Optical properties of PVA films with diamond and titania nanoparticles

I Vlaeva1, T Yovcheva2, S Sainov1, V Dragostinova1 and S Stavrev3

1 Institute of Optical Materials and Technologies “Acad. J. Malinovski”, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Bl. 101/109, 1113 Sofia, Bulgaria
2 Department of Experimental Physics, University of Plovdiv “P. Hilendarski”, 24 Tsar Assen Street, 4000 Plovdiv, Bulgaria
3 “Nano” SS Ltd., 4700 Smolyan, Bulgaria

E-mail: vlaeva@optics.bas.bg

Abstract. Polymer nanocomposite materials have attracted increasing attention because of their unique optical properties. Of practical interest is the controllable increase in the refractive index (RI) values of the polymer nanocomposite materials by using nanoparticle inclusions with high refractive index values. This paper presents a study of the optical characteristics of polymer nanocomposites with diamond and titanium dioxide (titania) spherical nanoparticles with different diameters (2 nm and 15 nm) and very close refractive index values – 2.50 and 2.42, respectively. The investigated samples are with different concentration of the particles varying from 0 wt% to 3 wt.%. The refractive indices are measured by a laser refractometer at two wavelengths, 532 nm and 632.8 nm. The results obtained show that the RI increases with the increase in the concentration of the inclusions of titania and diamond in the PVA matrix.

1. Introduction

Organic-inorganic hybrid materials have attracted considerable attention in recent years due to their novel physical and chemical properties. By using titania inclusions the RI is increased and the new materials have an optical dispersion behavior between that of organic polymers and inorganic glasses [1]. The refractive index (n) increases linearly with the increase in the titania content (more then 0.1 wt.%) of the aminoalkoxysilane-capped pyromellitic dianhydride (PMDA) – titania hybrid optical thin films [2]. The same behavior is observed in the polyamide-nanocrystalline-titania hybrid materials with titania contents from 20 wt.% to 90 wt.% [3]. The linear RI variation is also measured in acrylic polymer-titania hybrid films with titania content (up to 5 wt.%) before and after hydrothermal treatment [4], in titania nanocrystals into (3-glycidylxyloxypropyl) trimethoxysilane organic silica sol (10-50 wt.% titania inclusions) [5] and in photosensitive polyimide-nanocrystalline titania hybrid (up to 30 wt.% titania inclusions) [6].

In [7, 8] the optical transmittance and RI of the titania/epoxy nanocomposites coatings were presented and the authors noted that the transmittance and RI of pure epoxy were 99 % and 1.48, respectively. The refractive index of pure titania nanoparticles – i. e. 100 wt.% titania content was measured to be 2.6, while the RI of hybrid nanocomposite films at 633 nm increased from 2.19 (10 wt.% titania content) to 2.38 (30 wt.% titania content). When adding amorphous-titania nanoparticles to the epoxy matrix, where titania is dispersed directly into the polymer matrix without
the use of organic surfactant, the transmittance and RI of nano-titania/epoxy nanocomposite coating increase more than 90 % and become 1.607 (for 10 wt.% titania) and 1.668 (for 30 wt.% titania), respectively (see [8]).

The refractive index of acid-modified poly (bisphenol A carbonate) with titania nanocomposites at 486 nm, 589 nm and 656 nm is investigated and the experimental results are predicted based on Maxwell-Garnett and Lorentz-Lorenz theories [9]. The concentrations of titania in the cited references vary from 10 to 90 wt.%. At small concentrations (0-0.5 wt.%) the reverse relation is observed – a decrease in the refractive index at 514.5 nm [10].

As far as we know, diamond has not been used for polymer nanocomposites yet. The optical properties of nanocrystalline diamond films are investigated in [11] by a single-oscillator Sellmeier model that we also use in the present work.

In this paper we present optical investigations of polyvinyl alcohol thin films with small concentrations of both titania (up to 1 wt.%) and diamond (up to 3 wt.%) nanoparticles.

