Dielectric function of polymer nanocomposites in small filling factor approximation

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Abstract. The dielectric function of polymer nanocomposites is examined in a small filling factor approximation (SFFA). The linear concentration dependence on SFFA is experimentally confirmed by refractometric investigations of PVA thin films doped with titania and diamond nano-sized particles.

1. Introduction

Due to their interesting optical properties, ease of production, low cost, light weight, etc., organic-inorganic hybrid materials have attracted extensive scientific interest [1]. Nano-sized dopants offer ways to improve their mechanical properties together with good transparency and tunable refractive index [2]. For this purpose, high refractive index ($RI$) inorganic nanoparticles with no absorption in the visible region have been used (see [3] and references therein). The most widely used are titania (TiO$_2$) nanoparticles, that increase considerably the holographic diffraction efficiency, as was announced in [4, 5]. The technological advance in this field is very impressive: if twenty years ago TiO$_2$-containing polymer nanocomposites had a tunable $RI$ up to 1.76 [6], recently, synthesis of optically transparent polyimide-TiO$_2$ thin films was reported with tunable $RI$ in the range 1.583 - 2.029 [7]. Transparent TiO$_2$-epoxy nanocomposite film with extremely high $RI$ in the range 2.18 - 2.38 was prepared three years ago [8]. The investigation of the effective dielectric function $\varepsilon$ of these nanocomposite materials can elucidate the interaction between the polymer matrix and the embedded inorganic high refractive index nanoparticles. The technology of obtaining high $RI$ polymer nanocomposites is a real challenge, but at the same time small $RI$ changes are very important for optical applications.

In the theoretical background of the present investigation we use a small filling factor approximation (SFFA) to compare the most well known Maxwell Garnett [9], Bruggeman [10] and Odelevskii [11] mixing rules. The theoretical conclusions are confirmed experimentally by the refractive index ($RI$) measurements of polyvinyl alcohol (PVA) thin films 7 µm thick, containing different concentration of both 0 – 3 wt.% diamond and 0 – 2 wt.% TiO$_2$ nano-particles.
2. Theoretical background
Following [12], we shall consider dielectric spherical particles with dielectric function $\varepsilon_i$ and diameter $d$ embedded in a polymer matrix with dielectric function $\varepsilon_m$. The filling factor is determined by the next relation:

$$f = \frac{p \pi d^3 / 6}{V_m + p \pi d^3 / 6} = \frac{V_i}{V_m + V_i},$$

(1)

where $V_m$ is the volume of the matrix, $p$ is the number of particles, $V_i$ is the total particles’ volume.

In the following consideration we shall use small filling factor approximation (SFFA) – $f << 1$.

From equation (1) using SFFA we get:

$$f = \frac{V_i}{V_m (1 + V_i / V_m)} \approx \frac{V_i}{V_m} = \frac{V_i}{V_m} \frac{\rho_i}{\rho_m} = \frac{m_i}{M_m} \frac{\rho_m}{\rho_i} = C \frac{\rho_m}{\rho_i},$$

(2)

where $C$ is the weight concentration, $M_m$, $m_i$ are the weights of the matrix and inclusions, respectively. Accordingly, $\rho_m$ and $\rho_i$ are the specific weights of the matrix and inclusions.

The average electric field $\vec{E}_e$ in the polymer matrix containing spherical nanoparticles is the average of the electric fields inside the inclusions $\vec{E}_i$ and the host polymer matrix $\vec{E}_m$:

$$\vec{E}_e = f \vec{E}_i + (1 - f) \vec{E}_m.$$  

(3)

In the same way the average electric displacement is:

$$\vec{D}_e = \varepsilon_0 \varepsilon_e \vec{E}_e = f \varepsilon_0 \varepsilon_i \vec{E}_i + (1 - f) \varepsilon_0 \varepsilon_m \vec{E}_m,$$

(4)

where $\varepsilon_0$ is the vacuum permittivity and $\varepsilon_e$ is the effective dielectric function.

