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ORIGINAL ARTICLE

Estimation and prediction of optical properties of PA6/TiO2 nanocomposites

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Abstract Nanocomposites are used in many scientific and industrial applications in recent times. In polymer nanocomposites, nanoparticles are used as the main component in creation which has always been considerable. Nano TiO2 as a nanoparticle has a very strong light scattering effect which can replace the ordinary TiO2 in less amounts of usage.

In this research, optical properties of the PA6/nano TiO2 nanocomposite are studied using Mie scattering theory. Mie theory uses the relative refractive index of a small particle to calculate the light scattering efficiency of a material. At first, experimental and estimated properties of a nanocomposite film containing nano TiO2 particles with 40 nm radius are compared. Optical properties of nanocomposites are then predicted with various particle sizes as a result of this research.

Results show that by taking the refractive index as an intrinsic property of a particle, it is possible to estimate the optical properties with a defined size and in addition it can help to predict these properties for different particle sizes.

1. Introduction

Optical properties of particles are studied from very old time until recent years as one of their main characteristics. There are several theories and models alongside experimental tries in order to measure or calculate this property. Many general definitions are made for various conditions in which the particle and its medium take part in the light scattering. These conditions include single and multiple scattering, absorbent or nonabsorbent media, regular or irregular shaped particles and nonlinear optics. A common base for all these theories is the Maxwell's equations for electromagnetism as the light is an electromagnetic wave. These theories include Mie and Rayleigh light scattering models, effective medium theories (EMT), anomalous diffraction theory (ADT), T-Matrix, Monte-Carlo approximations and vice versa (Ulrich, 2006; Nelson and Deng, 2007; Bohren and Huffman, 1983; van de Hulst, 1957; Mishchenko et al., 2004; Mie, 1908; Kokhanovsky, 2010; Şahin and Miller, 1997).

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Mie theory is widely used among all those mentioned in order to obtain scattering properties of a single spherical particle. Therefore it can be used for single scattering where light scattering happens only from a single particle with no relation to neighboring ones. The fact is, Mie theory is a very complicated calculation and it can only be done by some modifications and restrictions (Mie, 1978). On the other hand in a material there are many scattering particles interacting with each other in light scattering so it is multiple scattering which really happens in the material. Researches usually combine a simple form of Mie theory for a single particle with a multiple scattering theory like Kubelka–Munk in order to calculate the scattering of the whole collection (Quinten, 2001).

In this study Mie's results are used as an input to the Kubelka–Munk theory in order to calculate the reflectance factor of the nanocomposite. These theories are briefly described in next sections.

2. Refractive index

Many of the previously explained theories act upon the material's refractive index as a basic input for their calculations. Refractive index is used in Mie theory in order to evaluate its coefficients and then those coefficients are the key parameters for calculating the Mie scattering efficiencies. Refractive index are measured or calculated in various ways such as ellipsometry as an instrumental method. However there are some theoretical methods for this purpose one of which is presented here (Azzam and Bashara, 1988).

Materials especially metals have a complex refractive index. This index contains two parts, a real and an imaginary part. The imaginary part of refractive index can be calculated from the Beer–Lambert's law of transmittance. According to this law, transmittance is related to the extinction coefficient and the number of absorbent particles.

$$T = 10^{-\varepsilon cl} \tag{1}$$

where T is transmittance, ε stands for the extinction coefficient, c is the concentration of absorbing material and l is the path length for the incident light.

From the above equation:

$$\varepsilon = \frac{4K}{\lambda} \tag{2}$$

where λ is the wavelength and K is the imaginary part of the refractive index.

Fresnel law is the scattered light from the surface of materials relevant to the refractive index. According to this law when the light is entering an environment perpendicularly, the reflected light intensity is:

$$R = \frac{[(n-1)^2 + K^2]}{[(n+1)^2 + K^2]} \tag{3}$$

where n is the real part of refractive index.

