# Increase of the Photoinduced Birefringence in Azopolymer Films Doped with $TiO_2$ Nanoparticles

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**Abstract.** In this article, we investigate the photoinduced birefringence in commercially available azopolymer PAZO doped with $TiO_2$ spherical nanoparticles (21 nm size). The films are prepared by spin-coating water solution of the polymer mixed with the nanoparticles with different concentrations from 0 to 10 wt %. To induce the birefringence we use He-Cd laser with wavelength 442 nm. For measurement of the effect, probe laser with wavelength 635 nm is used. The experimental setup includes also polarimeter, which measures the Stokes parameters in real time. We observe increase of the photoinduced birefringence in azopolymer films doped with $TiO_2$ nanoparticles. The maximal value of $\Delta n$ is achieved for the sample with 1 wt. % concentration.

**Keywords:** Birefringence, azopolymer, nanoparticles, $TiO_2$, nanocomposite.

## 1. INTRODUCTION

Azopolymers are investigated as one of the most efficient media for polarization recording (Nikolova and Ramanujam, 2009; Tripathy et at, 1999; Wang, 2017). Birefringence $(\Delta n)$ is induced in them through trans-cis-trans isomerization and reorientation of the molecules when they are illuminated with linearly polarized light. This processes provoke the interest of many research groups and many articles investigate the theory and practical use of that effect, the formation of the $\Delta n$ and so on (Natansohn and Rochon, 2002; Martinez-Ponce, 2016; Balazs et al, 2006). Acquiring high value of photoinduced birefringence $(\Delta n)$ allows further development of polarization holography and manufacture of unique optical polarizing devices (De Sio et al, 2016).

There are several ideas how to improve $\Delta n$ and one is to dope the azopolymer with appropriate nanoparticles (NP): Ag containing $TiO_2$ NP (Fernandez et al, 2015), Ag NP (Zhou et al, 2007; Wu et al, 2010). There is no yet established theory explaining of the process of increase of the birefringence, however a model is suggested how the doped NP can increase the $\Delta n$ (Nazarova et al, 2013; Kreibig and Voller, 1995; Bohren and Huffman, 1998). It presumes that if there is a significant difference in the refractive index of the polymer and the NP the scattering could reorient better the side chains of the polymer that leads to increased $\Delta n$.

Our group has investigated such nanocomposites with ZnO, goethite and silica NP and we established that there is an increase of the $\Delta n$ (Nedelchev et al, 2016; Nedelchev et al, 2012].

This encourages us to continue with investigations of similar nanocomposites based on commercially available (Sigma Aldrich) azopolymer PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzene-sulfonamido]-1,2-ethanediyl, sodium salt) and NP of $TiO_2$ because of the large difference between their refractive indices. There are other studies using $TiO_2$ NP in azopolymer (Fernandez et al, 2015), but our method of thin film preparation is different – we use spin-coating technology and we investigate concentrations of the $TiO_2$ NP between 0 and 10 wt % and we can compare the results with the results with another NP in the same azopolymer at the same conditions of formation (Nedelchev et al, 2016).

## 2. METHODOLOGY

### 2.1 Thin Films Preparation

Our goal was to produce samples with various concentrations of $TiO_2$ NP in PAZO in order to find the optimal concentration of the NP that leads to highest increase of $\Delta n$. Our method of preparing the samples consists of the following steps: First, we dissolve azopolymer PAZO in water and disperse the NP in various concentrations in water. After that, we mix the solution of the azopolymer and the suspension of the NP and sonicate them to ensure that they are evenly distributed in the water (Elmasonic P 60 H, frequency 37 kHz at room temperature for 1 hour). The concentration of the PAZO in the water is chosen according to our previous research (Nedelchev et al, 2015). When the suspensions of the nanocomposites are ready, we deposit them on a glass substrate (BK7) and then we continue with spin coating at 1500 rpm for 30 seconds. In this way, we obtain samples with 6 different concentrations (0, 0.5, 1, 2, 5, and 10 wt. %) of $TiO_2$ NP in the PAZO polymer.

### 2.2 Thickness Measurement

To calculate the birefringence, we need to first measure the thickness of the films and we do this using optical thin films analyzer "Filmetrics F20" (Fig. 1).

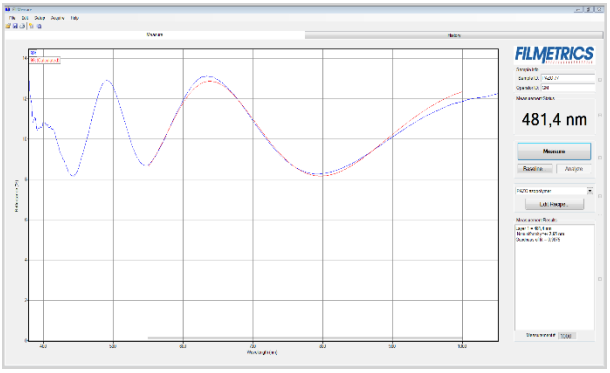


**Fig. 1** FILMeasure software window.

The device is using the principle of thin film interference. All of the samples have thicknesses in the range 450 – 550 nm.

