OPTICAL RESPONSE EVALUATION OF AZOPOLYMER THIN SOLID FILMS DOPED WITH GOLD NANOPARTICLES WITH DIFFERENT SIZES

Nataliya Berberova-Buhova[1], Lian Nedelchev[1,2], Elena Stoykova[1], Dimana Nazarova[1]

[1]Institute of Optical Materials and Technologies "Acad. J. Malinowski"
Bulgarian Academy of Sciences, Sofia, Bulgaria
[2]University of Telecommunications and Post, Sofia, Bulgaria
E-mail: natali.berberova@gmail.com

Received 01 July 2021
Accepted 04 February 2022

ABSTRACT

Azobenzene and azobenzene-containing polymers are intensively studied in the last decades because of their high potential for various applications: polarization holography, holographic optical polarization-sensitive elements, high-density storage by multiplexing, ptychography, etc. In this article are reported studies based on the optical response of azopolymer poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethan-ediyl, sodium salt], (PAZO) thin films with embedded Au spherical nanoparticles with different sizes. We found that effective medium approximations (Maxwell-Garnett and Bruggeman) are not satisfactory in evaluation of films optical response. The complex refractive index of the composite film is evaluated as a dependence on three factors: 1) the PAZO matrix complex refractive index; 2) volume scattering efficiency of the Au particle and 3) the filling factor of the composite film. The scattering of a single particle in the azopolymer matrix is calculated using the exact vector Maxwell equations. The particles with mean radius 10, 30 and 50 nm are treated as ensemble of non-aggregated spheres. Multiple scattering by individual particles was ignored. Three specific filling factors of 0.008, 0.010 and 0.030 are considered. The optical transmittance and absorption of a 440 nm thick composite film were evaluated. The algorithm is efficient and the results are robust. The photoinduced spectral response of the composite layers is under study.

Keywords: azopolymer, PAZO, gold nanoparticles, nanocomposites, optical response.

INTRODUCTION

Azobenzene and azobenzene-containing polymers are intensively studied in the last years because of their high potential for various applications: polarization holography, holographic optical polarization-sensitive elements, high-density storage by multiplexing, ptychography, etc. [1 - 6]. Azopolymer materials have the ability to record the polarization state of light as a result of film anisotropy induced under polarized illumination. Typically, the recording and reproduction of optical information in these materials is based on birefringence induced by preferential orientation of chromophores in the medium due to trans-cis-trans photoisomerization. In recent years, scientists have found that the combination of organic and inorganic materials could improve a number of properties of the obtained composites as electrical, optical and mechanical properties [7, 8]. In this article, we present numerical simulation of the optical response of thin azopolymer film (PAZO: (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethan-ediyl, sodium salt])) with embedded golden (Au) spherical nanoparticles with radius 10 to 50 nm and filling factors 0.008, 0.010, 0.030 by calculation of the complex refractive index of the composite film. Nanoparticles with a radius greater than 50 nm have no effect on photoinduced birefringence as shown in our previous study [9]. In this work, we studied three sizes of nanoparticles - 10, 30, 50 nm to determine the optimum of the studied effect. The new task in the future is to compare the obtained modeled optical characteristics with the experimental ones. This work is motivated by the search for the reason to increase the photoinduced birefringence in azopolymer layers doped with different nanoparticles [9 - 11]. The mechanism of this increase has not yet known. The aim to increase the photoinduced birefringence is related to the desire to improve the diffraction efficiency of polarization holographic recording. The scattering of particles in the polymer matrix is calculated using the exact vector Maxwell equations. We developed codes for numerical evaluation of the optical response: transmittance, absorption and reflectance of a composite film with thickness 440 nm. We show that the resonant peak location is a sensitive function of the characteristics of an Au particle - its size and refractive index. The potential use of azopolymers with embedded Au nanoparticles in photonics has also motivated studies of their material properties. This is because, along with the required optical characteristics, easy material processing is highly desirable for future applications.

Computational procedures and model for evaluation of the optical response

Our model assumes that Au spherical nanoparticles are embedded in a thin solid PAZO matrix and are homogeneously distributed. The PAZO complex refractive index N_{PAZO} is obtained from our previous calculations [12]. The Au complex refractive index N_{Au} is derived from [13]. We varied the sphere mean radius between 10 and 50 nm and the filling factors of the nanocomposite thin film used for the calculations are with values of 0.008, 0.010 and 0.030.

