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Optical properties of charged polymer with nano-sized zeolite inclusions

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The optical characteristics of photopolymer films doped with nanoparticles are studied. The investigated systems consist of a soft polymer matrix containing porous zeolite nanoparticles with concentrations varied in the range from 0wt.% to 7wt.%. 40µm thick layers are obtained by casting the photopolymer nanocomposite solution on glass substrates. The corona charging influence on the transmission spectra and on the surface and the effective refractive index of the dry layers is investigated.

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Keywords: Zeolite, Polymer, Optical properties, Corona discharge

1. Introduction

Nanoparticle doped polymers are the subject of increased research interest due to their unique and improved mechanical [1], electrical [2], optical [3-4] and thermal properties[5]. There are several advantages in using nanoparticles as dopants [6].The most exciting advantage is that the properties of the polymer nanocomposites are highly tunable due to their hybrid nature. Nanoparticles also introduce lower scattering than the microsized particles used as reinforcing agents. Another advantage is that when compared to traditional additives the loading requirements for nano-sized dopants are lower. The incorporation of nanodopants in a host matrix influences their optical characteristics. The effect of electrical field on the refractive index (RI) and on the permittivity of doped polymers, modified by external electrical field has recently been reported [7, 8]. It should be mentioned that nanocomposite RI measurement is not only the experimental challenge, but also need theoretical elucidation [9].

In this work, the influence of a corona discharge on the optical properties of photopolymer samples doped with nano-sized zeolite has been experimentally investigated. The surface refractive index (n_s) as well as the effective one (n_{eff}) have been measured by a laser refractometer and by a spectrophotometric method, respectively.

2. Experimental

2.1 Samples preparation

In the present work we have studied polymer samples with nano-sized zeolite inclusions. The investigated systems contain a soft photopolymer matrix with embedded porous nanoparticles. The standard photopolymer solution developed in Centre for Industrial and Engineering Optics-Dublin Institute of Technology [10] is used as a matrix. It consists of 9ml stock solution of Polyvinyl alcohol (20w/w%), 2ml triethanolamine, 0.6g acrylamide, 0.2g N,N-methylene bisacrylamide and 4ml Erythrosin B dye of 1.1mM dye stock solution. The nanoparticles used in this study were purchased from InnosLab Ltd. The Si-MFI zeolite nanoparticles (1.7wt.% H₂O colloidal solution) whose preparation is described in details elsewhere [11] are added in concentrations from 0wt.% to 7.0wt.%. In order to obtain equal thicknesses of the layers doped with different concentrations of zeolite nanoparticles, distilled water is added to obtain a total volume of 45ml. An amount of 0.7ml of the well mixed solution was gravity settled on a levelled 2.5cm x 7.5cm single glass substrate. The thickness of the layers after drying for 24h in dark under normal laboratory conditions ($t^{\circ} = (21-23)^{\circ}\text{C}$ and $\text{RH}=(40-60)\%$) was about 40µm. The dry layers were then exposed to UV light (LV202 Megaelectronics) with intensity 2.5mW/cm² for 30min to achieve complete photopolymerization.

2.2 Charging of the samples

Some of the samples were corona treated in a conventional point-to-plane three-electrode corona discharge system consisting of a corona electrode (needle), a grounded plate electrode, and a metal grid placed between them. Samples were placed on the grounded plate electrode. A positive or negative voltage of 5kV was applied to the corona electrode. 1kV voltage with the same polarity was supplied to the grid. The samples were charged under standard room conditions ($T = (21-23)^{\circ}\text{C}$ and $\text{RH} = (40-60)\%$) for 3min.

2.3 Measuring of the surface refractive index

The surface refractive indices (RI) n_s for all the samples were measured by the method of the disappearing diffraction pattern using two wavelengths laser refractometer. The method and the laboratory device were reported earlier in [12]. Two lasers were used as light sources: He-Ne "Spectra Physics" (0.5mW), and Laser pointer (0.1mW) generating at 632.8nm and 532nm, respectively. Methylene iodide CH_2I_2 was used as a contact liquid in order to minimize Fresnel losses. The thickness of the sub-surface layer where n_s was measured co-related to the evanescent wave penetration into the sample and was estimated to be about $1\mu\text{m}$. The experimental uncertainty was $\Delta n_s = \pm 0.0003$.

2.4 Measuring of the effective refractive index

The effective refractive index (RI) n_{eff} was determined by the iteration technique developed by Abeles and Theye [13] using two independent spectrophotometric measurements. For this purpose the transmission and the reflection measurements were carried out using a Cary 05E (USA) spectrophotometer in the spectral range from 400nm to 800nm. The transmittance, T and the reflectance, R_f and R_b (the indices f and b denote reflectance from the layer side and reflectance from the substrate side, respectively) at normal light incidence were measured with accuracy of 0.1% and 0.5%, respectively. The calculation was performed through minimization of the differences between the measured and the calculated spectrophotometric functions using the 2D Newton-Raphson algorithm. The uncertainty of the effective RI was estimated with accuracy better than $\Delta n_{\text{eff}} = \pm 0.02$ [14].

