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The Peculiarities of Photopolymerization in the Composite “Pre-polymer–TiO₂ Nanoparticles”

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The photo-conversion of pre-polymer mixture NOA65 (Norland, USA) doped with TiO₂ nanoparticles is studied by the method of dielectric spectroscopy. The photopolymerized composites show low frequency relaxation and ion conductivity typical for liquids. This is explained by the reaction of TiO₂ particles with components of NOA65 mixture that blocks photopolymerization of pre-polymer and increases concentration of ion carriers. In addition, strong photochromism of NOA65-TiO₂ composites is observed which makes this system quite attractive for non-linear optics and associated applications. It may be caused by formation of titanium mercaptide and its transfer from IV to III valency state under UV irradiation.

Keywords: dielectric permittivity; monodispersed nanoparticles; nanocomposite; photopolymer; titanium dioxide

1. INTRODUCTION

Per last years composite materials attract the rapt attention both in industry applications and in science. In these materials there is the possibility to combine mechanical, electric and optical properties of constituent components in one sample. From optical point of view, several fascinating properties of these composites can be obtained. First, addition of non-organic nanoparticles allows to extend drastically the

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refractive index range of polymers [1–3]. Second, as it is shown in Ref. [4], oriented arrays of metallic nanoparticles in polymer matrices may be used as color filters for polarized light. Third, the organic films doped with metallic or semiconductor nanoparticles are perspective materials for non-linear optics and associated applications [5–8]. At last, optical properties of nanoparticle doped polymers determine performance of polymer – nanoparticles – liquid crystal (LC) composites working in electrically controlled light scattering mode promising for display technologies [9].

In the cases when the polymer-nanoparticles composites are formed through the polymerization of pre-polymer, it is important to know, how nanoparticles influence on the polymerization process and general stability of the composites. We consider these questions in the present work.

Choosing the proper methods for the studies of polymerization we refused optical methods sensitive to optical homogeneity of the composites. Instead of them we selected dielectric spectroscopy sensitive to non-polymerized portion of pre-polymer. This liquid fraction of the composite results in ion current much higher than electronic current through the particles-polymer interface. In inhomogeneous mediums, the electronic conductivity has hopping character and stay in power dependence from frequency [10]. In contrast, the ion conductivity of liquid fraction does not depend on the field frequency [11,12]. This allows us to extract ion component of current from the general current of the composite. Assuming that this value is proportional to polymerization rate we judge about the efficiency of pre-polymer conversion for various contents of filler in the composite.

2. MATERIALS AND METHODS

As photo-polymerizing material we have been used commercial photo-curable mixture NOA65 from Norland Inc. (USA) [13]. It is transparent glue widely used in assembling of liquid crystal (LC) displays. Besides, this mixture is suitable for the preparation of LC – polymer composites also promising for the technologies of LC devices [9,14]. NOA65 includes three monomer constituents: trimethylolpropane diallyl ether, trimethylolpropane trithiol, and isophorone diisocyanate ester [15,16]. In the initial state, it is transparent, liquid and viscous mixture.

As filler we have been mainly used nanoparticles of TiO_2 with a size of primer particle of 5–10 nm. Some samples were made of nanoparticles of Sb_2O_5 and SiO_2 (size of primer particle 7–11 nm and 10–20 nm, respectively). TiO_2 nanoparticles were obtained from ANP Ltd.

(Korea) as colloidal dispersion in ethanol. The Sb_2O_5 and SiO_2 nanoparticles were provided by Nissan Chemicals Industries Ltd. (USA) as colloidal dispersions in methanol.

To prepare composites, the colloid solution was added to NOA65. The components were thoroughly mixed. Over this process, the alcohol was evaporated. For complete removal of alcohol the mixture was vacuumed at 10^{-2} Torr. A nanoparticles content in the composites was varied in the range of 5–50 wt. %

In contrast to colorless composites based on Sb_2O_5 and SiO_2 nanoparticles, the composites containing TiO_2 particles appeared yellow colored. This may be caused by chemical reaction of trimethylolpropane tristiol from pre-polymer NOA65 with TiO_2 filler (Fig. 1). The product of this reaction is titanium mercaptide, which has yellow appearance.

