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Estimation of Coloration Properties of PA6/TiO_2 Nanocomposites Based on Combined Light Scattering Theories

Amir Rastar*, Alireza Hoseinpour

Department of Textile Engineering, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

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Optical properties of nanocomposites are important and useful in their consumer satisfaction capacities. In this research, coloration properties of dyed PA6/nano TiO_2 nanocomposite is studied using a combined Mie and Kubelka-Munk light scattering theory. Mie theory uses the relative refractive index of a small particle to calculate the light scattering efficiency of a material while Kubelka-Munk theory inputs these efficiencies in order to evaluate the optical properties of a multiple scattering opaque object. Optical properties of a Polyamide 6/Nano Titanium Dioxide films containing 0.01% and 0.03% nano TiO_2 particles with 40nm and 50nm radius respectively, was investigated after dyeing with two different acid dyes and then compared to experimental measurements. Then the spectral reflectance and color values of nanocomposites with different particle sizes were predicted using the same method.

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

Keywords: Mie theory, Kubelka-Munk theory, TiO_2, nanoparticle, Color value.

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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 these characteristics. Many general definitions are made for various conditions in which the particle and its medium take part in the light scattering phenomena. [1-8].

Mie theory is widely used among all that mentioned in order to obtain scattering properties of a single spherical metal particle. Therefore it can be used for single scattering of light where the scattering happens only from a single particle with no relation to neighbor ones. [9]. On the other hand in a material, there are many scattering particles interacting and assisting each other in light scattering so it is the multiple scattering which really happens in the object. 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 efficiency of the whole collection [10].

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

1.1 Mie theory

Mie theory is one of the most basic theories among the light scattering models presented from 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 the size of particle, two main coefficients are derived and used to calculate the optical parameters of the material, such as optical efficiencies, cross sections and patterns [3].

$$Q_{ext} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\Re(a_n + b_n \qquad (1.1)$$

$$Q_{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n| + |b_n|) \qquad (1.2)$$

$$Q_{abs} = Q_{ext} - Q_{sca} \qquad (1.3)$$

$$x = \frac{2\pi r}{\lambda} \qquad (1.4)$$

in above formulas, Qext is the extinction efficiency, Qsca is the scattering efficiency, Qabs 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 which its maximum number is calculated according Bohren and Huffman as below [11]:

$$n_{max} = x + 4x^{1/3} + 2 \qquad (1.5)$$

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

$$a_n = \frac{m^2 j_n(mx)[xj_n(x)]' - j_n(x)[mxj_n(mx)]'}{m^2 j_n(mx)\left[xh_n^{(1)}(x)\right]' - h_n^{(1)}(x)[mxj_n(mx)]'} \qquad (1.6)$$

$$b_n = \frac{j_n(mx)[xj_n(x)]' - j_n(x)[mxj_n(mx)]'}{j_n(mx)\left[xh_n^{(1)}(x)\right]' - h_n^{(1)}(x)[mxj_n(mx)]'} \qquad (1.7)$$

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

$$Q_{ext} = \frac{C_{ext}}{G}, Q_{abs} = \frac{C_{abs}}{G}, Q_{sca} = \frac{C_{sca}}{G}, Q_{ext} = Q_{abs} + Q_{sca} \quad (1.8)$$

and G is the particle's across sectional area.

* amir.rastar@gmail.com

Finally the scattering patterns which demonstrate the amount of light scattering in different angles around the particles in the scattering plane are calculated from the results of above formulas [11].

1.2 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-Munkk theory is a multiple scattering theory which calculates the reflectance factor of a matte or semi-transparent material using its scattering (S) and absorption (K) coefficients.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1.9)$$

R is the reflectance factor in Eq. 1.9.

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

$$\mathrm{K} = \frac{\mathrm{Q_{ext}} - \mathrm{Q_{sca}}}{\mathrm{V_P}} = \frac{\mathrm{Q_{abs}}}{\mathrm{V_P}} \quad (1.10)$$

$$\mathrm{S} = \frac{3}{4}\frac{\mathrm{Q_{sca}}(1-\mathrm{g})}{\mathrm{V_P}} \quad (1.11)$$

Where $\mathrm{V_P}$ is the particle volume and g is the asymmetry parameter or weighted cosine of the scattering angle of the scattered light [10].

