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Coloring, Structuring, and Photopolymerization in the Composites "Pre-Polymer-TiO_2 Nanoparticles" Under the Action of an Electric Field

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The influence of an electric field on the color, structure, permittivity, and polymerization of the composite "pre-polymer NOA65-TiO_2 nanoparticles" is considered. The electrochromic effect which consists in the restructuring and coloring of NOA65 prepolymer-TiO_2 mixture under the action of DC voltage is revealed. The redistribution of TiO_2 nanoparticles results in the formation of an opaque structure near the cathode. At the same time, the AC voltage does not essentially influence the composite's structure. The structural and electrical properties of the composites polymerized under different irradiation conditions under the action of a DC voltage are investigated. The mechanisms of restructuring and coloring are discussed.

Keywords: conductivity; permittivity; polymer-nanoparticles composite; TiO_2 nanoparticles

1. INTRODUCTION

The "polymer–nanoparticles" composites are among the most important materials developed in the past century. They excite the permanent research and application interest because of a huge variety of properties which can be obtained. At present, the interest in these materials is multiplied by the recent achievements of nanotechnologies providing a great number of products with amazing characteristics.

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Doping with nanoparticles drastically changes the intrinsic properties of polymers allowing to obtained "polymers" with non-specific, sometimes astonishing characteristics. By this way, one can substantially improve the mechanical durability of polymers [1], modify the optical refraction and absorption [2,3], and introduce unusual electrical properties [4].

In our previous work [5], we discovered the photochromic effect in the composite "photopolymer NOA65-TiO_2 nanoparticles." It was revealed that such an effect is due to the chemical reaction between TiO_2 nanoparticles and the polymer under the action of UV light. According to the results of dielectric studies, the ionic conductivity of these composites is higher than that of the undoped polymer. The excess of ions in doped samples suggests the incomplete photoconversion in the polymer partially blocked by the chemical reaction between nanoparticles and polymer constituents.

We continue to investigate the electrical properties of these composites taking into account the dominating ionic mechanism of conductivity. The attention is paid to the mechanisms of charge transport under the action of a dc or ac electrical field and to the influence of these processes on the structure and photopolymerization. In parallel, we describe the electrochromic effect discovered in this system.

2. MATERIALS AND METHODS

As a photopolymer material, the photosensitive mixture of monomers named NOA65 from Norland Inc. (USA) was used. This photoadhesive material commonly used for the agglutination of optical parts [6] is suitable for the formation of polymer networks in liquid crystals [7,8]. NOA65 mixture consists of trimethylolpropane diallyl ether, trimethylolpropane tristhiol, and isophorone diisocianate ester. In the initial state, NOA65 is a transparent (refractive index is 1.524), liquid, viscous mixture.

As a filler for NOA65, we used colloidal TiO_2 nanoparticles with sizes 5–10 nm provided by ANP, Korea. These nanoparticles are supplied in the form of a 30 wt.% dispersion in ethanol. In the process of preparation, the dispersion of nanoparticles was added to monomer mixture NOA65 and mixed. Ethanol was evaporated during the mixing. The complete removing of alcohol from the mixture was achieved by applying vacuum at 10^{-2} Torr. To investigate the concentration dependences of permittivity, we prepared samples with the particles content from 5 to 70 wt.%. But a special attention was paid to the samples with 50 wt.% of TiO_2 nanoparticles, which are characterized by the strongest photochromic effect.

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The mixture obtained was placed between two glass plates covered by ITO from the inner side. The ITO layer was patterned to obtain two pixels independently switched and processed. For the reduction of edge effects, the protective grounded electrode was placed along the perimeter of a cell. The thickness of the obtained cell was fixed by a spacer tape at 20 μm. The cell was pressurized by an epoxy glue.

The mercury high-pressure lamp was used for the photopolymerization of samples. The irradiation was realized in two regimes with different irradiation doses. In regime 1, the samples were irradiated by $I = 20\,\mathrm{mW/cm^2}$ during 10 min. In regime 2, the intensity was $100\,\mathrm{mW/cm^2}$ and the irradiation time was 40 min. As earlier revealed [5], only regime 2 corresponds to photochromic changes in the composite.

The photopolymerization of samples was realized in the presence of an electric field and without it. Direct voltage was generated by a P4108 source of calibrated voltages. As a source of ac voltage, a sound generator was employed. The applied voltage was 100 V.