The suspension was placed between two glass substrates covered with ITO layers from the inner side. The cell gap was fixed by 100 μm spacer strips. The substrates were pressed and glued by an epoxy glue. For reduction of the edge effects in the dielectric studies, ITO layers were patterned, in order to have protective electrode along perimeter of cell. This electrode was earthed during measurements.

The photopolymerization in the samples was realized by irradiation with a high-pressure mercury lamp (50 mW/cm^2 , 10 min); the samples were irradiated 5 min from each side. After dielectric measurements

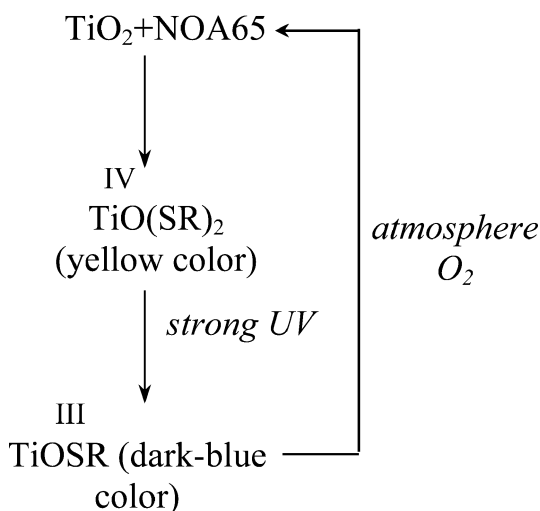


FIGURE 1 Scheme demonstrating most probable reactions in NOA65- TiO_2 composites.

were completed, the samples (or part of the samples) were irradiated with the more intensive light (100 mW/cm^2) during 20 min. In the strongly irradiated area, the color was changed from yellow to dark-blue (Fig. 2).

This photochromic effect for TiO_2 containing composites was earlier described in References [17,18]. It is caused by the transition of the Ti atoms from IV to III valency state. In our system, the photochromism may be caused by titanium mercaptide transfer from IV ($\text{TiO}(\text{SR})_2$) to III (TiOSR) valency state under the action of powerful UV light (Fig. 1). Due to oxidation, titanium III slowly returns back to titanium IV state, and so photochromic transition is reversible. In our samples, the time of photochromic relaxation was about several days. But non-sealed composite films were returned to IV valency state during 1 hour.

To evaluate the efficiency of photochromic changes in our composition, we prepared polymer- TiO_2 composites based on other polymers: polymethylmethacrylate, polystyrene, and polyvinylcinnamate. We revealed that photochromic effect in these composites is much weaker than in NOA65- TiO_2 samples. The photochromic changes in the samples based on Sb_2O_5 particles were rather poor, while in the SiO_2 containing composites they were not detected at all. This implies that, first, the observed photochromism is attributed to the photochemistry of titanium containing compounds and, second, NOA65 composition suits perfectly to TiO_2 particles to realize highly effective photochromic system.

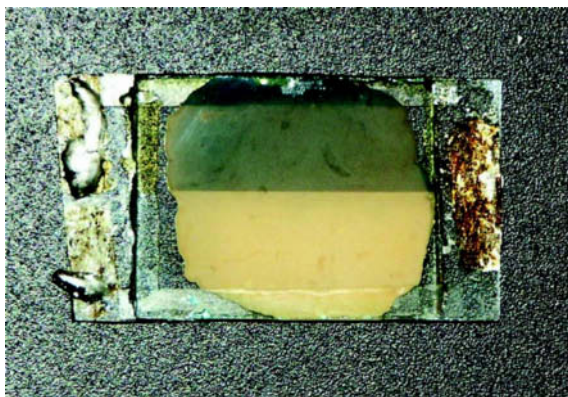


FIGURE 2 The photograph of NOA65- TiO_2 sample ($c_{\text{TiO}_2} = 50 \text{ wt.}\%$). The whole sample is cured with full spectrum irradiation of mercury lamp (50 mW/cm^2 , 10 min). Hereafter, the part of sample (upper part in Fig. 2) is subjected to stronger dose of the same light (100 mW/cm^2 , 20 min). One can see the change of color from yellow (bright section) to dark blue (dark section) in the strongly irradiated area.

