Improvement of the photoinduced birefringence in PAZO azopolymer doped with ZnO via electrospray deposition

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Abstract. We present a study of the birefringence photoinduced in thin nanocomposite films of an azopolymer (PAZO) doped with different concentrations of nanoparticles (NPs) of ZnO with spherical shape and size in the range 40 – 100 nm. The nanocomposite thin films were prepared by electrospray deposition of ZnO over a thin azopolymer film with a thickness below 200 nm. The different NPs concentrations were obtained through different electrospray deposition times varied from 0 to 10 minutes. Birefringence was induced by a He-Cd laser at a wavelength of 442 nm and measured by a probe diode pumped solid state (DPSS) laser at 635 nm. The birefringence dependence on the ZnO NP deposition time reached its maximum for a deposition time of 90 s.

1. Introduction

Azopolymers are known as very efficient materials for polarization recording [1-3]. One of the most important parameters of azopolymers is the photoinduced birefringence \( \Delta n \), defined as the difference between the component of the refractive index perpendicular to the polarization of the recording beam and the component parallel to it. It arises as a result of the trans-cis-trans isomerization and reorientation of the molecules under illumination with a linearly polarized light. This effect allows a variety of applications, for example in the field of polarization holography [4-6]. Obtaining high photoinduced birefringence in these materials is of crucial importance in the further development of polarization holography and creation of unique polarization optical devices [7-9].

In this article we present a study of the photoinduced birefringence in nanocomposite films of a PAZO azopolymer doped with ZnO nanoparticles (NPs). Our recent investigations on similar nanocomposites with ZnO, goethite, silica and TiO_2 NPs have shown an increase of the birefringence of the nanocomposites compared to the non-doped samples [10-13]. These results encouraged us to continue studying similar nanocomposites. Earlier, we have prepared the azopolymer nanocomposites by dispersing the NPs in an azopolymer solution and then spin-coating the suspension. In the present work, we used another method of embedding NPs in an already spin-coated thin film of the azopolymer – electrospraying ZnO on the azopolymer film surface for different deposition times [14-16].

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2. Experimental part

2.1 Preparation of the thin azopolymer films

The azopolymer used in the present study was PAZO (poly[1-{4-(3-carboxy-4-hydroxyphenylazo)benzene-sulfonamido]-1,2-ethanediyl, sodium salt), which we selected as it is commercially available, soluble in water, methanol etc., stable up to 300 °C and has high birefringence. Its chemical structure is shown in figure 1.

In order to produce samples with different concentrations of ZnO, we followed a two-step procedure. Initially, we produced thin layers of PAZO and then we added the ZnO nanoparticles via an electrospray technology. In the first step, we prepared an azopolymer solution in distilled water with a concentration of 50 mg/ml and then deposited 200 µl of the solution on a glass substrate (BK7).

According to our previous research [17], the expected thickness of the film spin-coated at 1500 rpm was 130 – 150 nm. Our aim was to obtain samples with a low thickness, in order to allow the ZnO NPs to penetrate into the sample during the electrospraying procedure and be evenly distributed in the volume of the film.

2.2. Electrospraying procedure

The Zn precursor was prepared by dissolving 0.400 g of zinc acetate dehydrate in 1.8 ml of deionized water. After 30 min of vigorous stirring, 12 ml of ethanol were added followed by few drops of acetic acid for clearing the solution. The solution was stirred for 2 hours and aged for 24 h at room temperature. The ZnO nanoparticles were deposited on the polymer surface by electrospraying using a vertical setup [15, 16]. The distance between the emitter and collector was 6 cm and a high voltage of 18 kV with positive polarity was applied by a DC power supply (Applied Kilovolts, UK). A syringe pump fed the solution continuously to the emitter. The glass substrate covered with the thin PAZO film was placed on the grounded collector; the spraying started when a temperature of 300 °C was reached. In order to obtain different ZnO phase concentrations, different deposition duration in the range 60 s – 10 min were used. A scanning electron microscope (SEM, Philips 515, 30 kV accelerating voltage) was used for characterization of the films’ surface morphology.