### 2. 3. Measurement of the Birefringence

According to the theory, we can calculate the photoinduced birefringence by the expression:

$$\Delta n = \frac{\lambda}{2\pi d}\arctan\left(\frac{S_3}{S_2}\right) \qquad (1)$$

where $\lambda$ is the wavelength of the probe laser beam (in our experiments 635 nm), $d$ is the sample's thickness and $S_3$ and $S_2$ are the Stokes parameters.

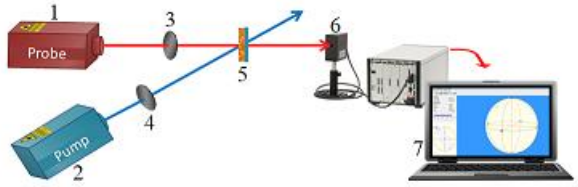


**Fig. 2** Experimental setup for measuring the birefringence. 1-probe laser (635 nm), 2-pump laser (442 nm), 3-vertical polarizer, 4-polarizer oriented at 45°, 5-sample, 6-polarmeter, 7-computer.

We can easily determine the Stokes parameters of light passed through the sample by using polarimeter (Thorlabs). The pump laser is He-Cd laser (Kimmon Koha) operating at 442 nm. With vertical polarizer we ensure that its light has vertical polarization. The probe beam is from diode laser at 635 nm. It passes through second linear polarizer oriented at 45°. The probe laser radiation is exactly perpendicular to the samples. The intensity of the pump laser is approximately 1 W/cm$^2$. The probe radiation passes through the film and is measured by the polarimeter.

All the samples go through the same steps – first we measure the background of the probe laser for 1 minute. Then we turn on the pump laser. The initial state of every sample is isotropic because the azomolecules are oriented at random. However, when turning on the pump laser they start to reorient perpendicular to the polarization of light because of selective trans-cis-trans isomerization processes and the birefringence starts to increase. When all the molecules are reoriented (i. e. saturation is reached)

we turn off the pump laser and measure the relaxation for 5 minutes.

## 3. EXPERIMENTAL RESULTS

Fig. 3 shows the calculated results for the photoinduced birefringence in time for some samples. In Fig. 4 is shown the graph of the dependence of the maximal birefringence of the concentration of the NP.

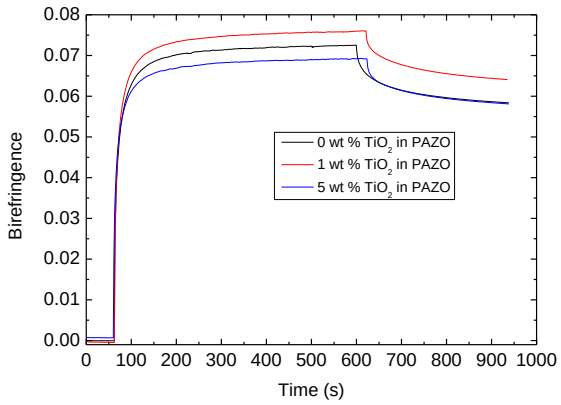


**Fig. 3** Time dependence of $\Delta n$ for the samples with 0, 1 and 5 wt % $TiO_2$ NP in PAZO.

As seen, the best results are achieved with the sample with 1 wt. % NP. For the sample with 5 wt. % $\Delta n$ is lower than for the sample with pure PAZO which is similar to the behavior observed in our earlier investigations (Nedelchev et al, 2016; Nedelchev et al, 2012).

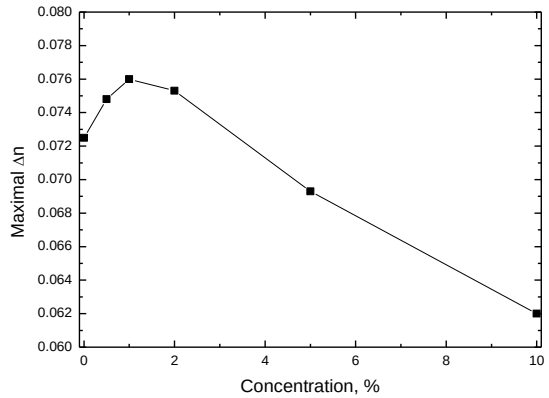


**Fig. 4** The dependence of the maximal $\Delta n$ on the concentration.

## 4. CONCLUSION

We have prepared nanocomposite thin films containing the azopolymer PAZO and $TiO_2$ NP with six different concentrations. All the samples have 450-550 nm thickness. The experiments showed that the highest value of $\Delta n$ is achieved for the samples with 1 wt. % $TiO_2$ and it is 0.076. The dependence of the $\Delta n$ on the NP concentration is similar to the dependences on the concentration of other spherical NP in azopolymer.

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