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Mechanisms of interaction of polyvinyl alcohol molecules and carbon nanoparticles in aqueous solutions

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The paper presents the results of the study of the spectral characteristics and viscosity parameters of aqueous solutions of polyvinyl alcohol (PVA) sensitized with an aqueous solution of graphene oxide at various concentrations (with reference to the dry substance of PVA) and carbon nanoparticles (fullerene C_{70} and single-walled carbon nanotubes (SWCNT)) at a concentration of 0.1 wt.%. The obtained electronic spectra of PVA clear solutions exhibit absorption at a wavelength of 275–280 nm of the functional carbonyl group (C=O), which is a part of polyvinyl alcohol. The graphene oxide applied in the form of an aqueous solution neutralizes the electronic transition of the carbonyl group, which results in the absence of an absorption peak in the UV band. Sensitization with C_{70} nanoparticles and SWCNT preserves all the transitions typical of polyvinyl alcohol. The decrease in viscosity of PVA-graphene oxide solutions is associated with the increased spacing between polyvinyl alcohol molecules due to the graphene oxide layers placed between them. The increase in viscosity for PVA aqueous solutions sensitized with C_{70} and SWCNT is due to the presence of large clusters of carbon nanoparticles that do not interact with PVA polymer molecules.

Keywords: polyvinyl alcohol; graphene oxide; carbon nanotubes; fullerenes; electronic transitions; dynamic viscosity.

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Introduction

Polyvinyl alcohol is a polymer material featuring unique characteristics that make it an attractive item to be researched with an aim of improving mechanical, optical, electrical and other parameters [1–5]. An ability to form flexible and durable

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optically transparent films can be distinguished among main advantages of PVA. Due to its film-forming properties, PVA can be used as a basis for creating thin-film polarizers. It should be noted that the ability to control the polarized light is widely used in modern optoelectronic applications, for example, in liquid crystal displays [6, 7].

A number of earlier studies have shown the progress in optical characteristics of polarizers based on polyvinyl alcohol, the volume of which was sensitized with carbon (graphene oxide, C_{70} fullerene and shungite) and quartz nanoparticles [8, 9]. The results of the work demonstrate an increase in the transmission of the parallel light component in the wavelength range of 500–750 nm. To explain the data observed, an assumption has been made that PVA polymer chains are oriented more uniaxially due to the formation of an additional orienting framework of carbon nanoparticles. According to the classic technology of producing iodine-polyvinyl alcohol polarizers, after the transparent PVA film is colored in the iodine solution, moistened films are exposed to mechanical stretching. The degree of stretching impacts the arrangement of PVA lamellas relative to each other. Since PVA chains where iodine atoms are built in are oriented strictly in parallel, maximum absorption of the crossed light component takes place. If molecules are located at certain angles, the resulting polarization will be partial.

The aim of this work was to study the mechanisms of interaction of PVA polymer molecules and carbon nanomaterials by measuring the dynamic viscosity and absorbency of PVA-carbon sensitizer solutions.

Experimental section

To study the mechanisms of interaction of a PVA polymer molecule with carbon nanosensitizers, the optical parameters of 1 % aqueous solutions of polyvinyl alcohol were analyzed. PVA grade 40/2 was used for preparing a solution [10]. The above-mentioned grade of polyvinyl alcohol is recommended for making optical polarizers based on Russian-manufactured components. The PVA concentration was 1 wt.% of a solvent (distilled water). The required amount of dry PVA was left in distilled water for twenty-four hours for the polymer molecules to swell, after which a homogeneous transparent aqueous solution of PVA was obtained by stirring at a water bath temperature of 100 °C for four hours continuously. Carbon sensitizers were added to the main solution after it had cooled down to a temperature of about 35 °C (Fig. 1). The sensitized solution of PVA was mixed additionally. An aqueous solution of graphene oxide, C_{70} fullerenes and single-walled carbon nanotubes played a role of sensitizers. The concentration of fullerene and SWCNTs was 0.1 wt.% relative to dry PVA. Fullerene C_{70} powder with a mixture purity of 97%, as well as carbon nanotubes (SWCNTs, type #704121, with a diameter varying in the range of 0.7–1.1 nm), were purchased from Aldrich Co. A polyvinyl alcohol solution with graphene oxide was studied at three concentrations of the sensitizer: 0.05, 0.1, and 0.15 wt.%. These concentrations were considered as part of earlier studies of polarization characteristics of iodine-polyvinyl alcohol polarizers [11]. It should be noted that graphene oxide was purchased from a Russian manufacturer, NanoTechCenter LLC in Tambov. After analyzing the data shown in Figure 1 (see bottles Nos. 2–4) for such compounds, on can say that homogeneous composites were obtained, and the change in their color is associated with an increased concentration of the graphene sensitizer.