3. Mie theory

Mie theory is one of the most basic theories among the light scattering models presented about a hundred years ago. It returns to 1908 when Lorentz Mie published an article about optical properties of spherical metal particles based on their complex refractive index. In this theory from the relative refractive index and size of the particle, two main coefficients are derived and used to calculate the optical parameters of the material like optical efficiencies, cross sections and patterns (Bohren and Huffman, 1983).

$$Q_{ext} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\Re(a_n + b_n) \tag{4}$$

$$Q_{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n| + |b_n|) \tag{5}$$

$$Q_{abs} = Q_{ext} - Q_{sca} \tag{6}$$

$$x = \frac{2\pi r}{\lambda} \tag{7}$$

in above formulas, Q_{ext} is the extinction efficiency, Q_{sca} is the scattering efficiency, Q_{abs} is the absorption efficiency, r is replaced by the particle radius and x represents the size parameter which is a factor of particle size and the incident light's wavelength.

a_n and b_n are Mie coefficients and n is the number of iterations in these functions where its maximum number is calculated according to Bohren and Huffman as below (Matzler, XXXX):

$$n_{max} = x + 4x^{1/3} + 2 \tag{8}$$

Mie coefficients can be estimated as the Bessel functions of the particle's relative complex refractive index.

$$a_n = \frac{m^2 j_n(mx)[xj_n(x)]' - j_n(x)[mxj_n(mx)]'}{m^2 j_n(mx)\left[xh_n^{(1)}(x)\right]' - h_n^{(1)}(x)[mxj_n(mx)]'} \tag{9}$$

$$b_n = \frac{j_n(mx)[xj_n(x)]' - j_n(x)[mxj_n(mx)]'}{j_n(mx)\left[xh_n^{(1)}(x)\right]' - h_n^{(1)}(x)[mxj_n(mx)]'} \tag{10}$$

From efficiencies, cross sections which are the area in which the light has its effects efficiently are calculated.

$$Q_{ext} = \frac{C_{ext}}{G}, Q_{abs} = \frac{C_{abs}}{G}, Q_{sca} = \frac{C_{sca}}{G}, Q_{ext} = Q_{abs} + Q_{sca} \tag{11}$$

and G is the particle's cross sectional area.

Finally the scattering patterns which demonstrate the amount of light scattering in different angles around the particles in the scattering plane are calculated from above formulas (Matzler, XXXX).

4. Kubelka–Munk theory

When multiple scattering occurs a single particle takes part in its own scattering behavior while in the light scattering of many neighbor particles. Kubelka–Munk theory is a multiple scattering theory which calculates the reflectance factor of a matter or semi-transparent material using its scattering (S) and absorption (K) coefficients.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{12}$$

R is the reflectance factor in formula 12.

These coefficients can be calculated by the efficiencies of other single scattering theories like Mie theory as an input.

$$K = \frac{Q_{ext} - Q_{sca}}{V_P} = \frac{Q_{abs}}{V_P} \quad (13)$$

$$S = \frac{3}{4}\frac{Q_{sca}(1-g)}{V_P} \quad (14)$$

where V_P is the particle volume and g is the asymmetry parameter or weighted cosine of the scattering angle of the scattered light (Quinten, 2001).

5. Materials and method

Polyamide 6 chips were provided from RTP company with the code number RTP200A and then mixed with nano Titanium Dioxide particles from Degussa with the average radius of 21 nm. Then the mixed material was fed to the Coperion Wener and Pfleiderer twin screw extruder at 235 °C in order to create the blended PA6/TiO2 chips. These chips were converted into thin films using a Toyoseiki hot pressing machine by pressing 7 g of prepared chips at 235 °C in 25 bar pressure forming a 30 × 30 cm film. Five thin films were produced and from each film a 10 × 10 cm film was extracted considering best places in evenness and uniformity. TEM photos were taken by Philips Transmission scanning microscope and then the diffuse reflectance, Fresnel reflectance and transmittance of the film were measured by a Cary 500 and two different Xrite ColorEye 7000a spectrophotometers so the approximate equality of the results proves the accuracy of the measuring instruments. Each film here was measured in five points, four in its corners and one in the center. Mean data from one of the Xrite spectrophotometers was chosen as the measured valuesof the film. Fresnel reflectance was measured for the samples by placing the film on the black background of the sample holder in the instruments and the diffuse reflectance was measured by placing a white tile under the samples. All computational evaluations were performed with MATLAB software from MathWorks.