3. Results

The optical properties (surface RI, n_s and effective RI, n_{eff}) of the corona charged nano-composite photopolymer samples with different zeolite nanoparticles concentrations (0, 1, 3, 5, 7)wt.% were investigated.

All samples were divided into two groups according to their charging conditions (polarity of the corona voltage – positive or negative). A control group (non-charged samples) – samples that were not corona charged – was

measured as well. We studied 5 samples from each of the groups and calculated the average value.

Table 1 represents the experimental data for the average value of the surface RI (n_s), obtained at different zeolite concentration C .

Table 1. The experimental data for surface RI (n_s).

$\lambda = 532\text{nm}$			
n_s C (wt.%)	Non-charged	Negatively charged	Positively charged
0	1.5130	1.5000	1.4995
1	1.5130	1.4990	1.4980
3	1.5010	1.4990	1.4985
5	1.5000	1.4985	1.4980
7	1.4950	1.4965	1.4960
$\lambda = 632.8\text{nm}$			
n_s C (wt.%)	Non-charged	Negatively charged	Positively charged
0	1.5080	1.4960	1.4955
1	1.5080	1.4950	1.4940
3	1.4960	1.4950	1.4945
5	1.4950	1.4945	1.4940
7	1.4900	1.4925	1.4920

The measured values were used to obtain the dispersion coefficients from the one-oscillatory model of Sellmeier and to plot the dependence of surface RI (n_s) on the wavelength $n_s(\lambda)$. The dispersion dependences for non-charged samples are plotted in Fig. 1, and for the charged samples – in Fig. 2.

The effective RI, n_{eff} is determined by double (T, R) spectrophotometric method using the Newton-Raphson's iterative algorithm. The obtained spectral dispersion of the effective RI is extrapolated using the Sellmeier equation.

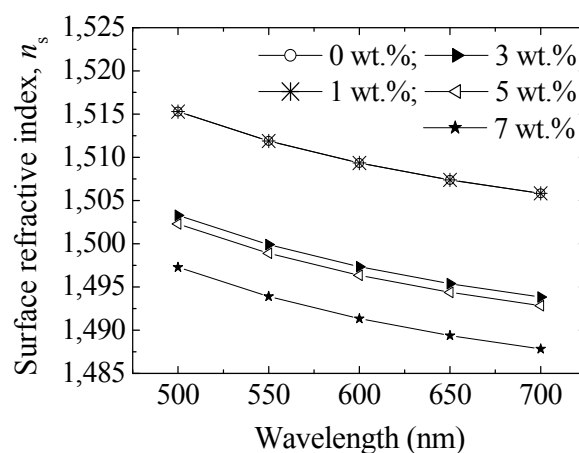


Fig. 1. Surface RI dispersion of non-charged samples with different zeolite concentrations.

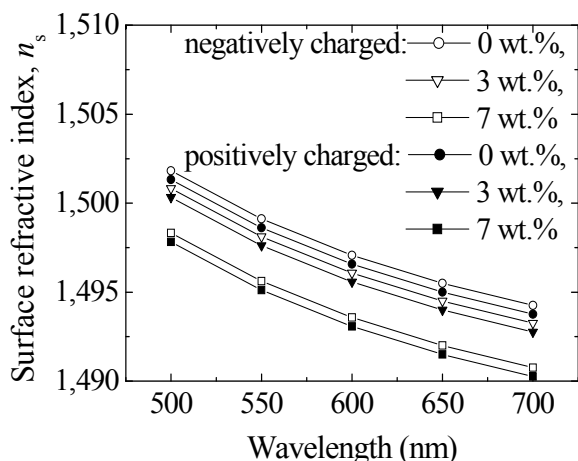


Fig. 2. Surface RI dispersion of charged samples with different zeolite concentrations.

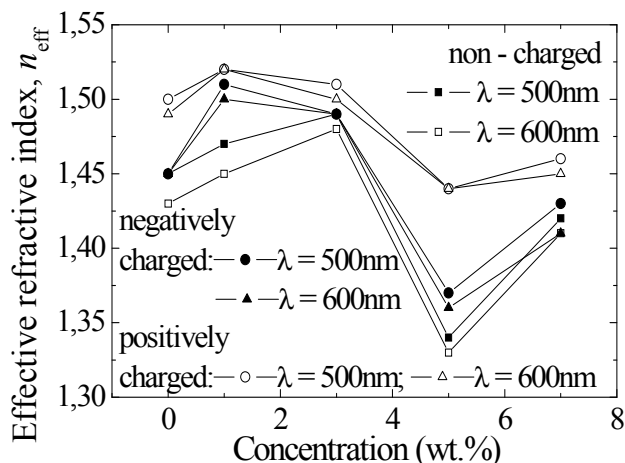


Fig. 3. Effective RI as a function of zeolite concentrations of all the samples conditions at two wavelengths.