Particle optical response in our model is analyzed by the exact vector Maxwell equations [14]. The solutions for two fields are obtained (the far-field scattered, internal and near-field external electromagnetic fields). Our model is based on separation of variables approach, which is modified and applied on particles embedded in azopolymer matrix. We use expansion coefficients, which are also called multipole electric and magnetic modes for estimation of the scattered fields. These modes are functions of the particle size parameter x = $2\pi r \times N_{PAZO}/\lambda$, where r is the sphere radius, N_{PAZO} is the refractive index of our azopolymer, and λ is the wavelength in vacuum.

Set of codes has been developed for calculation of optical response of the composite film. The sums are truncated when the machine precision or saturation is reached. The film optical characteristics (absorbance, transmittance at normal light incidence and effective refractive index N_{eff}) are found automatically by a special program. The particles are considered as ensemble of non-aggregated spheres. Further, we have ignored multiple scattering by individual particles.

The transmittance of the composite film is evaluated using the nanocomposite effective refractive index N_{eff}:

$$N_{eff} = N_{PAZO} \frac{1 + i\pi f S\,(0)/k^3\,\nu_p}{1 - i\pi f S\,(0)/k^3\,\nu_p} \qquad (1)$$

where $S(0)$ is the amplitude scattered by a particle in the forward direction, υ_p is the sphere volume and f is the filling factor (ratio of υ_p to sample volume) [15, 16]. When the thin film is non-doped, i.e. no particles are incorporated in the film, then the filling factor is zero $f = 0$. The maximum filling factor for Au spheres is $f = 0.03$. Values of $f \sim 0.3$ - 0.4 are considered as high [15]. A low filling factor means that multiple scattering between particles can be neglected.

RESULTS AND DISCUSSION

In this section we give the main results of our model simulation and present some graphical illustrations. In order to evaluate the effective refractive index of the nanocomposite film we first calculate the scattering amplitude matrix of a single Au sphere in PAZO environment. The optical constants are found as function of wavelength. We introduce the composite film filling factor f as parameter. f is the ratio of the volume of all embedded particles to the volume of the film. In Figs. 1 and 2 we present the results for the spectral transmittance and absorption change for f = 0.008; 0.010 and 0.030 and compare it to $f = 0$, that is no particles in the film in case of three different particle sizes: radius of 10 nm, 30 nm and 50 nm.

In Fig. 1, the transmittance of nanocomposite thin film as obtained from our model is shown. Fig. 1(a) represents the case of 10 nm radius of nanoparticles, Fig. 1(b) - 30 nm and Fig. 1(c) - 50 nm radius of NP. The transmittance minimum obtains bathochromic shift i.e. it is shifted towards red. Besides, the small filling factor produce a higher transmission of the nanocomposite film (curve pure PAZO and 0.008). For a filling factor $f \geq 0.03$, the peak of transmission is reduced twice as compared to the curve 0.01 of nanocomposite film with a smaller filling factor and reduced three times for curve pure PAZO of pure azo polymer film without particles. In conclusion, the optical behavior of transmission spectrum depends highly on the composite film components ratio i.e. filling factor and the size of the nanoparticles.

Fig. 2 shows the absorption changes of nanocomposite with three nanoparticle sizes of the mean radius (10 nm, 30 nm and 50 nm) and different filling factors (0.008, 0.01, 0.03). For larger particles and large filling factor, the changes in absorption spectrum decrease almost twice (curve 0.03).

In Fig. 3 the transmittances of nanocomposite films doped with 3 different radii NPs depending on the filling factor are compared. Three cases of filling factors are considered. For larger filling factor, the peak of transmission decreased twice. The minimum in the transmission spectrum corresponds to maximum in the absorption spectrum (Fig. 4).