2.3. Birefringence measurement

The photoinduced birefringence was calculated using the following equation [2, 13]:

\[ \Delta n = \frac{\lambda}{2nd} \tan \left( \frac{S_3}{S_2} \right), \]

where \( S_3 \) and \( S_2 \) are the Stokes parameters, \( \lambda \) is the wavelength of the probe laser and \( d \) is the thickness of the sample. The film thickness was determined using a Talystep profilometer; it was in the range 120 – 160 nm for all samples.

The photoinduced birefringence was measured by the polarimetric setup shown in figure 2. A He-Cd laser (Kimmon Koha) emitting vertically polarized light at 442 nm (\( I_{442} = 500 \text{ mW/cm}^2 \)) was used as a pump laser. To measure the photoinduced birefringence, a probe beam linearly polarized at 45° was used emitted by a DPSS laser (B&W TEK) at 635 nm (\( I_{635} < 50 \text{ mW/cm}^2 \)). It was steered through the pump laser spot on the sample (approximate spot area of 0.2 cm²); the Stokes parameters of the output beam were measured in real time by a PAX5710 polarization analyzing system (Thorlabs).

The experimental procedure for every sample was the following: 60-s measurement of the probe laser signal before starting the pump laser. At that moment, the film is isotropic because the azomolecules are oriented randomly. Then, the pump laser is turned on to illuminate the sample. When the pump laser is turned on, the processes of trans-cis-trans isomerization and reorientation of the
azomolecules begin; since these processes depend on the angle between the axis of the azo chromophore and the polarization of the laser, the birefringence starts increasing. After 240 s saturation is reached, all molecules are reoriented and the processes of isomerization stop. From this point on, the experiment continues with 300-s relaxation after the pump laser is turned off. Using equation (1), we calculated $\Delta n(t)$ and determined the maximal photoinduced birefringence ($\Delta n_{\text{max}}$).

![Figure 2. Experimental setup for measuring the birefringence.](image)

1 – probe laser, $\lambda = 635$ nm; 2 – pump laser, $\lambda = 442$ nm; 3 – polarizer, oriented at 45°; 4 – vertical polarizer; 5 – sample; 6 – polarimeter.

3. Results and discussion

SEM images of the PAZO polymer surface covered with ZnO nanoparticles sprayed for 300 s are shown in figure 3. It is seen that at this deposition time the ZnO particles are organized in micron-sized areas randomly spread over the surface. A closer look shows that each area comprises particles with spherical shapes and sizes in the range 40 – 100 nm. As the deposition time is increased, the distance between the ZnO areas decreases and the surface of polymer becomes more homogenously covered. Because of the high voltage (18 kV) used in the electrospraying deposition, we assume that some particles penetrate through the surface and become partially or fully embedded in the azopolymer.

![Figure 3. SEM image of PAZO sample surface with electrosprayed ZnO particles (a) and selected area with a magnified view of the surface (b).](image)

![Figure 4. Birefringence kinetics of the samples obtained at different electrospraying times: 0 – 10 min (a), and 60 – 120 s (b).](image)
Figure 4(a) shows the birefringence curves recorded for polymer samples doped with ZnO nanoparticles sprayed for different durations from 2 to 10 minutes. The samples are always isotropic at the start of the experiment. As seen, the highest maximal birefringence is that of the sample electrospayed for 2 minutes. Longer electrospaying times lead to a decrease in the $\Delta n_{\text{max}}$. We thus decided to produce another series of samples with electrospaying time between 1 and 2 minutes. The results for these samples are shown in figure 4(b). The highest birefringence is exhibited by the sample doped through ZnO electrospaying for 90 s. The results for all spraying durations are summarized in figure 5, where the maximal birefringence values are plotted as a function of the spraying time. As seen, the optimal spraying time is 90 s, as this spraying duration results in the highest birefringence value.

4. Conclusions
The kinetics of photoinduced birefringence are measured for a series of nanocomposite films obtained by electrospaying ZnO over a spin-coated layer of an azopolymer. The dependence of the saturated value of the birefringence on the electrospaying time is determined; it is found that the optimal time for deposition of ZnO NPs by electrospaying is 90 s. In this case, $\Delta n_{\text{max}} = 0.083$, which corresponds to an increase in the birefringence of more than 25% compared to the film that was not electrospayed.

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