Abnormally High Optical Transmittance of Refractive-Index Modified ZnO / Organic Hybrid Films

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***Abstract*— Hybrid films consisting of ZnO nanoparticles and organic matrices were fabricated at particle concentration levels of up to 60 wt%. The correlation between the refractive index and optical transmittance in the visible light region was investigated. The refractive index of the hybrid films was modified in a continuous manner in the range from 1.44 to 1.55. The refractive index increased linearly as a function of particle concentration. On the other hand, optical transmittance showed little change above the particle volume fraction of 0.08.**

Keywords - Nanocomposites; inorganic organic hybrid; refractive index; optical transmittance

I. INTRODUCTION

Uniform dispersion of nanoparticles in organic materials enables modification of the overall refractive index of the nanocomposites in the range between the indices of nanoparticle and organic materials [1]. Such hybrid materials have been attracting much attention as novel refractive index engineering materials for a wide range of optical applications including planar-gradient index lenses, reflectors, optical-wave guides, optical adhesives, anti-reflection films, holographic information storage devices and optical coupling materials [2]. Of particular importance for those applications is high optical transmittance at the wavelength of interest [1]. However, there is a trade-off between high refractive indices and high transparency. A high particle loading level not only leads to a high refractive index of the hybrid films but also increases light-scattering intensity, leading to low transparency [3].

To date, many studies have been conducted on the refractive index engineering of nanocomposites [2]. However, detailed investigation of the correlation between optical transmittance and the refractive index at particle concentrations higher than 30 wt% has been scarcely reported for visibly transparent nanocomposite films [4-7]. This is due to the difficulty in achieving high particle concentration levels without particle agglomeration. The agglomerates cause increased light scattering, resulting in higher turbidity and lower transparency [8]. In this study, the correlation between the refractive index and optical transmittance in the visible light region is investigated at particle concentration levels up to 60 wt% using ZnO nanoparticle dispersion systems having a low degree of agglomeration.

II. EXPERIMENTAL

ZnO nanoparticles were synthesised by mechanochemical processing as described in [9]. Hybrid films were made in two ways. In the first sample, ZnO nanoparticles were coated with stearic acid and dispersed into C12-15 alkyl benzoate. In the second sample, ZnO nanoparticles were coated with polymethylsilsesquioxane and dispersed into caprylic capric triglyceride. Since ZnO absorbs UV light, ZnO / organic nanocomposites are of particular interest as UV-screening visibly transparent films and coatings. C12-15 alkyl benzoate and caprylic capric triglyceride were selected as matrix materials for their optically transparent nature in the visible light region and the ability to disperse ZnO nanoparticles that are coated with stearic acid and polymethylsilsesquioxane, respectively [10].

The ZnO - alkyl benzoate hybrid system was prepared using the following flushing technique. Stearic acid 2g was dissolved in C12-15 alkyl benzoate 13g at 60°C and then 95g of ZnO nanoparticle aqueous suspension with a particle concentration of 14 wt% was added into the solution. During continuous agitation of the mixture, ZnO nanoparticles were transferred from aqueous to organic phases by developing stearic acid coatings on the particle surface. Then the supernatant water phase was decanted and a polyhydroxystearic acid dispersant was added into the organic phase. The resulting hybrid system had a particle concentration of 47 wt%, which was diluted with C12-15 alkyl benzoate to obtain a desired particle concentration. ZnO / caprylic capric triglyceride hybrid system was prepared using the method described elsewhere [11].

The particle size of coated ZnO was measured by photo-correlation spectroscopy (PCS) using a Nicomp 380ZLS particle sizer. Particle morphology was studied by transmission electron microscopy (TEM) using a JEOL 2000FX-II microscope with a beam energy of 80 keV. The crystallite size and crystal structure of the uncoated powder were examined by X-ray diffractometry (XRD) using a Siemens D5000 X-ray diffraction spectrophotometer with Cu-Kα radiation. The mean crystallite size was estimated from the width of the (100) diffraction peak using the Scherrer equation [12]. The specific surface area of the uncoated powder was measured via Brunauer-Emmett-Teller nitrogen-gas absorption method (BET) at 77 K, using a Micromeritics Tristar 3000 surface area analyser. The mean particle size was estimated from the specific surface area using the following equation;