6. Results and discussion

TEM pictures taken from the produced film is shown in Fig. 1. As seen the diameter of the particle is about 80 nm therefore it can be supposed that there are some clusters of particles in the polymer medium. Each cluster contains four particles however, in this research the cluster is assumed to be a single scattering particle. Therefore the calculations are based on the particles with 40 nm radius.

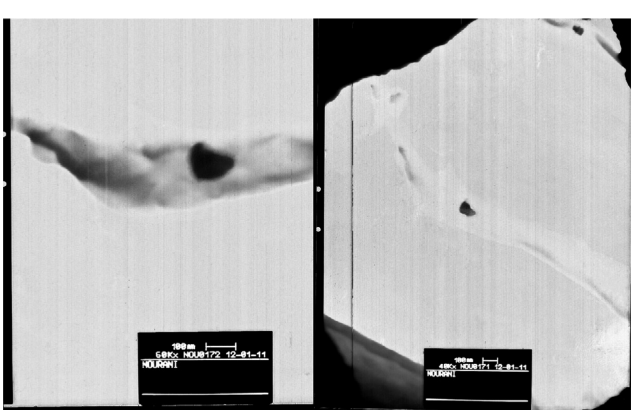

Figure 1 TEM pictures for PA6/nano TiO2 nanocomposite.

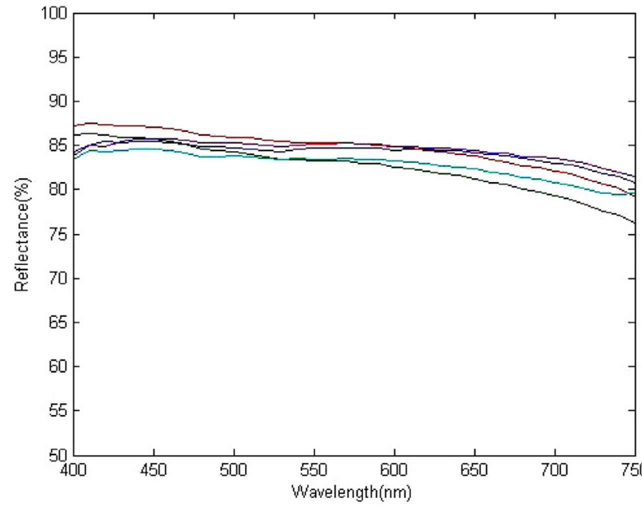

Figure 2 Spectral reflectance for five selected samples.

Fig. 2 shows the spectral reflectance for five selected film samples. As observed the reflectance factors are near to each other where their difference from their mean values is 99% insignificant for each wavelength step.

Fig. 3 shows the transmittance, Fresnel reflectance and diffuse reflectance of the film. It can be observed that the Fresnel reflectance is less than the diffuse one since the light reflectance only occurs from the film surface in the Fresnel reflectance according to the difference between the refractive indices of two environments.

From Eqs. (1) and (2) the imaginary part of the refractive index can be calculated for the film. This parameter is derived from the transmittance of nanocomposite film and then from Eq. (3) and the Fresnel reflectance of the film it is possible to acquire the real part.

Table 1 shows the imaginary part of the refractive index in different wavelength steps. A graph of the real part against light wavelength is observed in Fig. 4.

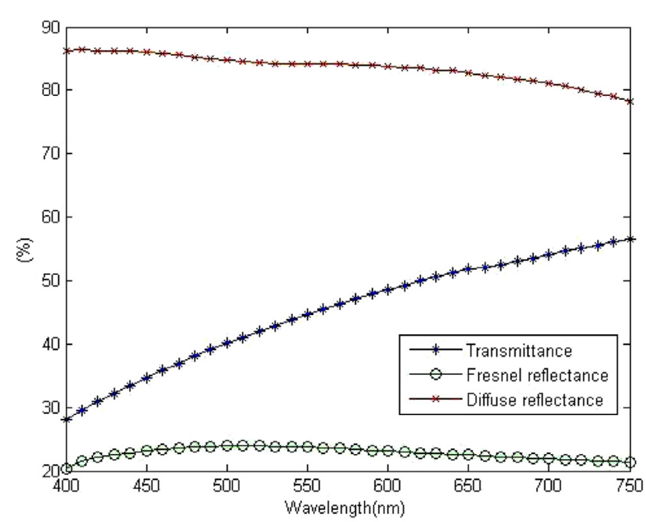

Figure 3 Optical properties of nanocomposite film.