2. MATERIALS AND METHOD

Virgin Polyamide 6 chips were provided from RTP Company with code number RTP200A and then mixed with P25 nano Titanium Dioxide particles from Degussa with the average radius of 21nm after proper drying. Virgin polyamide chips were separately mixed with the ratios of 0.01% and 0.03% per weight of the chips. Then the mixed material was fed to the Coperion Wener and Pfleiderer twin screw extruder in the average 235^{o}C in order to create the blended PA6/TiO_2 chips. These chips were converted to thin films using a Toyoseiki hotplate by pressing 7g of mixed material under 25mpa pressure and 235^{o}C temperature for each film forming an approximate 30×30cm film. Philips EM208 transmission electron microscope was used to capture images from the samples in order to evaluate the particle cluster sizes in the films. Five individual films were produced for each percent of nanoparticles. Each film was cropped to two 10×10cm film for the dyeing process. Then, the produced films were dyed with two different Acid dyes, Telon Blue RR 01(C.I. Acid Blue 62) and Telon Red BN 03(C.I. Acid Red 42) manufactured by Dystar company. In this case, films were introduced to warm dye bathes with 40^{o}C temperature and then the temperature was raised to boiling point in 20 minutes and dyeing was continued for 45 minutes after that. Finally, spectral reflectance of the dyed films was measured by an Xrite ColorEye 7000a spectrophotometers. These measurements were performed for five positions for each film, four in the corners and one in the center. The mean value of all five measurements was reported as the experimental data. All computational evaluations were performed with MATLAB software from MathWorks.

3. RESULTS AND DISCUSSION

After mixing and extruding the films, aggregation of particles may take place in them therefore the particles form clusters in their media. The cluster size is used in the calculation as it is assumed that all clustered particles are a single unit which led to single scattering of the light by them in their field. In order to access the size of particle clusters in the samples, TEM pictures were taken from the produced films. In Fig. 1 it is observed that the radius of particle cluster sizes for two different amounts of used nano TiO_2 particles are approximately 40 and 50 nanometers approximately. Then the 40nm particle size is used for the 0.01% nano TiO_2 and the 50nm is used as the radius for 0.03% nanoparticles.

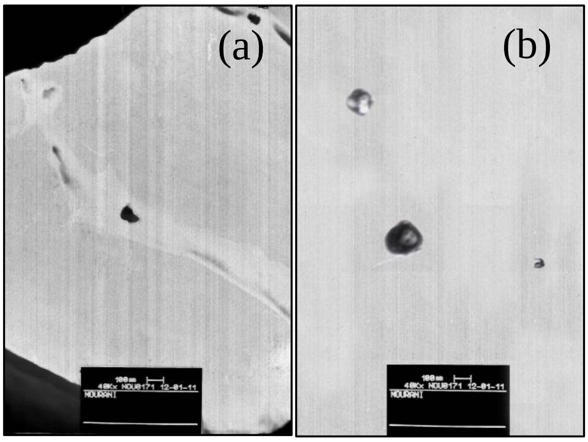

Fig. 1 – TEM picture of nanocomposite films: (a) 0.01% nano TiO_2 (b) 0.03% nano TiO_2

Single scattering is based on this fact that the distance among particles are large enough so the light scattered from one particle does not interfere with the scattered light from another one. So, it can be assumed that by increasing the amount on particles the accuracy of the result would be decreased due to the lower distances among the nanoparticles.

Spectral reflectance of two different dyed nanocomposite films are measured and observed in Fig. 2. As shown in this Fig. two different dyes were used with different spectral data in order to evaluate the method for different color values. The dyes were selected for their contrast so they would cover the whole steps of the visible light's wavelength range.