$$d = 6000 / (S \cdot \rho) \quad (1)$$

where d is the mean particle size, S is the BET specific surface area and ρ is the density of ZnO particles, 5.61 g/cm^3. UV-Vis optical transmittance was measured in the range of 250 – 800 nm using a Varian Cary 300 Bio UV-Vis spectrophotometer. The samples were placed in a quartz optical cell having an optical path length of 20 µm. Refractive index measurements were carried out using an Abbe refractometer equipped with a tungsten white lamp, at a constant temperature of 30 ^{o}C.

III. Results and discussion

The XRD study confirmed that the ZnO nanoparticles had the wurtzite crystal structure. The mean crystallite size estimated by XRD study was 26 nm. Fig. 1 shows the TEM image of ZnO nanoparticles coated with stearic acid. It is evident that the particles had equiaxed shapes with sizes in the range of 10 – 80 nm. The degree of agglomeration appeared to be low. Fig. 2 shows the number-weighted particle size distributions measured by PCS, where a monomodal size distribution with a narrow distribution width was evident. The number-weighted average diameter was 32 nm. The BET surface area of the uncoated ZnO powder was 34 m^2/g that corresponds to a spherical particle size of 31 nm. The good agreement between those particle and crystallite sizes is indicative of a narrow particle size distribution having a low degree of agglomeration [13]. However, as shown in Fig. 3, the light-scattering-intensity-weighted size distribution measured by PCS was bimodal, with peaks at 44 nm and 114 nm and the relative peak areas of 35 % and 65%, respectively. Those two peaks correspond to the primary and secondary particles, indicating the occurrence of particle agglomeration.

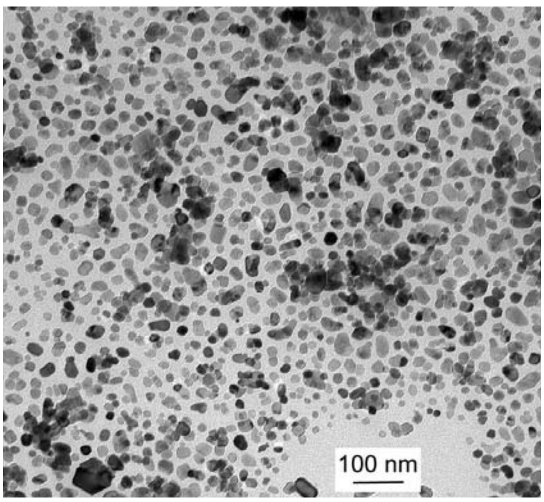

Figure 1. Transmission electron microscopy image of ZnO nanoparticles coated with stearic acid.

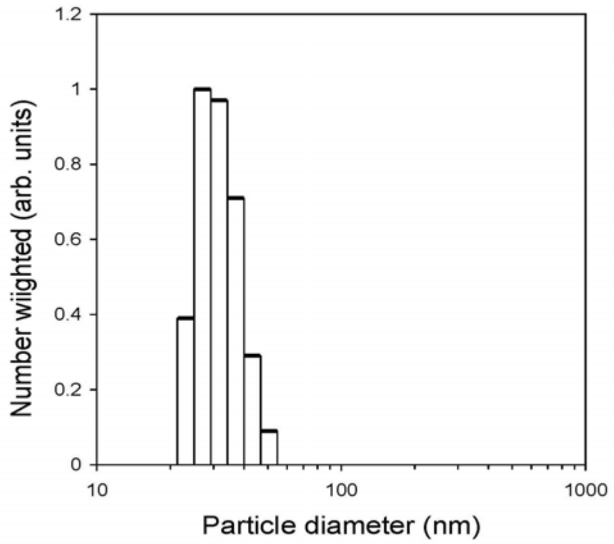

Figure 2. Number-weighted size distribution of ZnO nanoparticles.