Dielectric properties of samples were measured in frequency range 10^{-2} – 10^6 Hz by oscilloscope method [19,20]. The measured signal was delta shaped with a maximum value of 0.25 V. All measurements were carried out at 293 K. We defined capacity C and resistance R of samples by analysis of the oscillogram obtained. Knowing C and R, we calculated real ϵ' and imaginary ϵ'' parts of dielectric permittivity. In these calculations, the electrical field along the thickness of the sample was considered as homogeneous. The dielectric measurements were carried out for the samples before irradiation, as well as after moderate (50 mW/cm^2 , 10 min) and strong (100 mW/cm^2 , 20 min) irradiation.

3. EXPERIMENTAL RESULTS

Let us first consider the results obtained for the samples irradiated with the light of moderate intensity (50 mW/cm^2). Figure 3 shows frequency dependences $\epsilon'(f)$ and $\epsilon''(f)$ for the composites with 5 wt.% and 50 wt.% of TiO_2 respectively. In both cases the dependence $\epsilon''(f)$ contains a part where ϵ'' linearly decreases with the frequency growth. This means that conductivity does not depend on the field frequency. Such behavior is typical for the ion conductivity of liquids [10,11].

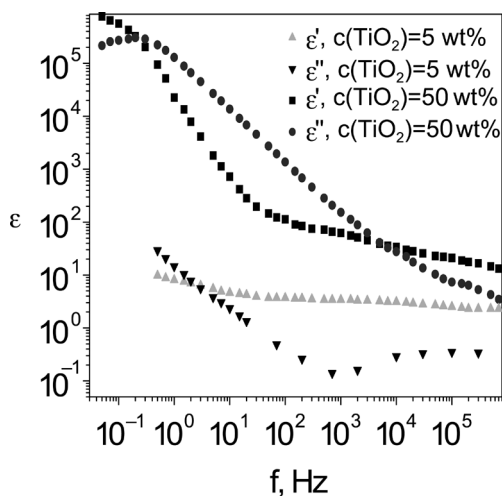


FIGURE 3 Frequency dependences of real $\epsilon'(f)$ and imaginary $\epsilon''(f)$ parts of dielectric permittivity for the composites of NOA65 filled with 5 and 50 wt.% of TiO_2 nanoparticles. The hardening of pre-polymer is initiated by full spectrum irradiation of mercury lamp (50 mW/cm^2 , 10 min).

In the discussed linear part, sample conductivity can be expressed as

$$\sigma \approx \sigma_i = 2\pi\epsilon_0\epsilon''f \quad (1)$$

where ϵ_0 is dielectric constant.

Figure 4 shows σ_i as a function of TiO_2 concentration in the composite for the samples polymerised with moderate UV light. Evidently, the increase of TiO_2 content results in the linear growth of the ion conductivity of the composites – from $\sigma_i = 4.7 \times 10^{-9} \text{Ohm}^{-1} \times \text{m}^{-1}$ at 5 wt.% of TiO_2 to $\sigma_i = 7.6 \times 10^{-6} \text{Ohm}^{-1} \times \text{m}^{-1}$ at 50 wt.% of TiO_2 filler.

The conductivity of pure NOA65 mixture was also measured. Before irradiation, the value $4.5 \times 10^{-8} \text{Ohm}^{-1} \times \text{m}^{-1}$ was obtained. However, for UV cured NOA65 samples the ion conductivity was not revealed. This gives us a ground to believe that big conductivity of the UV cured NOA65- TiO_2 samples is caused by incomplete polymerization of some reactive components. The possible reasons of this process are discussed below.