With respect to the complex relative refractive index of the nanoparticles which changes against the light wavelength and according to equation 6 and 7 the Mie coefficients were calculated using MATLAB software's Bessel functions. Then using these coefficients, the optical efficiencies of nanoparticles were calculated based on equation 1 and 2. The scattering efficiency and the absorption efficiency are used in acquiring the Keubelka-Munk's absorption and scattering coefficients.

In addition the scattering patterns are calculated in each wavelength step which demonstrates the amount of light scattering around the particle in each wavelength.

The Kubelka-Munk's coefficients are computed according to formula 10 and 11. These coefficients (K/S) are in a direct relation with the material's spectral reflectance based on formula 9.

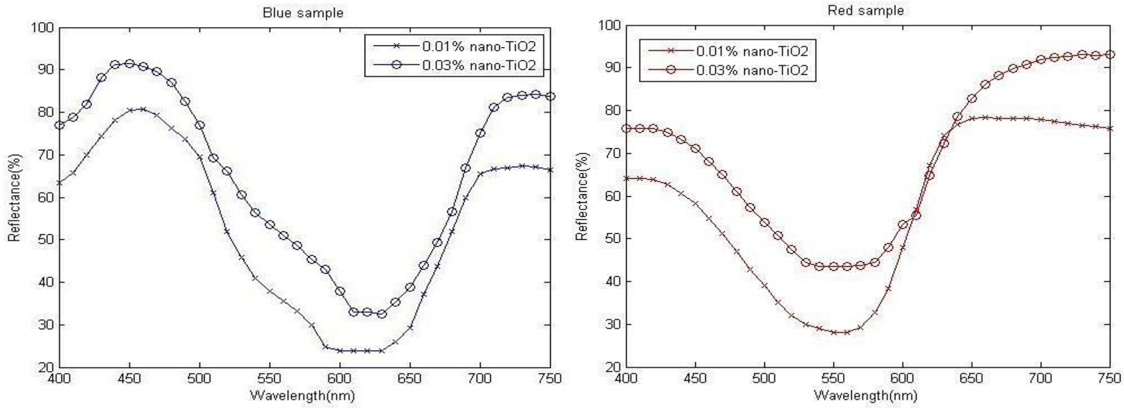

Fig. 2 – Spectral reflectance of two different dyed films

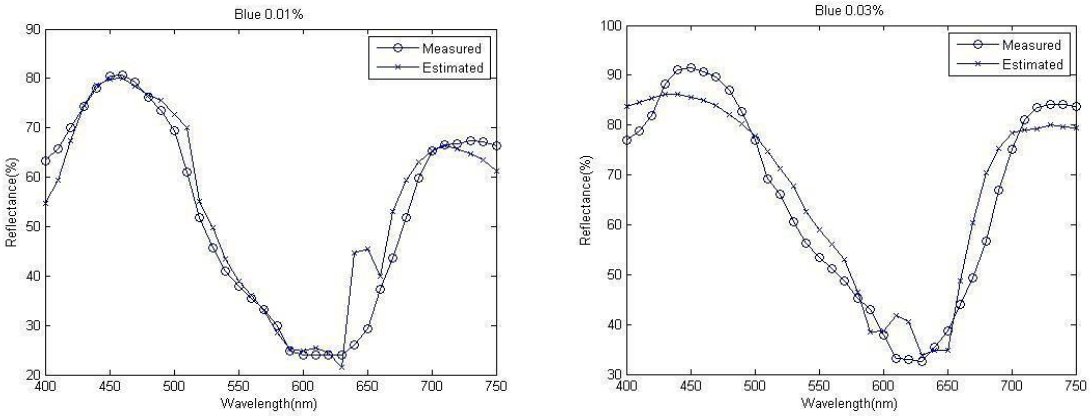

Fig. 3 – The measured spectral reflectance in comparison with the estimated one for the blue dyestuff