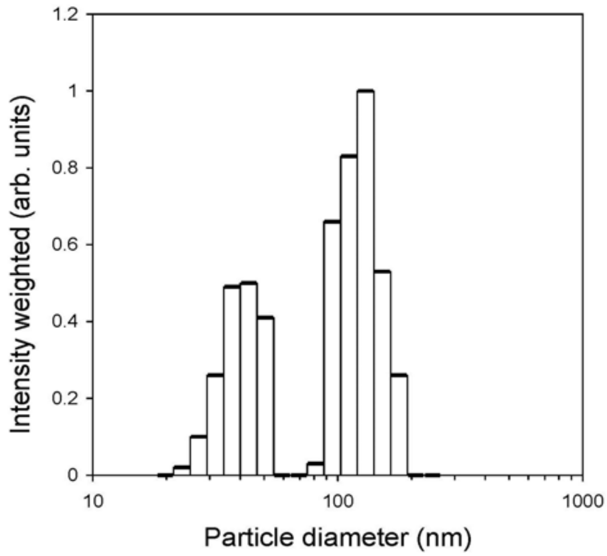

Figure 3. Light-scattering-intensity-weighted size distribution of ZnO nanoparticles.

Fig. 4 shows the refractive indices of the ZnO / alkyl benzoate films as a function of the volume fraction of nanoparticles. It is evident that the refractive index increased almost linearly as the particle concentration increased.

Assuming that the nanoparticles were randomly distributed in the film and that the particle size is much smaller than the wavelength of light, one can treat the material as a macroscopically homogeneous effective medium [14]. In this approximation, the film is regarded as an array of two components, where a single spherical grain of one component having a refractive index of n_p and the rest of the film is regarded as a homogenous medium having a refractive index of n_{hybrid}.

The effective medium approximations most commonly used for the refractive indices of nanocomposite films are Maxwell-Garnett and Bruggemann expressions [14]. Since the Maxwell-Garnett approximation is developed for very diluted collections of small particles, it will not be suitable to apply onto the high-particle loading systems that were used in this study. Hence the theoretical curves deduced from the following Bruggemann formula was used to compare the effective medium theory with the experimental data;

$$f_V \cdot \left(\frac{n_p^{\ 2} - n_{hybrid}^{\ \ 2}}{n_p^{\ 2} + 2n_{hybrid}^{\ \ 2}} \right) + (1 - f_V) \cdot \left(\frac{n_m^{\ 2} - n_{hybrid}^{\ \ 2}}{n_m^{\ 2} + 2n_{hybrid}^{\ \ 2}} \right) = 0 \quad (2),$$

where n_{hybrid}, n_p and n_m are the refractive indices of the hybrid system, particles and organic host matrix, respectively, and f_V is the volume fraction of nanoparticles. The values $n_p \sim 2.04$ and $n_m \sim 1.478$ were used for the calculation. As shown in Fig. 4, the experimental data were in good agreement with the theoretical curve.

Fig. 5 shows the specular transmittance of the ZnO / alkyl benzoate hybrid films at 550 nm. Since the sensitivity of the human eye is the highest around 550 nm [15], this wavelength was used to assess the visual transparency of the film. As the particle volume fraction increased, the transmittance values initially decreased but reached a minimum at $f_V \sim 0.08$. Further increase in particle concentration resulted in slight increase in transmittance.

The specular transmittance is associated with light scattering by particles. The most basic description of light scattering by small particles is by the Rayleigh scattering approximation based on the single-scattering assumption [3];

$$T_{st} = \exp\left[-\frac{32\pi^4 d^3}{\lambda^4} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 f_V \cdot L \right] \quad (3),$$

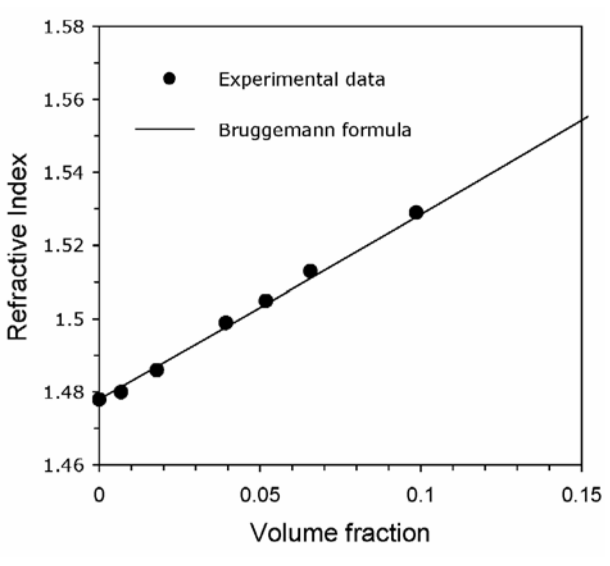

Figure 4. Refractive indices of ZnO / alkyl benzoate hybrid films.