Table 1 The imaginary part of refractive index for the nanocomposite film.

Wavelength (nm)	400	410	420	430	440	450	460	470	480	490	500	510
Refractive index	0.0015	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014	0.0013	0.0013	0.0013	0.0013	0.0013
Wavelength	520	530	540	550	560	570	580	590	600	610	620	630
Refractive index	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012
Wavelength	640	650	660	670	680	690	700	710	720	730	740	750
Refractive index	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012

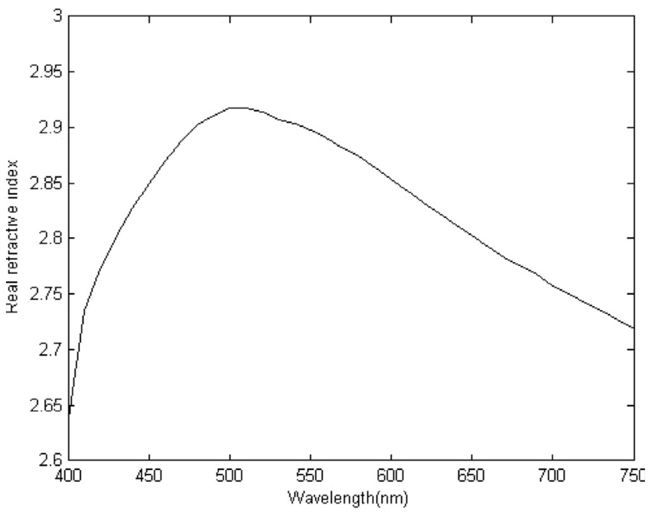

Figure 4 The real part of the refractive index.

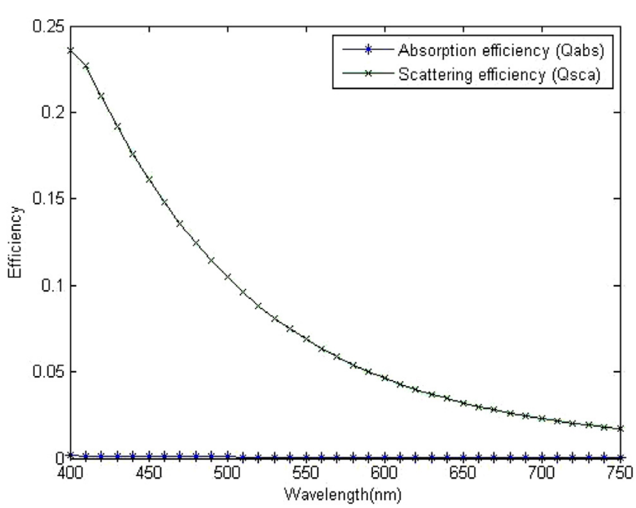

Figure 5 Efficiency functions against wavelength.

As observed in Fig. 4 the real part is increased against the wavelength until about 550 nm and then it is decreased. Therefore the particle mostly diffracts the light around 550 nm of light wavelength.

From the Mie approximation based on Eqs. ()()()(4)–(6) using computer programming various parameters such as efficiencies, cross sections and scattering patterns were estimated.

Q_{sca} and Q_{abs} are the efficiency functions that could be derived from the mentioned equations. These are the necessary functions for later estimation of the film's reflectance factor.