As one can see from Figure 3, at high frequencies of the applied field, $\epsilon''(f)$ curve becomes non-linear. This may be caused by the electronic conductivity of hopping type, σ_e , through the particles of TiO_2 . According to Reference [12], this conductivity obeys the law:

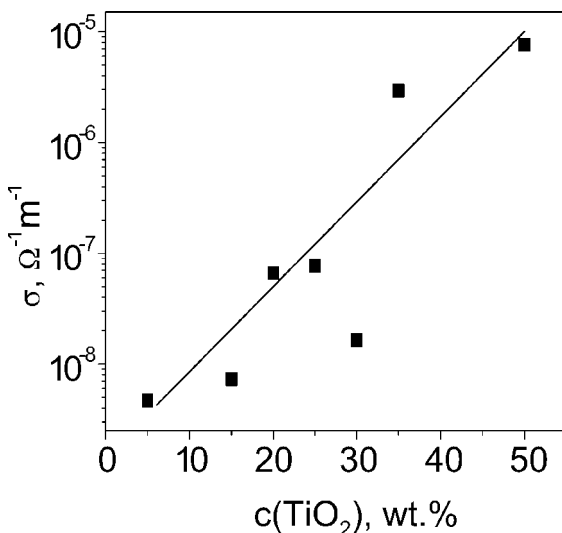


FIGURE 4 Ionic part of composite's conductivity vs. concentration of TiO_2 nanoparticles. The hardening of pre-polymer in all samples is realized by full spectrum irradiation of mercury lamp (50 mW/cm², 10 min).

$$\sigma_e = kf^m \quad (2)$$

where k is coefficient of proportionality, $0 < m < 1$.

If electronic and ionic conductivities are independent from each other and additivity principle for them in the respective frequency region is correct, ε'' based on (1)–(2) can be expressed as:

$$\varepsilon'' = \frac{\sigma_i + kf^m}{2\pi\varepsilon_0 f} \quad (3)$$

The function $\varepsilon''(f)$ has maximum. In agreement with this, the $\varepsilon''(f)$ curve experimentally obtained for the composite with 5 wt.% of TiO_2 also goes through maximum (Fig. 3). This may be one more proof of the correctness of our interpretation.

Finally, let us explain low relaxation process observed in Figure 3. The $\varepsilon''(\varepsilon')$ plots (Cole-Cole diagrams) for NOA65- TiO_2 samples are fitted well with the arch curves.

According to Reference [21], this relaxation corresponds to the charge exchange on the electrode-liquid interface. It obeys Debye's law:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (2\pi i f \tau)^{1-\alpha}} \quad (4)$$

where ε^* is the complex dielectric permittivity, ε_s and ε_∞ are the values of dielectric permittivity for the frequencies $f = \infty$ and $f = 0$ correspondingly, τ is dielectric relaxation time, and α is Cole-Cole parameter. For the composite doped with 50 wt.% of TiO_2 (Fig. 1) one can obtain $\varepsilon_\infty = 9.5$, $\varepsilon_s = 5.0 \times 10^5$, $\tau = 0.83$ s and $\alpha \approx 0.07$.

The high values of permittivity ($\varepsilon' > 10^5$) in the low frequency region might be caused by the non-uniform distribution of electrical field, because of blocking the electro-chemical processes of charge exchange at the interfaces [20,22]. Assuming that electric field is applied mainly to anode [20,22] and taking into account the approximation made in References [23,24] one can calculate thickness of the near-electrode charge exchange layers, d_e :

$$d_e = d \frac{\varepsilon_\infty}{\varepsilon_s} \quad (5)$$

where d is the thickness of the sample. For NOA65- TiO_2 composite with 50 wt.% of TiO_2 formula (5) gives $d_e \approx 2$ nm. It is in agreement with data earlier obtained for other liquids [22,25].

The strong irradiation with a mercury lamp (100 mW/cm², 20 min) resulted in decrease of ion conductivity by factor 4–5 as compared with the moderate irradiation (50 mW/cm², 10 min). The exception is only sample with small concentration of TiO_2 (5 wt.%) for which no any

substantial change of sample conductivity is detected. This means that practically for all concentrations the conductivity of NOA65-TiO₂ composites does not approach the conductivity of pure NOA65, even for strong irradiation doses.