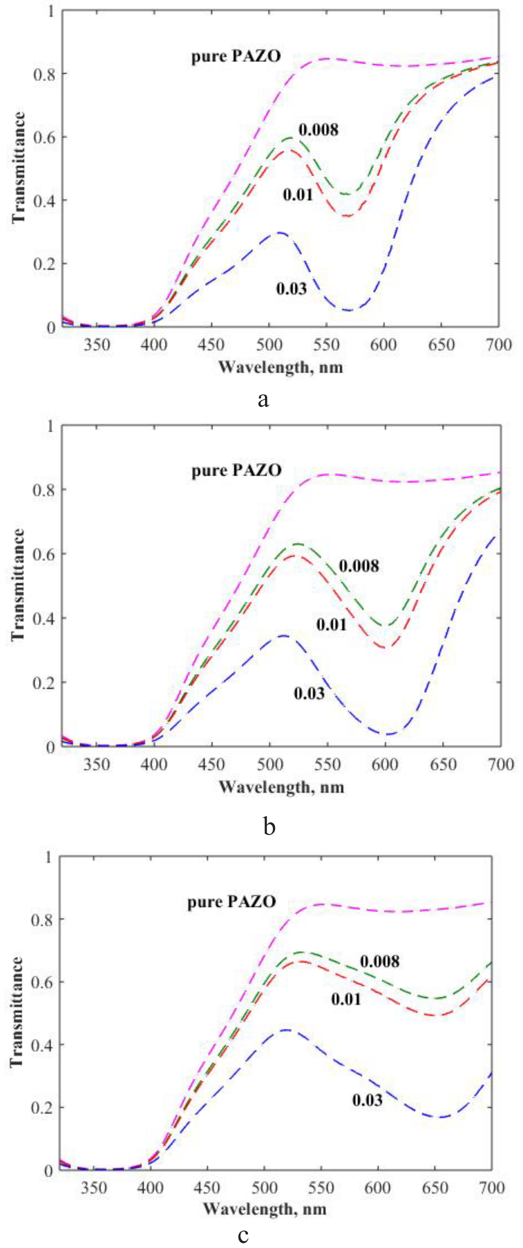


Fig. 1. Transmittance of nanocomposite film - PAZO with Au nanoparticles (mean radius of 10 nm (a); 30 nm (b) and 50 nm (c) and filling factor 0.008, 0.010 and 0.030).

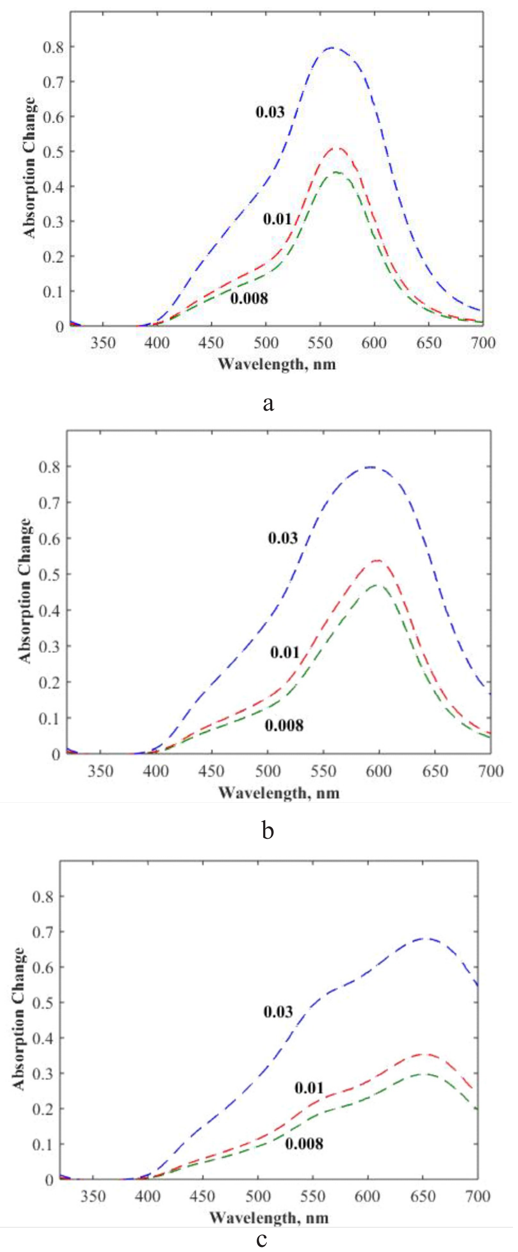
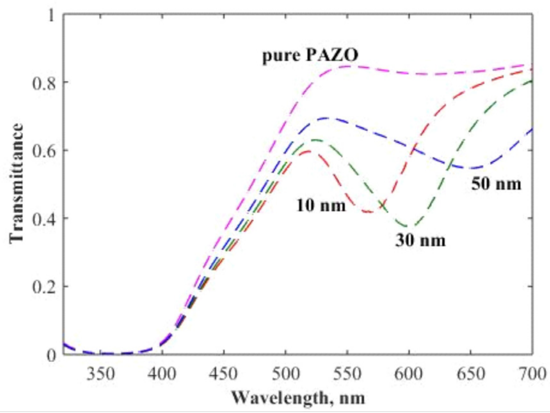
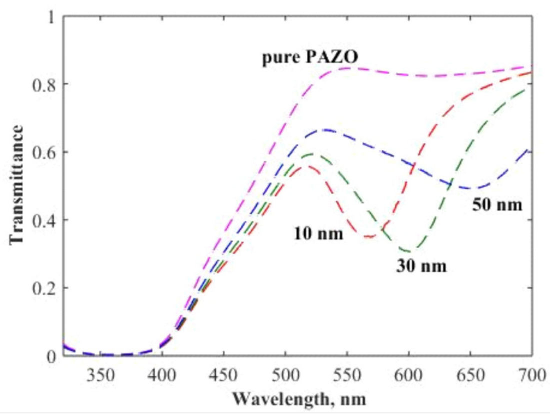