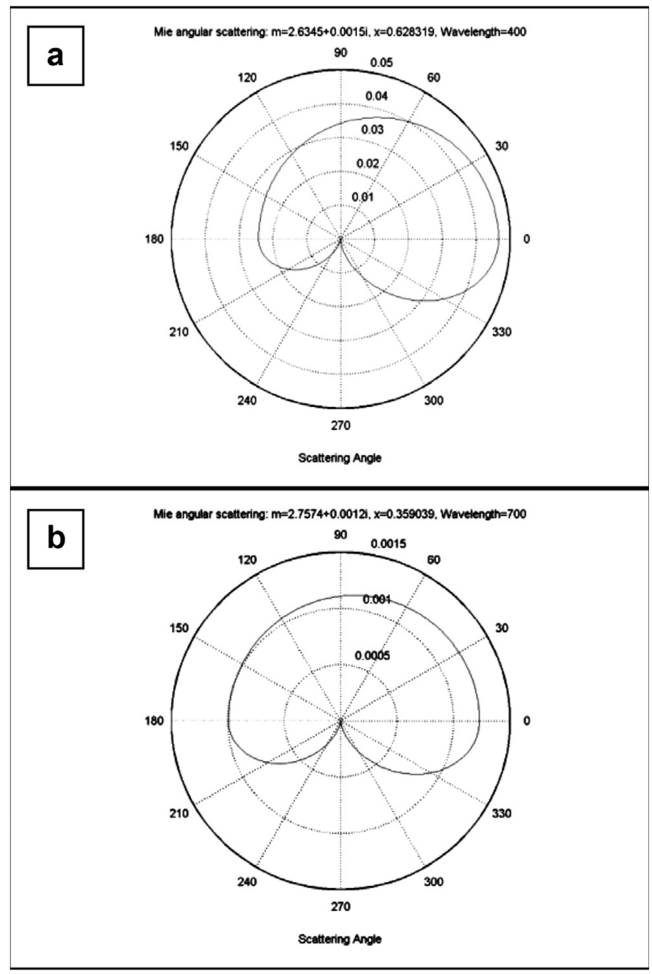

Figure 6 The scattering pattern for the nanoparticles in two different wavelengths: 400 nm (a) and 700 nm (b).

Fig. 5 shows the mean efficiency functions for the produced films.

It can be seen obviously that the scattering efficiency function is greater than the absorption function since the semi-transparent film is scattering the light more than it absorbs. Since Q_{sca} is decreasing by increasing the wavelength then the film is scattering more light in lower wavelengths than the higher ones.

Also as seen in Fig. 6 the scattering pattern is evaluated in different steps of the wavelength.

Scattering patterns show the amount of scattered light in each wavelength and angle. Fig. 6 shows that the scattering occurs mainly in the upper quarters. A three dimensional view of these changes among the angle, scattering and wavelength is

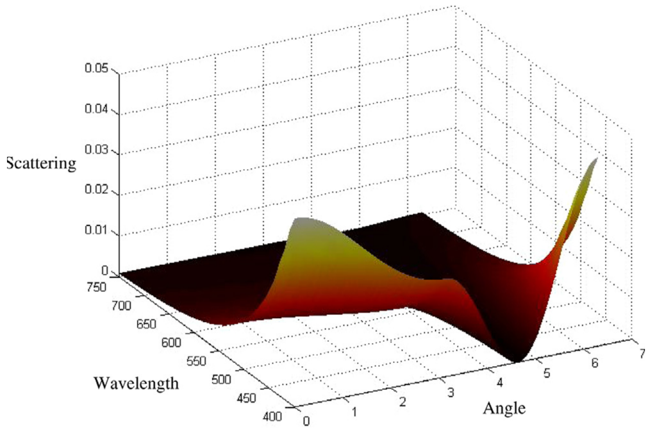

Figure 7 Scattering pattern versus angle (radians) and wavelength (nm).

shown in Fig. 7. As observed, the pattern varies by changing the wavelength and the angle.

After calculating the Mie parameters, using Kubelka–Munk theory the K/S parameter was estimated based on formula 12 and the reflectance is then obtained from Eqs. (13) and (14).

