# SURFACE MORPHOLOGY STUDY OF AZOPOLYMER-BASED NANOCOMPOSITES AS A FUNCTION OF NANOPARTICLE CONCENTRATION USING AFM

## STUDIUL MORFOLOGIG AL SUPRAFEȚEI NANOCOMPOZITELOR PE BAZĂ DE AZOPOLIMERI ÎN FUNCȚIE DE CONCENTRAȚIA DE NANOPARTICULE UTILIZÂND MICROSCOPIA DE FORŢĂ ATOMICA (AFM)

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***Sumar.*** *Nanocompozitele pe bază de azopolimeri dopate cu nanoparticule metalice atrag un interes tot mai mare datorită potențialului lor de utilizare în aplicații fotonice și optice difractive. În acest studiu, au fost sintetizate și depuse pe substraturi transparente pelicule*

*subțiri de azopolimeri care încorporează nanoparticule de aur cu concentrații variate. Morfologia suprafeței și nanostructura straturilor compozite au fost investigate utilizând Microscopia de Forță Atomică (AFM). Analiza topografică a evidențiat modificări semnificative în rugozitatea suprafeței, uniformitatea și organizarea structurală, în funcție de concentrația de nanoparticule utilizată. Rezultatele experimentale demonstrează că doparea cu nanoparticule influențează procesele de auto-organizare și capacitățile de modulare a suprafeței peliculelor de azopolimer. Aceste constatări contribuie la optimizarea compoziției și fabricării materialelor nanocompozite pentru dispozitive avansate fotoreactive și holografice.*

***Cuvinte-cheie:*** *nanocompozite pe bază de azopolimeri, microscopie de forță atomică, topografia suprafeței, nanoparticule de aur, pelicule subțiri, materiale fotonice, concentrație de nanoparticule.*

## 1. INTRODUCTION

Azopolymers are a class of photosensitive materials capable of undergoing reversible structural changes upon exposure to light, primarily due to the *trans–cis* photoisomerization of azobenzene units. This property makes them suitable for a wide range of optical applications, including the fabrication of diffractive optical elements (DOEs), data storage media, and surface patterning technologies. In recent years, the integration of metal nanoparticles, especially gold nanoparticles (AuNPs), into azopolymer matrices has opened new avenues for enhancing the optical and morphological properties of these materials. Such nanocomposites combine the photosensitivity of azopolymers with the plasmonic and light-scattering properties of metal nanoparticles, leading to improved sensitivity, surface relief formation, and refractive index modulation [1].

One of the key aspects of the development and optimization of azopolymer-based nanocomposites is understanding the effect of nanoparticle concentration on the surface morphology of the resulting films. Surface topography plays a significant role in determining the efficiency of optical modulation and diffraction, particularly in holographic applications [2]. AFM is a powerful technique for evaluating nanometer-scale surface features, offering detailed insight into the structural organization and roughness variations of thin films.

This study focuses on investigating the influence of various concentrations of gold nanoparticles embedded in azopolymer films on their surface morphology using AFM. By analyzing the topographic parameters and structural features of these nanocomposites, we aim to correlate the nanoparticle content with surface modulation behavior, contributing to the rational design of light-responsive nanostructured materials.

## 2. MATERIAL AND METHODS

### 2.1 Synthesis of azopolymer and gold nanoparticles

The azopolymer used in this study, poly-n-epoxypropylcarbazole_SY3 (PEPC-co-Sy3), was synthesized via a reflux method (fig. 1).

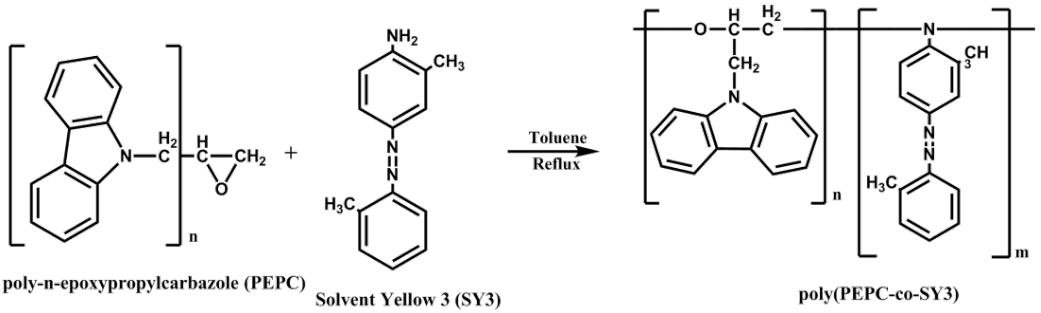



**Figure 1. Synthesis of PEPC-coSY3 azopolymer**

The chemical reaction shown in the previously presented scheme proceeds under reflux at a temperature of 220°C in the solvent toluene, for 8 hours, with continuous stirring at 500 rpm using a magnetic stirrer to ensure solution homogeneity and prevent sedimentation of the azo dye [3]. For the synthesis, the polymer matrix poly-N-epoxypropylcarbazole (PEPC) – 2 g, and the azo dye Solvent Yellow 3 (SY3) – 0.6 g were used, both substances being dissolved in 12 mL of toluene.