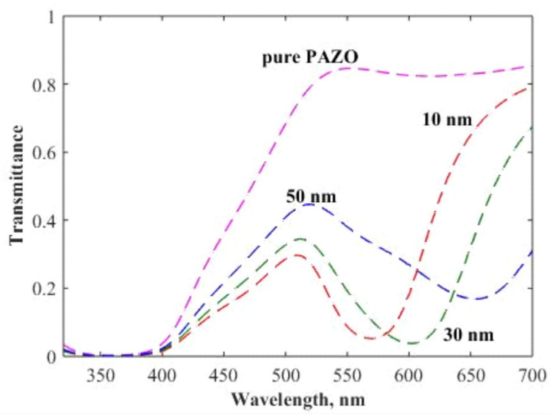
Fig. 2. Absorption change for the nanocomposite films with Au nanoparticles with mean radius of 10 nm (a), 30 nm (b) and 50 nm (c) and the filling factor of the film 0.008 (curve 0.008), 0.010 (curve 0.01) and 0.030 (curve 0.03).



a

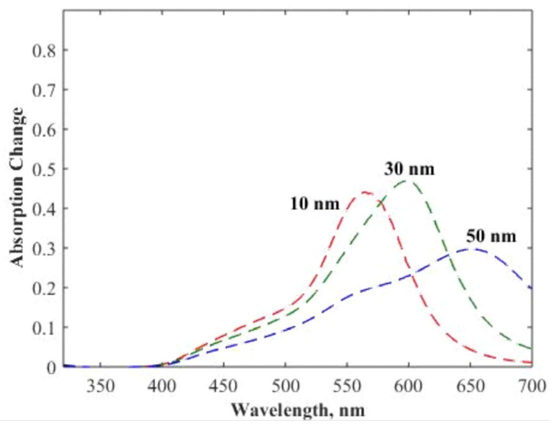


b

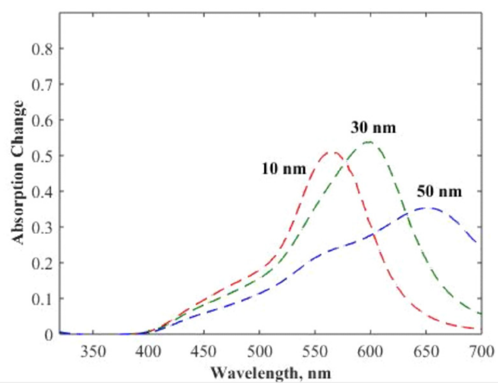


c

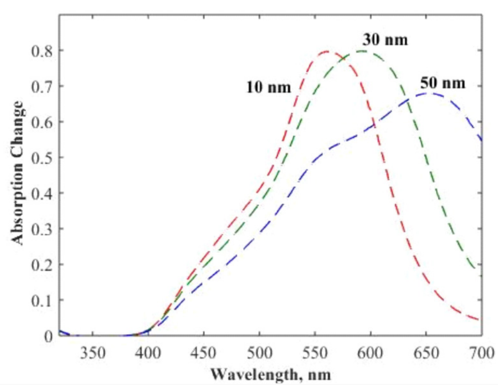
Fig. 3. Transmittance of the nanocomposite films with filling factor (a) $f = 0.008$, (b) $f = 0.01$, (c) $f = 0.03$; for the pure PAZO thin film and nanocomposite films with Au nanoparticles with mean radius of 10 nm, 30 nm and 50 nm.



a



b



c

Fig. 4. Change of absorption of the nanocomposite films with filling factor (a) f = 0.008, (b) f = 0.010 and f = 0.030, for the nanocomposite films with Au nanoparticles with mean radius of 10 nm, 30 nm and 50 nm.