2. Experimental details

2.1. Sample preparation
The films used in the experiments contained particles of titania with a diameter D = 15 nm and diamond nano-particles with a diameter of 2 nm. The nano-particles were imbedded in a matrix of polyvinyl alcohol (PVA), which is a solid colourless polymer:

\[
\left[-\text{CH}_2 - \text{CH(OH)}_2 \right]_n.
\]

In the experiment, polyvinyl alcohol with a molecular mass 22 000 of the “Fluka” company was used, from which suspensions of 6 wt.% water solution of PVA with different quantities of titania and diamond nano-particles were prepared.

The titania and the diamond nano-particles are in various weight proportions relative to PVA. Their concentrations vary from 0 wt.% to 1 wt.% and from 0 wt.% to 3wt.%, respectively.

Glass substrates are used with a conductive coating of tin dioxide of the “Merck” company production. The glass substrates are washed and dipped in a 1 % – alcohol solution of polyvinyl pyrrolidone (PVP). This contributes to the improvement of the film adhesion. On a leveled table at a temperature of 20°C certain quantities of the prepared suspensions are deposited which are then dried for 24 hours at room temperature. The films obtained are 10 μm thick.

2.2. Refractive index measurement
The surface refractive indices \( n \) for all the samples were measured by the method of the disappearing diffraction pattern using two wavelengths laser refractometer. The principle set-up of the two wavelengths laser refractometer is shown in figure 1.
Two lasers were used as light sources: He–Ne “Spectra Physics” (0.5 mW), and Laser pointer (0.1 mW) generating at 632.8 nm and 532 nm, respectively. A sample was placed between the glass prism and the reflecting grating. Benzyl alcohol was used as a contact liquid in order to minimize Fresnel losses. The thickness of the sub-surface layer where \( n \) was measured co-related to the evanescent wave penetration into the sample was estimated to be about 1 \( \mu \)m [12]. The value of the critical angle \( \varphi_{cr} \) was measured in the air at a chosen wavelength. After that \( n \) was calculated from the formula:

\[
 n = N \sin \left( A \pm \arcsin \left( \frac{\sin \varphi_{cr}}{N} \right) \right).
\]  

The signs (+) and (−) correspond to clockwise and counter-clockwise determination of \( \varphi_{cr} \), respectively. In our case the sign is (−). In equation (1) \( A = 65^\circ \) is the refraction angle of the prism, \( N \) is the refractive index of the prism for the used wavelength – 1.7347 and 1.7480 for 632.8 nm and 532 nm, respectively.

The uncertainty in determination of the critical angle \( \varphi_{cr} \) is the main source of error in evaluation of the refractive index. In our experiments “Micro Control” rotary stage with 1 arcmin resolution was used. The theoretical RI uncertainty is:

\[
 \Delta n = N \cos \left( A - \arcsin \left( \frac{\sin \varphi_{cr}}{N} \right) \right) \left( N^2 - \sin^2 \varphi_{cr} \right)^{-1/2} \cos \varphi_{cr} \Delta \varphi_{cr}.
\]  

In our experiments \( \Delta \varphi_{cr} = \pm 2.10^{-3} \) (± 5 arcmin) and uncertainty is \( \Delta n = \pm 1.10^{-3} \).

3. Results and discussion
In figures 2 and 3 the dispersion curves in the range 400 nm – 800 nm are plotted.

![Figure 2. RI dispersion curves of the PVA matrix with diamond nanoparticles (D = 2 nm).](image1)

![Figure 3. RI dispersion curves of the PVA matrix with titania nanoparticles (D = 15 nm).](image2)

The surface refractive index was measured at 532 nm and 632.8 nm and the dispersion relationships were presented by Sellmeier one-oscillator model:
\[ n^2 - 1 = \frac{s}{1 - \left(\frac{\lambda_s}{\lambda}\right)^2}, \]  

where \( s \) and \( \lambda_s \) are Sellmeier’s coefficients.

In comparison to the samples without nanoparticles an increase of RI values was observed when nano-sized particles of diamond and titania were embedded into the PVA matrix. It was established that the percentage rise of the nanoparticles results in an increase of the RI values. This effect was stronger for the samples with 1 wt.% that contained titania nanoparticles, and weaker for those containing diamond ones. The relationships for the investigated samples as a function of the nanoparticles concentration in the PVA matrix are presented in figures 4 and 5.