When the particle’s diameter $d$ is too small, the phase of the electromagnetic wave with wavelength $\lambda$ is constant when passing through the particle, i. e. $\frac{2 \pi \sqrt{\varepsilon_i d}}{\lambda} << 1$, and one can use the quasi-static approximation [13] in order to obtain the electric field inside the inclusions:

$$\vec{E}_i = \frac{3\varepsilon_m}{(\varepsilon_i + 2\varepsilon_m)} \vec{E}_m.$$  

(5)

From the equations (2-4), the Maxwell Garnett effective medium relation [9] is obtained:

$$\varepsilon_e = \varepsilon_m \left[ 1 + \frac{3f(\varepsilon_i - \varepsilon_m)}{(\varepsilon_i + 2\varepsilon_m) - f(\varepsilon_i - \varepsilon_m)} \right].$$

(6)

In 1935, Bruggeman [10] proposed that inclusions are embedded in the effective medium where $\varepsilon_i = \varepsilon_m$ and obtained the following expression from the Lorentz-Lorenz relation [14]:

2
\[
f \frac{(\varepsilon_i - \varepsilon_e)}{(\varepsilon_i + 2\varepsilon_e)} + (1-f) \frac{(\varepsilon_m - \varepsilon_e)}{(\varepsilon_m + 2\varepsilon_e)} = 0. \tag{7}
\]

From equation (6) the following quadratic equation can be obtained:

\[
\varepsilon_e^2 - 2A\varepsilon_e - \frac{\varepsilon_i \varepsilon_m}{2} = 0,
\]

\[
A = \frac{3f(\varepsilon_i - \varepsilon_m) + (2\varepsilon_m - \varepsilon_i)}{4} \tag{8}
\]

The solution of (7) yields:

\[
\varepsilon_e = A + \left( A^2 + \frac{\varepsilon_i \varepsilon_m}{2} \right)^{1/2}. \tag{9}
\]

The same result was obtained by Odolevskii in 1951 \[11\].

Solving the equation (8), we can use Taylor expansion up to the first order of \( f << 1 \) and after some transformations we obtain:

\[
\left( A^2 + \frac{\varepsilon_i \varepsilon_m}{2} \right)^{1/2} = \frac{2\varepsilon_m + \varepsilon_i}{4} \left[ 1 + 3f \left( \frac{\varepsilon_i - \varepsilon_m}{(2\varepsilon_m + \varepsilon_i)^2} \right) \right]. \tag{10}
\]

Finally, we obtain for the effective dielectric function:

\[
\varepsilon_e = \varepsilon_m + 3f \left( \frac{\varepsilon_i - \varepsilon_m}{(\varepsilon_i + 2\varepsilon_m)^2} \right). \tag{11}
\]

The same result can be achieved from equation (5), neglecting the second term in the denominator \( f << 1 \). In the visible spectral region far from the absorption band, refractive index \( RI \) is a square root of the dielectric function (dielectric constant or relative permittivity) from Maxwell’s electromagnetic theory \( \varepsilon^{1/2} = RI \). The relation (11) can be easily transformed into:

\[
RI = \varepsilon_e^{1/2} = \varepsilon_m^{1/2} \left[ 1 + \frac{3f}{2} \left( \frac{\varepsilon_i - \varepsilon_m}{(\varepsilon_i + 2\varepsilon_m)^2} \right) \right]. \tag{12}
\]

Despite the different approach used in the Maxwell Garnett, Bruggeman and Odolevskii’s mixing theories, in the small filling factor approximation the final results coincide (equations (11) and (12)). Using SFFA, we can represent the dependence of the nanocomposite film \( RI \) on the particle concentration. The relative difference of refractive indices of polymer nanocomposite \( n_e \) and polymer matrix \( n_m \) is a linear function of the concentration in a first approximation. From (2) and (12) we have:
\[
\frac{n_c - n_m}{n_m} = \text{const} \cdot C.
\] (13)

This can be experimentally proved by the refractometric measurements in the visible spectral region (400 nm – 800 nm). Hence, the simple relation (13) is convenient for experimental confirmation of the obtained theoretical results.