The dielectric properties of samples were measured in the frequency range 10^{-1}–10^{6} Hz by the oscilloscope method [9,10]. The measuring signal was delta-shaped, and its amplitude was 0.25 V. The temperature during the all measurements was 293 K. The experimental oscillograms (current vs. voltage dependences) allowed us to calculate the capacity and resistance of the investigated samples. Based on these data, one can calculate the real and imaginary parts of permittivity. These calculations were carried out assuming a uniform electric field in the volume of the cells.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Influence of an Electrical Field on the Parameters of Unpolymerized NOA65-TiO_2 Mixtures

The DC voltage was applied to the mixture “NOA65 pre-polymer-TiO_2 nanoparticles” (1:1). In the initially transparent mixture, the muddy light scattering structure is formed, when the field is switched-on (Fig. 1a). The muddy area is darker from the side of the cathode. By the microscopic observation, one can see a structural transition under the field action; the sample becomes optically non-uniform with the average size of non-uniformities of about 20 μm. This non-uniformity can be caused by the field-initiated transport of nanoparticles accompanied with their aggregation. The sample darkening near the cathode can be a result of the electrochemical reduction of titanium atoms obtaining electrons from the cathode. This is confirmed by the fact that the observed effect is very weak in the low-frequency field

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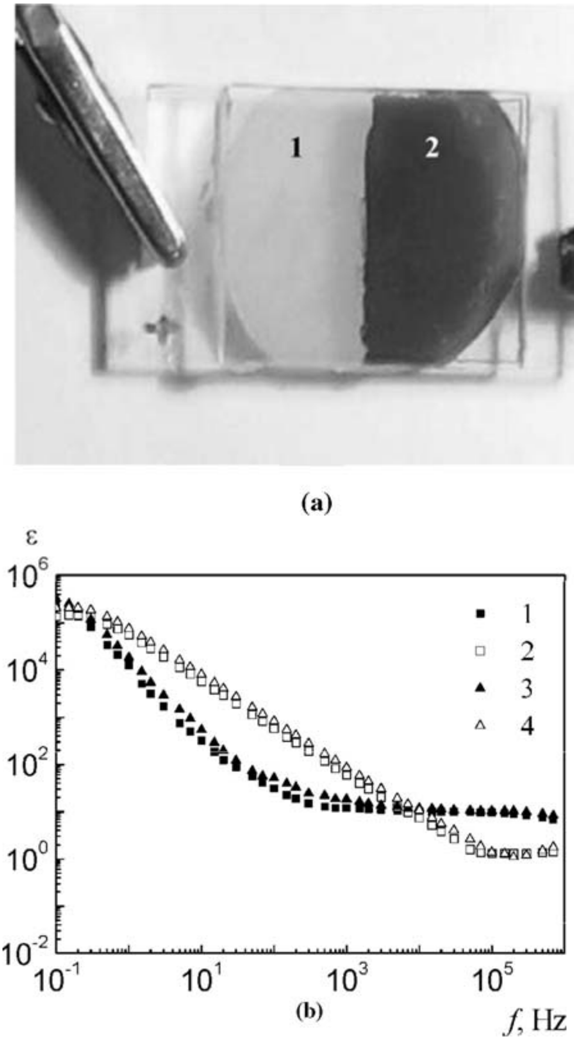

FIGURE 1 (a) Photograph of the NOA65 prepolymer-TiO_2 composite (1:1) cell: (1) unpowered area; (2) powered area (dc voltage, $U = 100\,V$, $t = 10\,min$); (b) Frequency dependences of the real $\varepsilon'(f)$ (curves 1 and 3) and imaginary $\varepsilon''(f)$ (curves 2 and 4) parts of the permittivity for the NOA65 prepolymer-TiO_2 composite (1:1). Curves 1 and 2 correspond to the unpowered state, while curves 3 and 4 correspond to the powered state.

($f < 100\,Hz$) and absent in the field of higher frequencies. All features of the discovered electrochromic effect will be separately considered in the forthcoming article.

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The frequency dependences of the real ε' and imaginary ε'' parts of permittivity before (curves 1, 2) and after (curves 3, 4) the application of a DC field are presented in Figure 1b. The character of these curves obeys the laws typical of weak electrolytes, particularly for liquid crystals [9–12] and water [13]. One can see that ε' and ε'' change with frequency essentially.

