Enhanced photoanisotropic response in azopolymer doped with elongated goethite nanoparticles

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Abstract: We present a study of the photoinduced birefringence in nanocomposite films of an azopolymer (PAZO) doped with goethite (α-FeOOH, a characteristic antiferromagnetic material) nanoparticles (NPs). The NPs had an elongated shape with a size 15×150 nm, i.e., a ratio of 1:10. Samples were prepared with different concentrations of the NPs in the azopolymer varying from 0\% (undoped azopolymer film) to 15 wt \%. An unusual dependence of the birefringence on the concentration was observed – two peaks of enhancement at 1\% and at 10\% concentration. Our previous studies on ZnO and SiO\textsubscript{2} NP have indicated only one peak of increase at low concentrations – 0.5 wt \% and 2 wt \%, respectively. This effect could be related to the elongated shape of the nanoparticles and the presence of two characteristic NPs sizes – 15 and 150 nm. Moreover, the birefringence increase for the samples with 10 wt \% NPs concentration (compared with the non-doped samples) was rather significant – nearly 70\%.

1. Introduction
Azobenzene and its numerous derivatives, including azopolymers, are well-known as one of the most efficient media for polarization recording [1,2]. One of the most significant optical characteristics of the azopolymers is the birefringence \(Δn\) that can be induced in them upon illumination. This is 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 \(Δn = n_\perp - n_\parallel\).

Recently it has been reported that nanocomposites based on an azopolymer and inorganic dopants – silver nanoparticles [3], ZnO NP with different sizes [4,5], as well as silica NPs [6] – show an increased birefringence compared with the non-doped azopolymer. In all of these studies, however, nanoparticles with spherical shape have been used which possess only one characteristic dimension – their diameter.

In order to establish the influence of the shape of the nanoparticles on the birefringence enhancement, we studied the photoinduced birefringence in nanocomposite films of an azopolymer doped with elongated nanoparticles (nanorods) of the magnetic material goethite (α-FeOOH) in

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concentrations varying from 0 wt % (pure azopolymer) to 15 wt %. The nanorods had dimensions 15×150 nm, i.e. a ratio of 1:10.

2. Experimental results and discussion

2.1. Samples preparation

In the present study we used the commercially available azopolymer poly[1-4-(3-carboxy-4-hydrophenylazo) benzensulfonamido]-1,2-ethanediyl, sodium salt] (Sigma Aldrich) or PAZO, for short. Its chemical structure is shown in figure 1(a). An aqueous dispersion of goethite nanorods was synthesized by co-precipitation of ferrous and ferric ions solutions at acid pH (pH<4) [7]. 20 mL of aqueous 1 M FeCl$_3$ and 5 mL of 2 M FeSO$_4$·7H$_2$O in 1.3 M HCl were simultaneously injected into 250 mL of 0.4 M NH$_4$OH under rapid mechanical stirring. Stirring was allowed to continue for 30 min, and then the yellow-brown solid product was allowed to precipitate. The sediment was redispersed in 50 mL distilled water, and subsequently three 30 mL aliquots of tetramethylammonium hydroxide solution (1 M) in 50 mL of water were added, again with rapid stirring. Finally, water was added to the dispersion up to a total volume of 250 mL. Figure 1(b) shows a transmission electron microscope (TEM) image of the goethite NPs used in the experiments. Their dimensions were 150±40 nm by 15±4 nm. Finally, three thin films from each concentration were prepared.

![Figure 1](image1.png)

**Figure 1.** (a) Chemical structure of the azopolymer matrix. (b) TEM image of the goethite NPs.

In order to produce samples with various concentrations of goethite in the azopolymer, we used the following procedure: we dissolved PAZO in water and, to ensure complete dissolution of the polymer, we heated the solutions to 60 °C. The nanoparticles were separately dispersed in water by sonication. Then the polymer solutions and the nanoparticles dispersions were combined to achieve the desired concentration ($C$) of the goethite nanoparticles in the azopolymer. Seven different concentrations were obtained in this way: $C = 0, 0.5, 1, 2, 5, 7.5, 10$ and $15$ wt %. Finally, thin films were prepared by depositing the solutions on a glass substrate (BK7) and spin-coating at 1500 rpm for 30 seconds.

2.2. Characterisation of the films

As it will be seen, to calculate both the absorbance and birefringence, it is necessary to know the precise value of each sample’s thickness. For this purpose, we used a Talystep profiler with 1 nm vertical and 0.1 µm horizontal resolution, additionally upgraded with a digital recording device connected to a PC. A groove was made on the surface, with the distance between the “plateau” and the bottom of the groove corresponding to the film’s thickness. Figure 2 shows a typical profile obtained from such measurements.