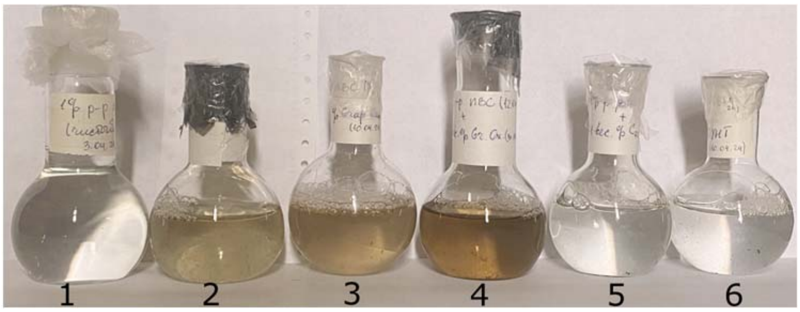

Fig. 1 Aqueous solutions of 1% polyvinyl alcohol after being sensitized: 1 – non-sensitized PVA solution; 2 – 0.05 wt. % of graphene oxide; 3 – 0.1 wt. % of graphene oxide; 4 – 0.15 wt. % of graphene oxide; 5 – 0.1 wt. % of C_{70} fullerene; 6 – 0.1 wt. % single-walled carbon nanotubes

The transmittance spectra in the UV and visible bands of 1% PVA solutions with carbon sensitizers were studied with SF-26 spectrophotometer. The absorbency (*D*) of samples was calculated based on the transmittance values obtained. The data are shown in Figure 2.

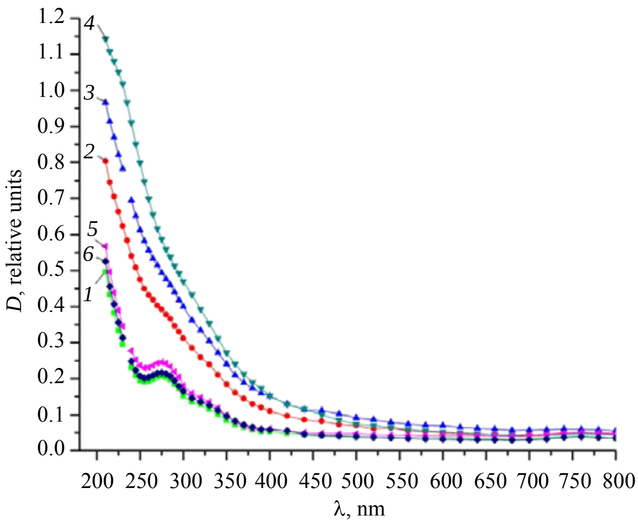

Fig. 2 Absorbency of 1% aqueous solutions of polyvinyl alcohol after being sensitized: 1 – non-sensitized PVA solution; 2 – 0.05 wt. % of graphene oxide; 3 – 0.1 wt. % of graphene oxide; 4 – 0.15 wt. % of graphene oxide; 5 – 0.1 wt. % of C_{70} fullerene; 6 – 0.1 wt. % single-walled carbon nanotubes

Analysis of the curves has shown that sensitization with graphene oxide results in the change of solutions' absorbency in the UV band. For a 1 % solution of polyvinyl alcohol with graphene oxide, at a wavelength of 275–280 nm and at all the considered concentrations of the nanomaterial, there are no peaks (Fig. 2, curves 2–4) typical of non-sensitized PVA (curve 1). The dynamic viscosity of the solutions was also measured using SV-1A vibroviscometer (A&D Company Limited (Japan)). The dynamic viscosity values in the work are expressed in relative units (η), because the task was to compare the data for sensitized and non-sensitized 1 % solution of polyvinyl alcohol (Fig. 3).

Sensitization of an aqueous 1 % solution of polyvinyl alcohol with graphene oxide reduces the viscosity by 5–13 % relative to the non-sensitized PVA solution. The PVA solutions with C_{70} fullerene and SWCNTs have a higher viscosity value differing by 13 % and 8 %, respectively.

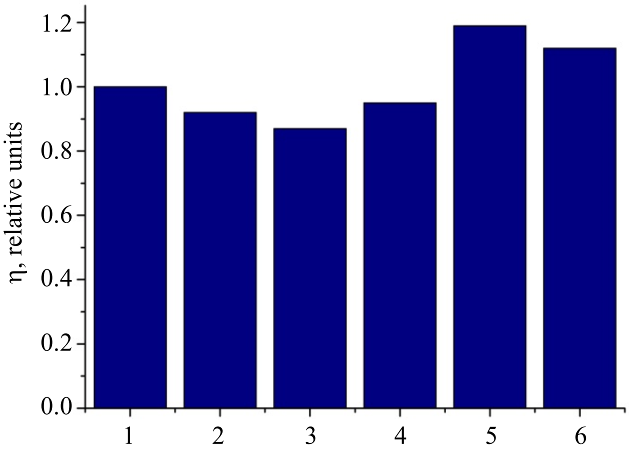

Fig. 3. Dynamic viscosity of 1% aqueous solutions of polyvinyl alcohol after being sensitized: 1 – non-sensitized PVA solution; 2 – 0.05 wt. % of graphene oxide; 3 – 0.1 wt. % of graphene oxide; 4 – 0.15 wt. % of graphene oxide; 5 – 0.1 wt. % of C70 fullerene; 6 – 0.1 wt. % single-walled carbon nanotubes