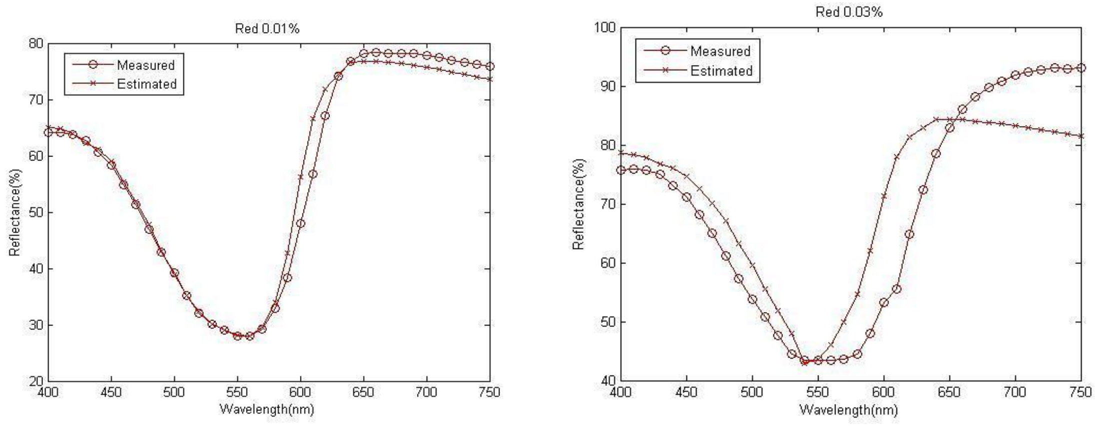

Fig. 4 – The measured spectral reflectance in comparison with the estimated one for the red dyestuff

Finally the spectral reflectance for the dyestuffs is calculated. Then these results are compared with the actual results measured by the experimental instruments. The results for each dye are shown in Fig. 3 and Fig. 4.

It can be observed that the combined Mie and Kubelka-Munk method is able to estimate the optical properties of colored materials as nanocomposite films with an acceptable precision. The color values and color differences for these two dyes which are shown in Table 1 also proves the above conclusion.

It is observed in Table 1 that the lower amounts of nanoparticles leads to more accurate results. By considering the color differences it is shown that the samples with 0.01% nano TiO_2 have less color difference compared to the other sample. The color difference for the low amount of nanoparticles are good but for the sample with higher amounts of nanoparticles, this difference is not very acceptable however, the correlation coefficient between the measured and the estimated data shows good correspondence between them. The correlation coefficient for the blue sample with 0.01% nanoparticle was 0.9631 while this number was 0.9048 for the sample with 0.03% TiO_2. Again, the coefficient for the red sample containing

Table 1 – The color values and color differences for two dyestuffs

	0.01% nano TiO_2			
	Measured red	Estimated red	Measured blue	Estimated blue
L*	68.5608	69.4894	71.2824	72.4123
a*	28.0317	30.1926	-10.5597	-10.7595
b*	-19.2000	-17.9983	-32.5463	-30.4258
Color difference	2.6412		2.4110	
	0.03% nano TiO_2			
	Measured red	Estimated red	Measured blue	Estimated blue
L*	76.5010	80.1922	79.6224	81.2981
a*	16.4229	20.5237	-10.0136	-12.0783
b*	-17.3786	-14.2280	-26.8290	-21.3408
Color difference	6.3536		6.0984	

0.01% nanoparticles was 0.9904 versus 0.8978 for the red sample with 0.03% TiO_2. This result is based on the distance among the particles in their medium which is lower in the sample containing higher amounts of nanoparticles. Therefore, it can be mentioned overally that the combined method of Mie and Kubelka-Munk theory is a good technique for estimating the coloration properties of nanocomposite films using the relative refractive index and the radius of particles as their intrinsic characteristics.

4. 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 dyed Polyamide nanocomposites containing nano TiO_2 particles however, the lower the amount of used nanoparticle is, the better the accuracy of the method would be. It is possible to estimate the reflectance factor of a polymer film using the particle's relative refractive index to its medium. 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 calculations which may not be actually very practical. Particle shape was assumed to be spherical while in fact, it is produced in an irregular shape. Other methods like T-matrix or EMT are able to estimate the properties of an irregular shaped particle. Other dyestuffs could also be used in order to investigate the results of this method.

This study investigated the optical prediction of dyed polyamide 6 nanocomposites containing nano TiO_2 particles which shows adequate and acceptable results.

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