![Figure 2](image2.png)

**Figure 2.** Profile for a sample with 0.5 wt % NP concentration. The thickness measured is 460 nm.
Besides the thickness, we also measured the absorbance spectra of the samples. This is essential for choosing correctly the wavelengths of the pump and the probe lasers for measuring the birefringence. The wavelength of the pump laser has to be within the absorbance band, but not at the peak, because then the recording light will not penetrate into the depth of the film. On the other hand, the probe laser’s wavelength has to be outside the absorbance band, so that it only measures the birefringence but does not destroy it.

The absorbance spectra were determined using a Varian Cary 5E spectrophotometer. The data directly obtained from the measurement were the transmittance spectra \( T(\lambda) \), which were then transformed to absorbance using \( \alpha = -(1/d) \log(T) \). Typical spectra of the absorbance coefficient are shown in figure 3.

As seen, the peak of absorbance is at 360 nm for all samples. The arrows in the figure indicate the selected wavelengths for the pump and probe lasers.

### 2.3. Measurement of the photoinduced birefringence

Figure 4 shows the experimental setup used to measure the birefringence.

![Diagram](image)

**Figure 4.** Setup for birefringence measurement. 1 – probe He-Ne laser (\( \lambda = 633 \) nm), 2 – DPSS laser (\( \lambda = 473 \) nm), 3 – polarizers, 4 – Glan prism, 5 – sample, 6 – photodetector and 7 – PC.

Birefringence was induced by a vertically polarized beam from a diode-pumped solid-state laser (DPSSL) with an intensity of 400 mW/cm\(^2\). The sample was placed between two crossed polarizers oriented at ±45º with respect to the vertical. The probe beam passed through the system polarizer-sample-polarizer and was measured by a digital optical power meter (Thorlabs). The birefringence was calculated from the intensity using the following expression [1]:

\[
\Delta n(t) = \frac{\lambda}{\pi d} \arcsin \left( \frac{I_\parallel(t)}{I_\perp} \right),
\]

where \( \lambda \) is the wavelength of the probe laser (633 nm), \( I_\parallel \) is the intensity of the probe beam transmitted through the system “crossed polarizers – sample”, and \( I_\perp \) is the intensity of the probe beam transmitted through the parallel polarizers and the sample before the start of the recording. We thus obtained the time dependence of the photoinduced birefringence \( \Delta n(t) \), graphically presented for three of the samples in figure 5(a).
Each data point on figure 5(b) was averaged over three samples with the same NP concentration. Each measurement consisted of three stages. Initially, we measured the probe laser signal for 60 seconds before starting the pump beam in order to take into account the background light noise.

Then the pump laser was started and the birefringence began to increase. When it approached saturation after 300 s of irradiation, the pump laser was stopped and the birefringence relaxation was measured for another 240 seconds. Thus, it was observed that more than 90 % of the birefringence was retained after the relaxation period.

The samples thicknesses and the maximal values of the photoinduced birefringence ($\Delta n_{\text{max}}$) for all samples are summarized in table 1. We studied three samples of each concentration.

The dependence of $\Delta n_{\text{max}}$ on the concentration of goethite nanoparticles in the PAZO azopolymer is plotted in figure 5b. Two peaks of birefringence enhancement can be clearly observed. The first one is at $C = 1$ wt %, which corresponds to a 32 % increase of the birefringence compared to the undoped azopolymer. The second peak is at 10 wt % concentration, where the birefringence is enhanced by nearly 70 %. A possible reason for the presence of two peaks in the $\Delta n_{\text{max}} (C)$ dependence may be the geometry of the nanorods and the two characteristic dimensions – 15 and 150 nm. In order to confirm this, further experiments will be focused on determining how the size of the nanoparticles used for doping the azopolymer influences the birefringence.

### Table 1. Samples thicknesses and the maximal values of the photoinduced birefringence ($\Delta n_{\text{max}}$).

| Concentration, wt % | $d$, µm | $\Delta n_{\text{max}}$ |
|---------------------|---------|------------------------|
| 0                   | 0.45    | 0.060                  |
| 0.5                 | 0.46    | 0.064                  |
| 1                   | 0.43    | 0.079                  |
| 2                   | 0.47    | 0.065                  |
| 5                   | 0.42    | 0.071                  |
| 7.5                 | 0.41    | 0.064                  |
| 10                  | 0.40    | 0.10                   |
| 15                  | 0.45    | 0.046                  |

3. Conclusions

Photoinduced birefringence was measured in nanocomposite films of an azopolymer doped with elongated nanoparticles (nanorods) of the magnetic material goethite ($\alpha$-FeOOH) in concentrations varying from 0 wt % (pure azopolymer) to 15 wt %. An unusual dependence of the birefringence on the concentration was observed – two peaks of enhancement were seen at 1 wt % and at 10 wt % concentration. Our previous studies with ZnO and SiO$_2$ NP have indicated only one peak of increase at low concentrations – 0.5 wt % and 2 wt % respectively. This effect could be related to the elongated shape of the nanoparticles and the presence of two characteristic NP sizes – 15 and 150 nm. The
birefringence increase for the samples with 10 wt % NP concentration compared with the undoped samples was about 70%.

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