Spherical gold nanoparticles, spheres with a diameter 25 nm (Au-NPs), was purchased on Sigma Aldrich. The colloidal Au-NPs solution was added to the PEPC-co-SY3 solution in toluene in various volumetric ratios to achieve uniform volume doping.

### 2.2 Nanocomposite films deposition

Thin films of PEPC-co-SY3 and PEPC-co-SY3 doped with Au-NPs were deposited onto pre-cleaned glass substrates using the rod-coating method (fig. 2), chosen for its simplicity and reproducibility in forming uniform thin layers over large areas. The coating was performed under ambient conditions, followed by solvent evaporation at room temperature for 24 hours [4].




**Figure 2. Thin Film Deposition Setup –Rod-Coater:**
1 – polished rod; 2 – azopolymer thin film; 3 – glass substrate; 4 – drop of azopolymer solution. Arrow shows substrate movement by step motor

### 2.3 Holographic recording setup

The holographic recording was performed using a two-beam interference configuration based DPSS laser emitting at a wavelength of 473 nm with an output power of 100 mW. The wavelength was chosen to match the absorption of the azopolymer at thicknesses of about 1 μm, ensuring efficient photoisomerization throughout the film thickness. Two coherent beams from the same laser source were directed onto the film surface at symmetric angles of incidence relative to the normal to the sample surface, creating an interference pattern with a spatial period of approximately 7 μm (fig. 3) [5].

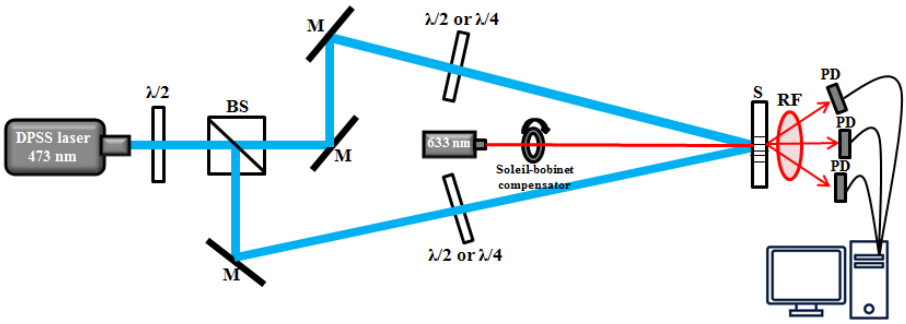



**Figure 3. Optical Setup for Polarization Holographic Recording**

The setup consists of a DPSS laser (473 nm, 100 mW), a beam splitter that divides laser beam into two coherent beams, and retardation plates (λ/2 and λ/4) used to achieve various beam polarization states configurations. A nonactinic laser diode wavelength of 633 nm, vertical polarization with a power of 1 mW is employed to monitor the kinetics of DE, along with a photodiodes currents-based data acquisition and storage system. The DE of the recorded grating is determined using the following relation:

$$\eta = \frac{I_1}{(I_1+I_{-1}+I_0)} * 100\% \quad (1)$$

where:

- $I_0$ – intensity in the 0th diffraction order,
- $I_1$ – intensity in the +1st diffraction orders ,
- $I_{-1}$ - intensity in the -1st diffraction orders.

Polarization control was achieved using a combination of linear polarizers and quarter-wave plates, allowing the formation of gratings under both linearly and circularly polarized light. An exposure time was 30 minutes. All recordings were performed under ambient conditions.

### 2.4 Atomic force microscopy (AFM)

To investigate the surface topography of azopolymer nanocomposites, Atomic Force Microscopy (AFM) was employed in non-contact mode, a high-resolution technique that enables detailed surface examination without damaging the sample. In this mode, the AFM tip oscillates near the surface of the sample without making direct contact. The van der Waals interactions between the tip and the sample surface cause changes in the cantilever's resonance frequency, which are used to reconstruct a three-dimensional image of the surface topography.

This method is particularly suitable for characterizing thin films and sensitive materials such as azopolymers, as it minimizes the risk of mechanical deformation during measurement. The acquired data provide precise information about surface roughness, the height of photoinduced relief structures, and the morphological distribution of features formed under polarized light exposure [6].

## 3. RESULTS AND DISCUSSIONS

The obtained azopolymer PEPC-co-SY3 with concentration of 30% mass ratio of azodye was doped with different colloidal Au-NPs solution for obtaining nanocomposite films with different concentration of Au-NPs.