**Figure 4.** Dependence of the refractive index on the concentration for the PVA matrix with diamond nanoparticles at a wavelength of 532 nm.

**Figure 5.** Dependence of the refractive index on the concentration for the PVA matrix with titania nanoparticles at a wavelength of 532 nm.

Our experimental results demonstrate that for concentrations of the diamond nanoparticles over 1 wt.% and of the titania nanoparticles over 0.2 wt.%, the concentration relationships are linear which is in good agreement with the reference data [2-6]. For lower nanoparticle concentrations, however, the concentration relationships do not have a clearly expressed linear nature, which, we assume, is due to the very low nanoparticle concentrations used in our investigations.
Investigations on the transmission spectra in the range 500 nm – 800 nm with “Cary 5E” spectrophotometer for the 10 µm polymer films are carried out, the data being presented in figure 6. The experimental uncertainty is ± 0.5 %.

![Transmission spectra for the PVA matrix with titania and diamond nanoparticles.](image)

The experimental results show that the PVA film transmittance diminishes when nano-sized particles are introduced in the polymer matrix. The samples with diamond nanoparticles have higher transmittance value than those with titania. We suggest that this is due to scattering caused by the introduction of nanoparticles with different sizes in the polymer matrix. The lower transmittance of the samples containing titania can be attributed to the larger diameter of titania particles (15 nm), as compared to that of the diamond particles (2 nm).

4. Conclusion
Based on the experimental results obtained the following conclusions can be drawn:
- the nano-sized particles embedding in a polymer matrix causes an increase in the refractive index of the polymer-nanoparticles composite material – from 1.488 to 1.505 at 532 nm for the samples that contain 1 wt.% diamond nanoparticles, and from 1.488 to 1.526 at 532 nm for the samples that contain 1 wt.% titania. The experimental uncertainty is ± 0.001;
- at very low concentrations of the nano-sized particles, the relationship of RI on the concentration at a wavelength of 532 nm has a non-linear nature, and at higher concentrations, the relationship is clearly linear;
- the samples that contain titania nanoparticles have lower transmittance as compared to those containing diamond particles. The reason for this is the different diameters of the investigated nanoparticles in the PVA matrix that causes increased scattering.

Acknowledgements
I. Vlaeva, S. Sainov, T. Yovcheva and V. Dragostinova are grateful for the financial support under Contract DO 02/155 by Ministry of Education and Science, Bulgaria

References
[1] Wang B, Wilkes G L, Hedrick J C, Liptak S C and McGrath J E 1991 Macromol. 24 3449-50
[2] Chang Ch-Ch and Chen W-C 2001 Inc. J. Polym. Sci. Part A: Polym. Chem. 39 3419-27
[3] Su H-W and Chen W-Ch 2008 J. Mater. Chem. 18 1139-45
[4] Su H-W and Chen W-Ch 2008 Macromol. Chem. Phys. 209 1778-86
[5] Liu Y, Lü Ch, Li M, Zhang L and Yang B 2008 Coll. Surf. A: Physicochem. Eng. Aspects 328 67-72
[6] Chang W-L, Su H-W and Chen W-Ch 2009 Europ. Polym. J. 45 2749-59
[7] Chau J L H, Lin Y-M, Li A-K, Su W-F, Chang K-Sh, Hsu S L-Ch and Li T-L 2007 Mat. Lett. 61 2908-10
[8] Chau J L H, Tung Ch-T, Lin Y-M and Li A-K 2008 Mat. Lett. 62 3416-18
[9] Imai Y, Terahara A, Hakuta Y, Matsui K, Hayashi H and Ueno N 2009 Europ. Polym. J. 45 630-38
[10] Jiménez Riobóo R J, De Andrés A, Kubacka A, Fernández-Garcia M, Cerrada M L, Serrano C and Fernández-Garcia M 2010 Europ. Polym. J. 46 397-403
[11] Hu Z G, Prunici P, Hess P and Chen K H 2007 J. Mater. Sci.: Mater. Electron. 18 S37-41
[12] Yovcheva T, Sainov S and Mekishev G 2007 J. Optoelectron. Adv. Mat. 9 2087-2090