Fig. 8 shows the comparison between the measured reflectance and the estimated one using theoretical method. The correlation coefficient is calculated between the measured and the estimated reflectance factors equal to 0.97 which shows the great correlation between them. As observed, there is a good correspondence between the two curves and therefore it can be concluded that the method is suitable for estimating the optical properties of a nanoparticle nanocomposite based on its intrinsic characteristic which is the refractive index.

In the next section, the properties of the nanocomposite film are predicted with different particle sizes which can help to design a favorite composite before the production by assuming a constant refractive index for different particle sizes.

Using the above approximation for various particle sizes, the final results for the desired nanocomposites are shown as their reflectance factor in Fig. 9.

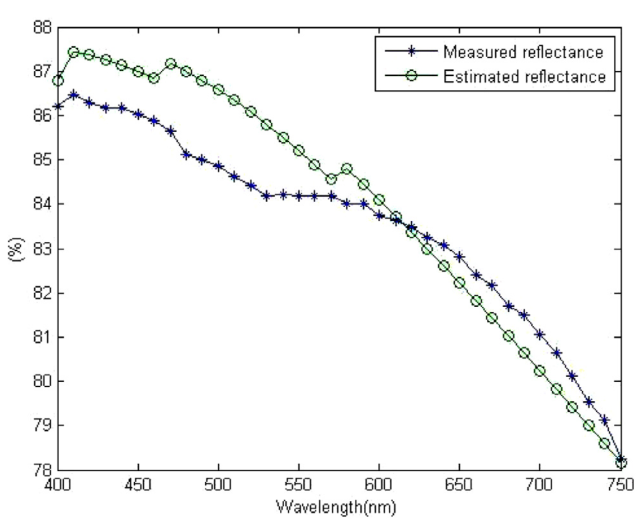

Figure 8 The real measured reflectance of the nanocomposite versus the theoretical model.

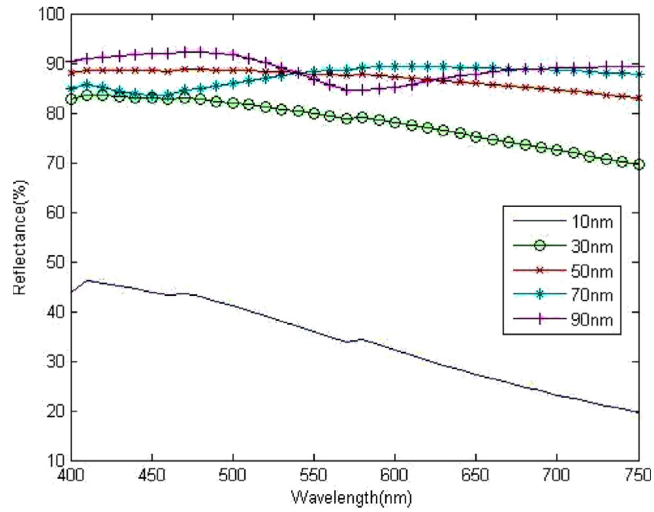

Figure 9 Estimated reflectance spectrums for nanocomposites containing different particle sizes.

As shown in Fig. 9, by having the relative refractive index of the particle and its size, it is possible to estimate and predict the optical properties of the nanocomposite.

7. Conclusion

Optical properties of particles are one of their main characteristics. There are many ways to measure these properties using various devices; however with careful considerations it is possible to use different theoretical methods. Results showed that Mie approximations combined with Kubelka–Munk theory is a good way to predict and estimate the optical properties of polyamide nanocomposites containing nano TiO2 particles. It is possible to estimate the reflectance factor of a polymer film using the particle's relative refractive index to its medium as seen in Fig. 8. It is also possible to predict these properties for various particle sizes which could help to predesign the favorite product.

There could be also better selections in order to attain better results. In this research the particle cluster was accepted to be one particle unit. It is possible to calculate and aggregate the properties of each individual particle in order to get better correspondence to the experimental data. However this method will significantly increase the complexity of the method. Particle shape was assumed to be spherical while it is actually not. Other methods like T-matrix or EMT are able to estimate the properties of an irregular shaped particle.

This study investigated the optical prediction of polyamide 6 nanocomposites containing nano TiO2 particles which shows adequate and acceptable results.

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