In the investigated spectral region, they manifested maximum absorption close to 500nm and maximum transmittance around 600nm. The dependence of the effective RI on zeolite concentration for non-charged samples and samples charged at different polarity was measured at 500nm and 600nm; the corresponding curves are plotted in Fig. 3.

For all of the studied samples the dependence of the effective RI on nanoparticle concentration was non-linear. The maximum values were found for the samples with 1wt.% zeolite nanoparticles concentrations, and the minimum – for those that had 5wt.% concentrations. The dispersion dependences for the non-charged and charged samples with fixed zeolite nanoparticles concentrations are nearly the same. The curves for 5wt.% zeolite concentrations are plotted in Fig. 4.

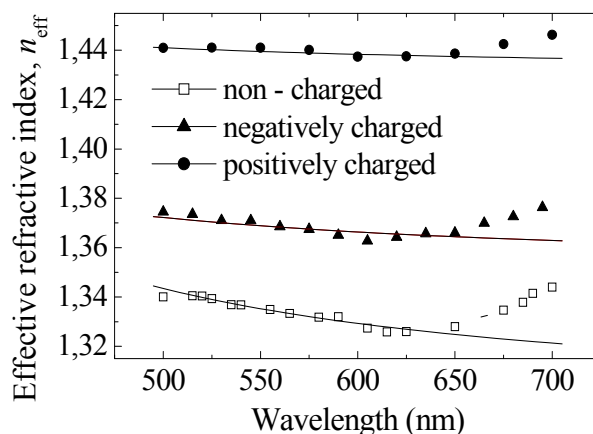


Fig. 4. Effective RI dispersion of all the samples with 5wt.% zeolite concentrations. Solid lines are Sellmeier fit.

4. Discussion

The surface RI (n_s) for non-charged samples with 0wt.% and 1wt.% nano-sized zeolite concentrations are practically the same. It is observed that the surface RI for non-charged samples decreases when nano-sized zeolite concentrations increase (Table 1, Fig. 1). For the charged samples with the increase of the zeolite nanoparticles concentrations, similar decrease of the surface RI is observed (Table 1, Fig. 2). It should be noticed that the drop in the surface RI is more pronounced for the samples with 7wt.% nano-sized zeolite concentrations. In the frame of our experimental uncertainty it is rather difficult to find out the surface RI dependence on the corona discharged polarity.

It is important to note, that the change of the surface RI in a narrow surface layer obtained by a positive or a negative corona discharge is comparable that obtained by addition of the zeolite nanoparticles with concentrations higher than 1wt.%. For all samples with concentrations of the zeolite nanoparticles below 7wt.% the corona charging causes a slight decrease of the surface RI. It is only for the samples with 7wt.% nano-sized zeolite concentrations that we observed increased values of the surface RI caused by the corona charging.

The effective RI (n_{eff}) displays a rather different behaviour. For all the samples, irrespective of the concentrations of the zeolite nanoparticles (0 – 7)wt.% the corona discharge gives rise to the effective RI (Fig. 3). The effective RI depends on the corona discharge polarity, and the values are higher for the positively charged samples compared to the negatively charged samples. Hence, the dispersion curves for the negatively charged samples are situated lower than those for the positively charged samples (Fig.4). A low dependence of the effective RI on the wavelength for all samples is observed. The zeolite nanoparticles have micro-porous molecular structure that can accommodate a wide variety of cations [15]. During the negative corona discharge, it is possible that some of these cations become neutral. This perhaps is the reason

for the lower effective RI values and the corresponding dispersion curves. In the case of the surface RI, where a 1 μm sub-surface layer is investigated, perhaps the amount of cations present at the surface is insufficient to cause corona discharge polarity influence.

The dependence of the effective RI on the zeolite nanoparticles concentrations is non-linear (Fig. 3). A similar behaviour of the effective RI of doped polymers (PS, PMMA) modified by electrical field was demonstrated in [7].

In both cases, surface and effective, the refractive index modulation is due to the different influences of two factors, namely the inclusion of zeolite nanoparticles with various concentrations in the host polymer matrix, and the changing polarizability of the samples as a consequence of corona charging. In this way the decrease of the surface RI with the increase of the nano-sized zeolite concentration (from 0wt.% to 5wt.%) could be explained by the fact that the zeolite's RI value is lower than the host polymer matrix RI value. On the other hand, the effective RI increases with the growth of the nano-sized zeolite concentration (from 0wt.% to 7wt.%), and the increased surface RI for the 7wt.% nano-sized zeolite concentration could be explained with the increase of the sample's polarizability.

5. Conclusions

The obtained results show clear influence of a corona discharge on optical properties of polymer samples doped with different nano-sized zeolite concentrations. This fact and the observed low dependence of the effective RI on the wavelength could be used for waveguide sensor applications.

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