To measure the thickness of the azopolymer applied on a transparent substrate, a scratch must be made on the surface of the azopolymer layer, reaching down to the substrate. This creates a step with well-defined boundaries. As a result, the interference pattern is obtained with a displacement, allowing the thickness of the azopolymer layer to be distinguished relative to the substrate. This approach enables measurement of the azopolymer layer thickness using the principles of interferometry. The MII-4 interferometric microscope was equipped with a Logitech HD Webcam C310 (1280x720 px). This setup allowed for clear image acquisition using the specialized OpticMeter software, which is based on mathematical model for determining the minima and maxima of the interferograms obtained via the least squares method [7]. Thicknesses of the sample is shown in table 1.

**Table 1.** Thickness of obtained nanocomposites samples

| Sample | PEPC-co-SY3(30%) 0 µgAu | PEPC-co-SY3(30%) 0,4 µgAu | PEPC-co-SY3(30%) 0,8 µgAu | PEPC-co-SY3(30%) 1,2 µgAu |
|---|---|---|---|---|
| Thickness, nm | 2120 | 998 | 990 | 946 |

In the figure 3 the kinetics of DE with linear (PP) states of polarizations of recording beams are presented for nanocomposites of various Au-NPs concentrations. Note that DE of azopolymers is dependent on the thickness of samples [4, 5]. Therefore, DE was recalculated to a thickness of 1 µm. When exposed to PP polarized lights (fig. 3) the polarization of reading beam was linear vertical polarization.

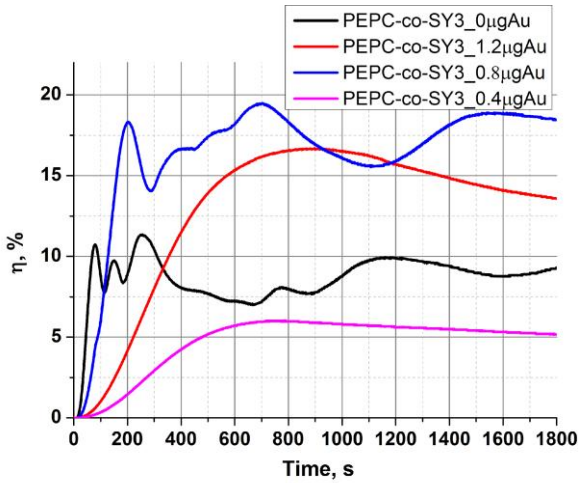
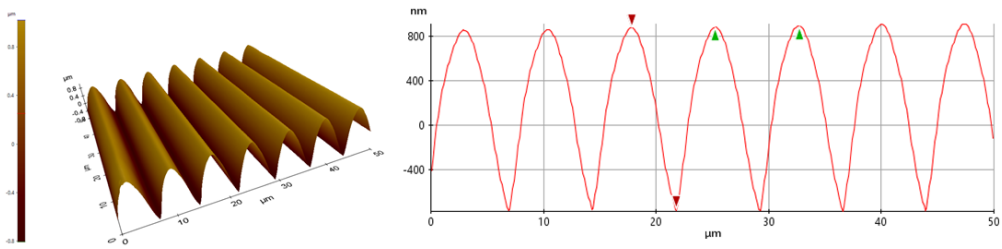


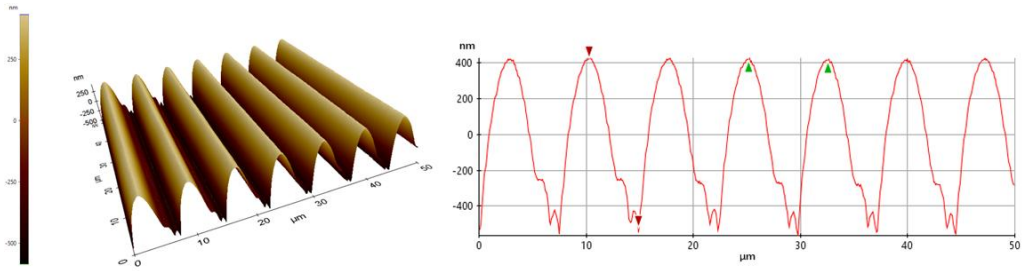

**Figure 4.** Diffraction efficiency during recording in PP polarized light

Following the exposure of the azopolymer samples to polarized light, atomic force microscopy (AFM) analysis revealed significant changes in surface topography. Non-contact mode imaging showed the formation of well-organized sinusoidal relief structures, typically associated with light-induced surface deformation. These surface patterns reflect the molecular reorganization driven by trans–cis–trans photoisomerization of azobenzene under polarized illumination. Variations in the amplitude and periodicity of the relief, depending on the sample composition (pure polymer versus nanocomposite), indicate a direct influence of nanoparticle doping on the photo-orientation efficiency and mass transport behavior within the material.