At low frequencies, the permittivities ε' and ε'' achieve values $\sim 10^5$. As shown in [9,10,12,13], these extremely high values are determined by the strong non-uniformity of the electrical field in a sample. Since the electrical charges accumulate near the electrodes forming double electrical layers, the electrical field is concentrated in the near-electrode volume of the mixture. The field uniformity increases with frequency because of a weaker influence of near-electrode charges.

In the medium frequency region (10–10^2 Hz), $\varepsilon'(f)$ is a power function, $\varepsilon' \sim f^{\alpha}$. It is evenly only for NOA65-TiO_2 composites, but not for pure NOA65. Probably, the dispersion of ε' is related to the dipole polarization of molecular groups adsorbed on TiO_2 nanoparticles.

The imaginary part of permittivity ε'' corresponding to the medium frequencies linearly decreases with the frequency. According to [14], such a dependence is typical of ionic conductivity and can be presented in the form

$$\sigma_i = \varepsilon_0 \varepsilon'' \omega, \tag{1}$$

where ε_0 – dielectric coefficient, and $\omega = 2\pi f$ – cyclic frequency.

Using (1), one can obtain that the conductivity before the field application is $3.2 \times 10^{-6}\,\mathrm{Ohm}^{-1} \times \mathrm{m}^{-1}$. After the application of dc voltage, the conductivity became $4.4 \times 10^{-6}\,\mathrm{Ohm}^{-1} \times \mathrm{m}^{-1}$. The growth in the conductivity might be connected with increase of the ion mobility caused by the aggregation of TiO_2 nanoparticles. Another reason is the dissociation of composite's molecules under the field action. This reason is however less probable, because the conductivity increase was not observed under the application of an alternative voltage (2 kHz).

3.2. Influence of an Electric Field on the Formation NOA65-TiO_2 Composites in the Case of Small Irradiation Doses

Let us consider the peculiarities of the photopolymerization in the composite NOA65-TiO_2 (1:1) under the action of small UV irradiation doses (regime 1) and a direct field. In this case, the transport of nanoparticles under the dc voltage is complicated due to an increase of the viscosity of the mixture. So the structural transition and aggregation of nanoparticles are considerably weaker (Fig. 2a).

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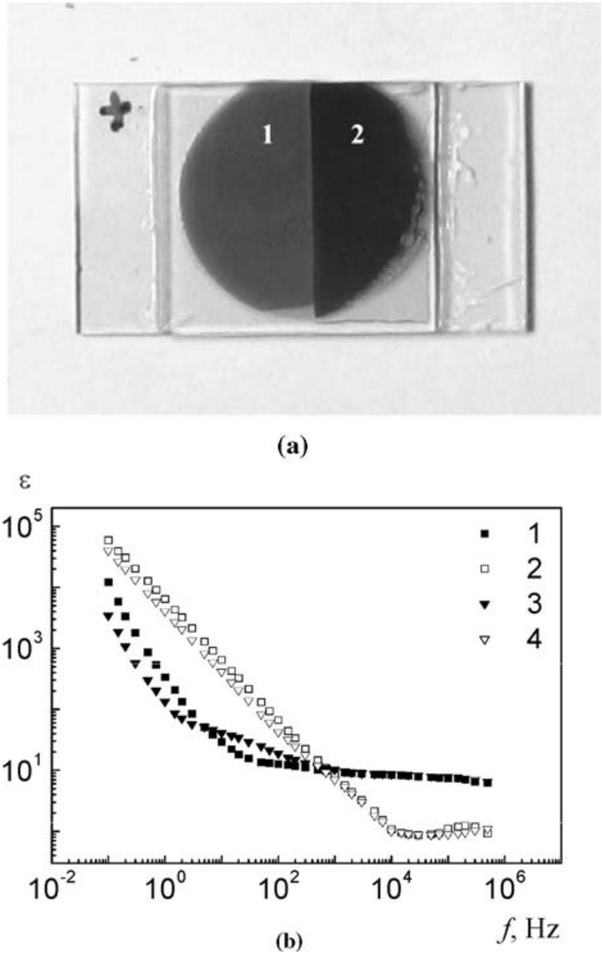