4. DISCUSSION

As we already mentioned in Section 3, the reason for the ion conductivity in our composites is the existence of liquid phase. This liquid can be a fraction of pre-polymer, which did not converse due to photo-irradiation. Several processes can be responsible for the incomplete photoconversion. One of them is non-uniform irradiation, when exciting UV light is mainly absorbed and scattered at the boundaries of the composite layer. In this case pre-polymer should be effectively converted in polymer at the boundaries, while the conversion in a bulk should be poor. However, if this mechanism plays decisive role, we should not detect layers of the non-reacted liquid at the electrodes (i.e., boundaries of the composite layer).

The second, more probable reason for existence of the liquid phase is blocking of photopolymerization of NOA65 by TiO₂ nanoparticles. As we believe, trimethylolpropane trithiol, one of the NOA65 components, reacts with TiO₂ phase and so is excluded from the polymerization process. This may result in non-polymerized fraction of NOA65. Naturally that increase of the content of TiO₂ particles in the composites should increase the fraction of non-hardened liquid monomers remained after irradiation. The particles should block pre-polymer conversion both in polymer bulk and on the polymer surface. Due to the latter fact we can detect the near-electrode layers typical for liquids.

It is noteworthy to admit that, before irradiation, the conductivity of NOA65-TiO₂ composites is higher then conductivity of pure NOA65 mixture. With irradiation, the conductivity of NOA65-TiO₂ composites reduces. At $c_{\text{TiO}_2} > 15 \text{ wt.}\%$ it remains, however, higher then conductivity of pure NOA65. For instance, the conductivity of NOA65-TiO₂ composite (20 wt.% of TiO₂) before and after irradiation is, respectively, $1.2 \times 10^{-5} \text{ Ohm}^{-1} \times \text{m}^{-1}$ and $6.6 \times 10^{-8} \text{ Ohm}^{-1} \times \text{m}^{-1}$. For comparison, the conductivity of pure NOA65 mixture is $4.5 \times 10^{-8} \text{ Ohm}^{-1} \times \text{m}^{-1}$. These results suggest that some amount of ions giving a rise of the ion conductivity in composites appear in the process of chemical reaction of NOA65 components with TiO₂. Thus, reaction of TiO₂ phase with NOA65 results in both blocking of polymerization and generation of ions leading to increase of the composite's conductivity.

The increase of conductivity of NOA65 can be initiated also with other types of particles. For instance, we detected substantial increase

of conductivity by adding particles of Sb_2O_5 . Similarly to TiO_2 based composites, this may be evidence of reactivity of Sb_2O_5 particles with some components of NOA65 mixture. By contrast, SiO_2 particles do not change substantially conductivity of pre-polymer that implies that SiO_2 surface is inert with regard to components of NOA65. These results show that dielectric method applied is quite universal and can be used for other types of composites to evaluate conversion rate of pre-polymer and its ability to react with nanoparticles.

CONCLUSIONS

It is shown that dielectric spectroscopy can be successively used to study the process of photo-polymerization in the photo-curable pre-polymers and their composites with non-organic nanoparticles. In case of incomplete photoconversion, liquid fraction of pre-polymer becomes apparent in the appearance of low frequency relaxation and substantial increase of ion conductivity. In case of the composites, the incomplete conversion of pre-polymer can be explained by the reaction of nanoparticles with pre-polymer's components that excludes some reactive ingredients thoroughly balanced from the polymerization process. These reactions can also increase concentration of ion carriers in the composition. The suggested model, of course, needs some additional experimental proofs. In progress are infrared spectroscopy studies for the NOA65- TiO_2 composites to prove chemical reactions assumed in the present work.

The influence of nanoparticles on the conversion rate of pre-polymers should be taken into account by preparation of pre-polymer – nanoparticles composites. Besides, this effect may substantially influences properties of liquid crystal – pre-polymer – nanoparticles composites recently suggested as a new medium for the electrooptic devices on a LC base [9].

For NOA65- TiO_2 composites strong photochromic effect is observed. The formation of titanium mercaptide and its transfer from IV to III valency state under UV irradiation might cause high efficiency of this effect. The strong photochromism makes NOA65- TiO_2 composites rather attractive for non-linear optical applications.

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