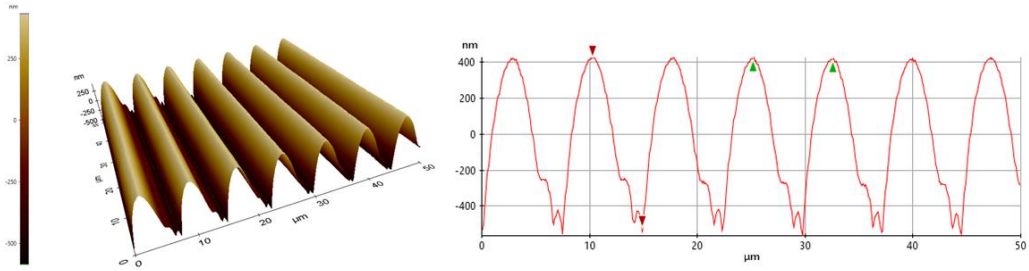
The analyzed samples consisted of thin films of the PEPC-co-SY3 azopolymer, both in pure form and doped with gold nanoparticles at various concentrations. The results revealed the formation of sinusoidal surface diffraction gratings, whose periodicity and amplitude were found to vary depending on the sample composition and exposure conditions shown in fig 5.



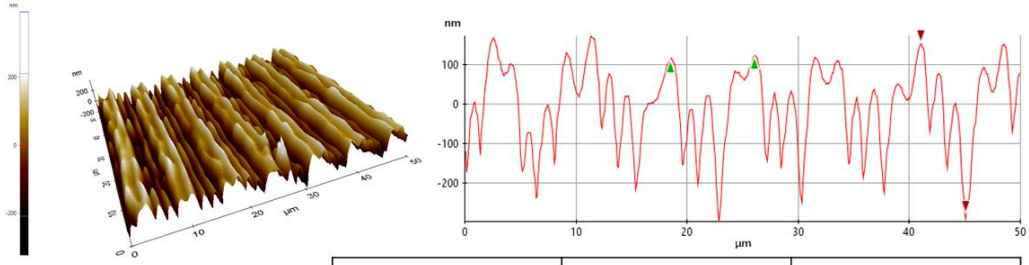

| | ΔX, μm | ΔY, μm |
|---|---|---|
| **Red** | 3.947 | 1.632 |
| **Green** | 7.401 | 0.014 |




| | ΔX, µm | ΔY, nm |
|---|---|---|
| **Red** | 4.605 | 945.826 |
| **Green** | 7.401 | 6.109 |




| | ΔX, µm | ΔY, nm |
|---|---|---|
| **Red** | 4.605 | 945.826 |
| **Green** | 7.401 | 6.109 |




| | ΔX, µm | ΔY, nm |
|---|---|---|
| **Red** | 4.030 | 433.015 |
| **Green** | 7.566 | 8.244 |

**Figure 5.** 3D Surface relief gratings and transversal sections for:
*a) PEPC-co-SY3_0mgAu, b) PEPC-co-SY3_0.4mgAu, c) PEPC-co-SY3_0.8mgAu, d)PEPC-co-SY3_1,2mgAu*

AFM measurements revealed significant differences in the depth of the light-induced surface relief depending on the composition of the analyzed samples. Azopolymer

films doped with gold nanoparticles exhibited much more pronounced surface structuring compared to the undoped film.

In particular, the sample doped with 0.8 μg of gold showed a surface relief depth of approximately 95% of the total film thickness, indicating an enhanced efficiency of the light-induced mass transport process. This behavior is attributed to the local enhancement of the electromagnetic field near the metallic nanoparticles, which promotes molecular reorganization within the azopolymer matrix. In contrast, the undoped sample exhibited a relief depth of approximately 75% of the total film thickness, reflecting a less efficient mass transport process in the absence of nanoparticle doping.

## CONCLUSIONS

- Azopolymer-based nanocomposites doped with gold nanoparticles exhibit significant changes in surface topography depending on the concentration of the dopant.
- AFM analysis revealed an increase in surface roughness and relief depth with higher AuNP concentrations, indicating active interaction between nanoparticles and the polymer matrix during photoisomerization.
- Well-defined and uniformly distributed surface structures were observed at optimal concentrations, enhancing the material's suitability for direct recording of diffractive optical elements.
- Excessively high concentrations of nanoparticles may lead to partial aggregation, negatively affecting film uniformity and optical performance, highlighting the importance of concentration optimization.
- AFM proved to be an essential technique for detailed characterization of morphological changes, providing valuable insights for controlling and tuning surface properties for optoelectronic applications.

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