3. Experimental

3.1. Sample preparation

The films used in the experiments contained particles of titanium dioxide 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:

\[
\begin{align*}
\text{[CH}_2 - CH(\text{OH})_2 \text{CH}_2 \text{CH}_2 \text{CH}_2]_n.
\end{align*}
\]

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 titanium dioxide and diamond nano-particles were prepared.

The titanium dioxide and the diamond nano-particles are in various weight proportions relative to PVA. Their concentrations vary from 0 wt.% to 2 wt.% (titania) and from 0 wt.% to 3 wt.%, (diamond).

Glass substrates with a conductive coating of tin dioxide of the “Merck” company are used. The glass substrates are washed and dipped in a 1 %-alcohol solution of polyvinyl pyrolidone (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 \(\mu\)m thick.

In our experiments, two types of nano-sized particles with close physical characteristics but with different diameters \(d\) are selected – titania and diamond. The main properties of the experimental materials are listed in table 1.

| Materials | \(\varepsilon\) | \(\rho, \text{g/cm}^3\) | \(d, \text{nm}\) |
|-----------|----------------|-----------------|----------|
| PVA       | 2.19           | 1.20            | -        |
| Titania   | 5.84           | 3.51            | 15       |
| Diamond   | 6.25           | 4.24            | 2        |

3.2. Refractive index measurements

The refractive index is measured with a laser microrefractometer [15] at a wavelength of 632.8 nm, illustrated schematically in figure 1.

The laboratory device works on the principle of the critical angle \(\phi_c\) determination by disappearing of the diffraction pattern on the screen (6), obtained by the diffraction from the reflection metal grating (2) placed behind the sample (1) and flint glass measuring prism (4) with \(RI = N\). The critical angle value when the diffraction pattern disappears is measured with a rotary table (5).
The sample refractive index is calculated by

$$n_c = \varepsilon_c^{1/2} = N \sin \left[ A - \arcsin \frac{\sin \varphi_c}{N} \right].$$

(14)

The experimental uncertainty for thin film measurement [15] is $\Delta n_c \leq 1.10^{-3}$.

3.3. Results and discussion

The surface refractive indices of the polymer nanocomposite $n_c$ and polymer matrix $n_m$ were measured at 632.8 nm with a He-Ne laser microrefractometer. The relative difference of refractive indices $(n_c - n_m)/n_m$ was calculated and the experimental uncertainty was found to be less than $\pm 3.10^{-3}$.

The experimentally obtained concentration dependence curves are plotted in figure 2 (a) – PVA with diamond nanoparticles, (b) – PVA with titania nanoparticles.

Figure 2. Dependence of the relative difference of refractive indices on the concentration for the PVA matrix with both diamond and titania nanoparticles at a wavelength of 632.8 nm.
Our experimental results demonstrate that for the diamond nanoparticle concentrations up to 3 wt.% and for the titania ones up to 2 wt.%, the dependence of the relative difference of refractive indices (polymer nanocomposite and polymer matrix) on the concentration is linear. Therefore, the theoretical linear dependence of the square root of the dielectric function (refractive index in the visible spectral region) of polymer nanocomposites in small filling factor approximation on the nano-particle concentration is confirmed in the limits of our experimental uncertainty.

4. Conclusion
Despite the different approach used in the Maxwell Garnett, Bruggeman and Odelevskii’s mixing theories, in the small filling factor approximation the final results coincide. The linear dependence of the square root of the dielectric function (refractive index in the visible spectral region), of polymer nanocomposite film for small filling factor values, is experimentally confirmed by refractive index measurements of polyvinyl alcohol (PVA) thin films, containing either diamond or TiO$_2$ nano-particles. The different size and corresponding polarizability of the spherical nanoparticles used has no influence on the effective refractive index of PVA polymer nanocomposites. The potential optical applications of the obtained results we foresee are in thin film waveguide techniques, anti-reflective coatings, holographic optical elements, etc.

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