Discussion of the results

Polyvinyl alcohol has the chemical formula $(CH_2CHOH)_n$. However, the molecule may contain small amounts of other chemical groups: carbonyl, acetate, ether bridges and other structural heterogeneities [12]. The absorbency curve shown in Figure 2 features an absorption peak at a wavelength of 270–280 nm for the non-sensitized PVA solution and PVA solutions with added C_{70} fullerene and SWCNTs (Fig. 1, curves 1, 5 and 6). This peak is attributed to the $n \rightarrow \pi^*$ transition of the carbonyl group C=O, which disappears in an acidic environment [13]. According to the literature data, aqueous solutions of graphene oxide have a high acidity [14, 15] with pH = 2.1–3.5. Thus, when polyvinyl alcohol is sensitized with the graphene oxide solution, an unshared electron pair in the oxygen atom of the PVA carbonyl group is exposed to protonation. One of the earlier studies [11] presented a model of intermolecular interaction between PVA and graphene oxide, which was based on the assumption that hydrogen bonds formed between the PVA hydroxyl groups and the oxygen ions of graphene functional groups. The relationship observed in this study between the molecules under study confirms their chemical interaction to form a stable compound. In terms of practical use, it is worth noting that a sensitizer based on graphene oxide suits more for enhancing the transmittance of a parallel light component during manufacture of thin-film light polarizers [11].

The results of viscosity measurements demonstrate its growth in solutions with fullerene nanoparticles and CNTs. The decrease in viscosity values for solutions with graphene oxide can be explained by the following reasons. First of all, the sensitizer under consideration, namely the graphene oxide, is used in the form of an aqueous solution. Thus, its addition to the PVA solution reduces the PVA concentration relative to water. The viscosity values do not decrease anymore because the volume of graphene oxide solution remains relatively small. As a second reason, a model of formation of a chemical compound between graphene oxide planes and PVA polymer molecules can be considered. Interaction including the formation of new bonds can result in an increased distance between polyvinyl alcohol chains, which, consequently, leads to lower resistance forces between PVA layers. The lowest viscosity (0.87 relative units relative to the non-sensitized solution) is observed for the PVA solution with 0.1 wt.% of graphene oxide; the use of a smaller (0.05 wt.%) and larger (0.15 wt.%) mass of the sensitizer results in the relative dynamic viscosity decreased by 8 % and 5 %, respectively. This dependence can be interpreted as estimation of the optimal concentration of the sensitizer – a small addition of graphene oxide is not sufficient to separate PVA layers most effectively, and with a larger addition, the viscosity is contributed by graphene oxide plates. A significant increase in viscosity of PVA with carbon nanoparticles is also associated with the presence of undissolved clusters of fullerenes and carbon nanotubes. The size of a single link of a polyvinyl alcohol molecule is about 0.257 nm [12], the diameter of a carbon nanotube varies from 0.5 to 2 nm [16], the size of an ellipsoidal C_{70} molecule is 0.69 nm×0.78 nm [17]; the thickness of graphene nanoplates is as large as 2–6 nm [18]. The operating principle of the viscometer is based on the simultaneous oscillation of two metal plates of the sensor. Accordingly, the viscosity increase can be caused by the presence of large particles in a solution, which interact with the sensor plates, thus exercising a higher resistance, and as a result, the viscosity value increases.

Conclusion

The work shows that sensitization of the polyvinyl alcohol aqueous solution with the graphene oxide solution, a bond is formed between PVA molecules and functional groups of graphene oxide. The new bond results in the change of absorbency in the sensitized PVA solution at the wavelength of 275–280 nm. Since PVA is a basis for producing optical polarizers and light filters, the observed effect, from a practical point of view, allows creating optical PVA elements with uniform increase in transmittance throughout the light spectrum.

Graphene oxide added to the PVA solution also results in decreased dynamic viscosity, while sensitization with fullerene and carbon nanotubes increases its value. Thus, it is possible to produce PVA solutions for further formation of optical films, including an option of varying the friction force between the polymer layers, and, therefore, the final thickness of resulting films.

Finally, we note that the earlier studies of the spectral and polarization characteristics of iodine-polyvinyl alcohol polarizers sensitized with carbon nanomaterials showed an increase in the listed characteristics. The findings of the studies presented in this work along with the earlier results allow considering the sensitization of polyvinyl alcohol with carbon nanoparticles as a method for obtaining optical elements with varying parameters (optical transmittance, thickness, polarization degree).

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