CONCLUSIONS

We have developed accurate and flexible calculation model for evaluation of the optical response of metal nanoparticle spheres embedded in a polymer matrix. Herein we considered the case with Au nanoparticles and azopolymer matrix. The optical behavior of composite thin film in our model has common features that strongly correlated with each other. Considering the absorption in the nanocomposite thin film, we find that the absorption peak decreases with increasing particle size and with a higher filling factor. This is due to light scattering from the particles. The transmittance and absorption depends highly on the composite film components ratio: filling factor and the size of the nanoparticles.

Acknowledgements

This work is financially supported by contract M38/2 with the National Science Fund of Bulgaria. Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science was used in this investigation.

REFERENCES

1. T. Todorov, L. Nikolova, N. Tomova, Polarization holography 1: A new high-efficiency organic material with reversible photoinduced birefringence, Appl. Opt. 23, 1984, 4309-4312.
2. A. Natansohn, P. Rochon, Photoinduced Motions in Azo-Containing, Polymers Chem. Rev., 102, 2002, 4139-4176.
3. L. Nikolova, P.S. Ramanujam, Polarization Holography, New York: Cambridge University Press, 2009.
4. A. Matharu, S. Jeeva, P.S. Ramanujam, Liquid crystals for holographic optical data storage, Chem. Soc. Rev., 36, 2007, 1868-1880.
5. D. Gindre, A. Boeglin, A. Fort, L. Magerand, K.D. Dorkenoo, Rewritable optical data storage in azobenzene copolymers, Opt. Express, 14, 2006, 9896-9901.
6. P. Forcen, L. Oriol, C. Sanchez, F. Rodriguez, R. Alcala, S. Hvisted, K. Jankova, Methacrylic azopolymers for holographic storage: A comparison among different polymer types, Europ. Pol. J., 43, 2007, 3292-3300.
7. A.C. Balaza, T. Emrick, T.P. Russell, Nanoparticles polymer composites: where two small world meet, Science, 314, 2006, 1107-1110.
8. Y. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A.R. Burns, D.Y. Sasaki, J. Shelnutt, C.J. Brinker, Self-assembly of mesoscopically ordered chromatic polydiacetylene/silica nanocomposites, Nature, 410, 2001, 913-917.
9. L. Nedelchev, D. Nazarova, V. Dragostinova, D. Karashanova, Increase of photoinduced birefringence in a new type of anisotropic nanocomposite: azopolymer doped with ZnO nanoparticles, Opt. Lett., 37, 2012, 2676-2678.
10. L. Nedelchev, D. Nazarova, V. Dragostinova, Photosensitive organic/inorganic azopolymer based nanocomposite materials with enhanced photoinduced birefringence, J. Photochem. Photobiol., A: Chem., 261, 2013, 26-30.
11. D. Nazarova, L. Nedelchev, P. Sharlandjiev, V. Dragostinova, Anisotropic hybrid organic/inorganic (azopolymer/SiO2 NP) materials with enhanced photoinduced birefringence, Appl. Opt., 52, 22, 2013, 28-33.
12. N. Berberova, P. Sharlandjiev, A. Stoilova, L. Nedelchev, D. Nazarova, B. Blagoeva, Optical constant of azopolymer PAZO thin films in the spectral range 320-800 nm, IOP Conf. Series: Journal of Physics: Conf. Series, 992, 2018, 012019.
13. P.B. Jonson, R.W. Christy, Optical Constants of the Noble Metals, Phys.Rev.B, 6, 1972, 4370-4379.
14. C.F. Bohren, D.P. Gilra, Extinction by a spherical particle in an absorbing medium, J.Coll.Interf.Sci., 72, 1979, 215-221.
15. A. Zayats, I. Smolyaninov, A. Maradudin, Nano-optics of surface plasmon polaritons, Phys. Rep., 408, 2005, 131-314.
16. C.F. Bohren, D.R. Huffman, Absorption and scatteing of light by small particles, John Wiley & Sons, New York, 1983.