FIGURE 2 (a) Photograph of the NOA65-TiO_2 composite (1:1) cell: (1) unpowered area polymerized in regime 1 (UV intensity $I = 20\,\mathrm{mW/cm^2}$, $t = 10\,\mathrm{min}$); (2) powered ($U = 100\,\mathrm{V}$, $t = 10\,\mathrm{min}$) area polymerized in regime 1; (b) Frequency dependences of the real $\varepsilon'(f)$ (curves 1 and 3) and imaginary $\varepsilon''(f)$ (curves 2 and 4) parts of the permittivity for the NOA65-TiO_2 composite (1:1). Curves 1 and 2 correspond to the unpowered state polymerized in regime 1, while curves 3 and 4 correspond to the powered state polymerized in regime 1.

The frequency dependences of ε' and ε'' for the NOA65-TiO_2 (1:1) sample irradiated in regime 1 under the action of a dc electric field and without field are presented in Figure 2b. The real part of the permittivity, ε', similarly to the previous case, is a power function of the frequency of the testing field. However, the value of α is slightly higher than in the case of a non-irradiated sample. The $\varepsilon''(f)$ curve for the part of a sample hardened under the direct field action has two regions differently inclined to the horizontal level (Fig. 2b, curve 3). Such a behavior implies two types of electric polarization: one of them can be attributed to TiO_2 nanoparticles, while the second one to NOA65 molecules.

On the basis of Eq. (1), one can obtain that sample's parts hardened under the action of direct field and without field have conductivities $2.1 \times 10^{-7}\,\mathrm{Ohm}^{-1} \times \mathrm{m}^{-1}$ and $3.6 \times 10^{-7}\,\mathrm{Ohm}^{-1} \times \mathrm{m}^{-1}$, respectively. In contrast to the case described in Section 1, the application of an electrical field during the photopolymerization leads to a decrease in the conductivity.

In what follows, we also consider the case where a dc electric field is applied 10 min before the photoirradiation. It is obtained that the conductivity of the NOA65-TiO_2 (1:1) sample irradiated after the application of a direct field was 3.5 times smaller than the conductivity of the sample hardened without field. Thus, the difference in the conductivities of the parts subjected to the action of the electric field/irradiation and only irradiation is even higher than that in the previous case when the field and light acted simultaneously.

The lower conductivity of the sample parts polymerized under the field is due to a diminution of the number of ions because of the phase separation making the polymer composition purer. Consequently, the photoconversion rate increases. The growth of the molecular mass and viscosity prevents the migration of nanoparticles. Therefore, the conductivity decrease is stronger for the samples affected by a DC voltage *before* the irradiation than that for the samples subjected to the action of a dc field and light *simultaneously*.

3.3. Influence of an Electrical Field on the Formation NOA65-TiO_2 Composites in the Case of High Doses of UV Irradiation

In the case of irradiation in regime 2, color of the composite becomes dark blue (Fig. 3a), similarly to our earlier observations [5]. The following difference between the powered and unpowered parts was observed:

1. The sample obtains dark color sooner if it is irradiated from the cathode side.
2. Even in the case of irradiation from the anode side, the color is more saturated from the cathode side.

