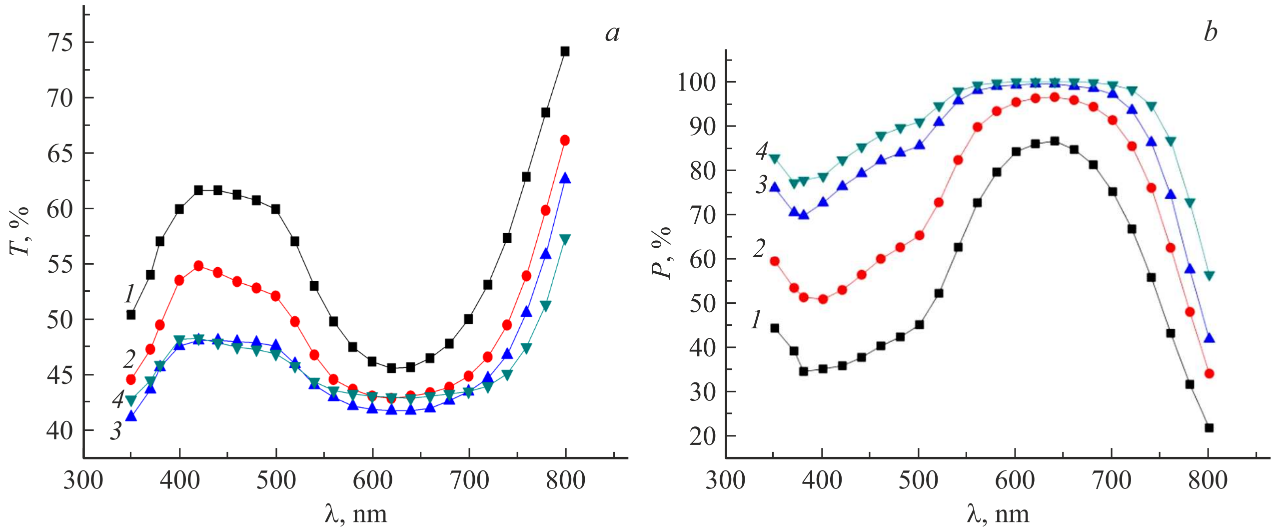

Figure 2. Optical transmission spectra of iodine-polyvinyl-alcohol polarizers at different iodization times (*a*), and polarization degree of the polarizers under consideration (*b*). *1* — 30 s, *2* — 1 min, *3* — 1.5 min, *4* — 2 min.

of iodization time, i.e. the time during which the PVA film stays in the I_2−KI solution, on the polarization characteristics and transmission of the total (unpolarized) light flux. Four time intervals during which the films were kept in the iodine solution were studied: 30 s, 1, 1.5 and 2 min.

The polarizers' transmission spectra were studied using the SF-26 spectrophotometer in the range of 350 to 800 nm. Transmission was measured for the total (unpolarized) light (T, %) and two polarized radiation components: parallel ($T_{\parallel}$, %) and orthogonal ($T_{\perp}$, %). Polarized light was obtained using a Nicolas prism placed between the spectrophotometer exit slit and polarizer under consideration. By rotating the prism about the light beam, radiation was polarized either parallelly to the sample polarization axis corresponding to the maximum $T_{\parallel}$ value or orthogonally with the minimum $T_{\perp}$ values.

Fig. 2 presents the measured transmission spectra of natural light (*a*) and the degree of polarization (*b*). The polarization degree P was calculated using the following formula [17]:

$$P = 100\% \cdot (T_{\parallel} - T_{\perp})/(T_{\parallel} + T_{\perp}). \quad (1)$$

The transmission spectra show that, when the iodization time increases from 30 s to 1.5−2 min, optical transmission of the polarizers decreases. The process of decreasing is nonuniform. At the wavelengths of 350 and 600−700 nm, films kept in the iodine solution 3−4 times longer (curves *3*, *4* in Fig. 2, *a*) transmit 4−10% less light than films with the iodization time of 30 s (curve *1*). A significant difference (up to 20%) in the transmission magnitude is observed at the wavelengths of 450−460 nm. Note that polarization degree of films with a lower iodine concentration is about 35−45% at the beginning of the considered spectral range (350−400 nm) (curve *1* in Fig. 2, *b*), which indicates poor polarization properties of the polarizers. At the wavelengths of 600−700 nm, polarization of low-iodized films increases to 80% but remains lower than that for films with higher iodine concentrations (curves *3*, *4* in Fig. 2, *b*).

The transmission reduction at the wavelengths of 350 and 600−650 nm corresponds to the absorption peaks of iodides I_3^- and I_5^-. Hence, an increase in the iodine concentration in the films leads to an increase in the quantity of these iodides. In a number of works [18,19], the iodine absorption peaks at the wavelengths of 450−460 nm are attributed to hydrated iodine molecules. Thus, as the iodization time increases, iodine molecules not only get included in the PVA polymer molecules in greater amounts, but also form the I_2−H_2O complex.

The paper demonstrates that the increase in the iodization time unsurprisingly results in transmission reduction due to an increase in the number of absorption centers at iodine ions and hydrated molecules I_2. Notice that an increase in the iodine concentration reduces the transmission by 3−4% in the range of 600−700 nm, i.e. concentration of I_5^- ions increases. Transmission in the vicinity of the ion I_3^- absorption peak (350 nm) decreases stronger (from 50 to 40%), which indicates formation of a larger amount of I_3^- due to reaction with ions I_5^- ($I_5^- + I^- \rightarrow 2I_3^-$) [12].

Formation of the I_2−H_2O complex with increasing iodization time is confirmed by an increase in absorption (decrease in transmission) at the wavelengths of 450−460 nm. Thus, the study has shown that an increase in the time of treatment with iodine to 1.5−2 min leads to an increase in the iodine concentration in polyvinyl alcohol films. Comparison of the polarization and transmission degrees demonstrates the key role of iodine in creating lightpolarizing materials. A lower iodine concentration in PVA films allows obtaining polarizers with a higher optical transparency; however, in this case the polarization degree decreases significantly (by 35–86%), its minimum is observed in the wavelength band of 400–500 nm. The strongest polarization (95–99%) is observed in iodine-polyvinyl-alcohol polarizers with iodization time of 1.5 to 2 min.

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Conflict of interest

The authors declare that they have no conflict of interests.

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