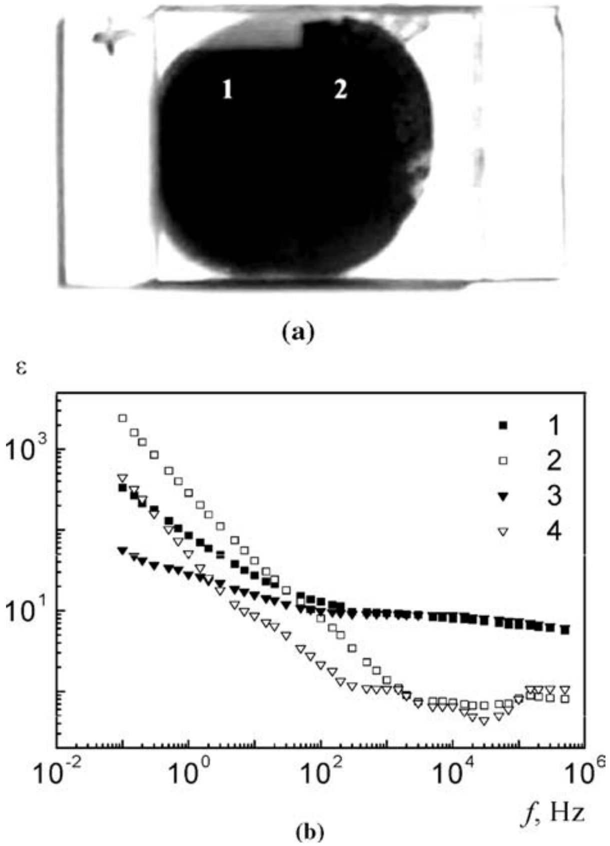

FIGURE 3 (a) Photograph of the NOA65-TiO_2 composite (1:1) cell: (1) unpowered area polymerized in regime 2 (UV intensity $I = 100\,\mathrm{mW/cm^2}$, $t = 40\,\mathrm{min}$); (2) powered ($U = 100\,\mathrm{V}$, $t = 40\,\mathrm{min}$) area polymerized in regime 2; (b) Frequency dependences of the real $\varepsilon'(f)$ (curves 1 and 3) and imaginary $\varepsilon''(f)$ (curves 2 and 4) parts of the permittivity for the NOA65-TiO_2 composite (1:1). Curves 1 and 2 correspond to unpowered state polymerized in regime 2, while curves 3 and 4 correspond to powered state polymerized in regime 2.

3. After the strong UV irradiation without electric field, the dark color of a sample retains during 1–3 days. In contrast to this, after the application of a direct field during the hardening, the dark color of a sample retains during several months and longer.

The first two features suggest that the photochromic effect is enhanced by the electrochromic one. According to the scheme of photochemical transformations proposed in [5], titanium recovers from the IV to III valency state accepting one electron from environmental atoms. Near the cathode, this photochemical process is enhanced by the electrochemical one, when titanium obtains an electron from the cathode. Because of this, the coloring effect is stronger near the cathode. The different stability of coloring changes in the powered and unpowered pixels might be caused by different relaxation rates of the photochromic and electrochromic processes.

The results of dielectric studies for the sample irradiated in regime 2 (high power irradiation) are presented in Figure 3b. Curves 1 and 2 correspond to the unpowered part of the sample, while curves 3 and 4 correspond to the sample part photopolymerized under a DC field. Same as at the low-power irradiation, $\varepsilon'(f)$ curves can be considered as a sum of two power functions. But the frequency dependences of ε' and ε'' are rather weak in contrast to the cases considered before. In turn, the difference in the dielectric constants of the samples hardened under the action of an electric field and without field is the largest.

As one can see from Figure 3b, the dependence $\varepsilon''(f)$ is essentially non-linear. Therefore, to estimate the value of ionic conductivity, we took that the magnitude of ε'' corresponded to the lowest measured frequency (10^{-1} Hz). It was obtained that the ionic conductivity of the sample part hardened under the action of a direct field is 6.3 times smaller than the conductivity of the part hardened without field. Qualitatively, this result agrees well with the results earlier described for low-power irradiated samples.

Interestingly, two weeks after the irradiation, the conductivity of the samples polymerized in regime 1 becomes close to the conductivity of mixtures polymerized with high-intensity light (regime 2). This means that the gradual hardening of samples continues even after the irradiation so that the system approaches the balanced state.

4. CONCLUSIONS

The influence of an electrical field on the coloring, structure, photopolymerization, and electric properties of the composite system consisting of commercial photopolymer NOA65 and TiO$_2$ nanoparticles is considered. It is determined that the direct and low frequency alternate fields increase the ionic conductivity of the non-hardened composite and result in the formation of light scattering structures caused by the phase separation.

Under the action of UV irradiation, the conductivity decreases, but this occurs faster for the composites photopolymerized in the presence

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of a direct electrical field. This suggests a higher degree of polymerization in the field due to the separation processes, in the course of which the polymer releases from TiO_2 particles inhibiting the polymerization.

It is experimentally shown that the direct electrical field causes the recovery of titanium from the IV valency to the III valency state due to the electron transfer from the cathode to titanium atoms. Such a recovery is accompanied by the color change more pronounced in the near-cathode area. Under the action of UV light, this electrochromic effect superposes with the photochromic one earlier described in [5]. The relaxation characteristics of the photochromic and electrochromic effects seem to be different.

The observed coloring effects are rather interesting for information displays and information storage systems. Our further efforts will be directed to the system optimization in order to enhance the contrast and switching characteristics of the potential devices.

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