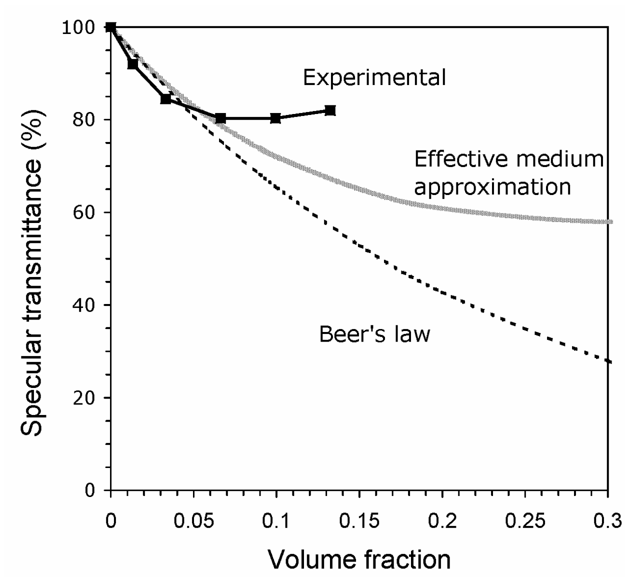

Figure 5. Specular transmittance of ZnO / alkyl benzoate hybrid films at 550 nm.

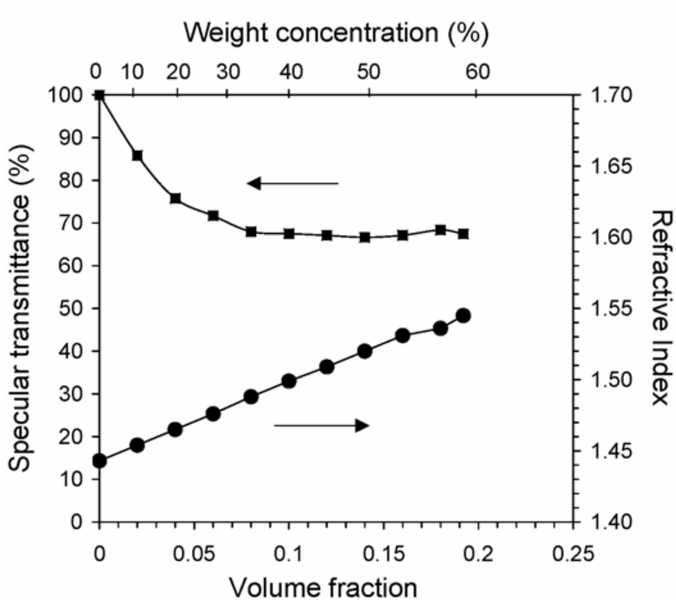

Figure 6. Refractive indices and specular transmittance of ZnO / caprylic capric triglyceride hybrid films at 550 nm.

where T_{st} is the optical specular transmittance, L is the optical path length, m is the relative refractive index defined as $m = n_p / n_m$ and λ is the wavelength of light (550 nm). In Fig. 5, the experimental data were compared with the values derived from (3) considering the light scattering by both primary and secondary particles that are evident in Fig. 3. The dotted line in Fig. 5 shows the T_{st} thus estimated. It is evident that the experimental data were much higher than the theoretical transmittance values at $f_V > 0.08$.

By introducing the effective medium theory into (3), n_m was replaced with n_{hybrid} and the relative refractive index is calculated as $m = n_p / n_{hybrid}$ [16]. According to this equation, n_{hybrid}, that is increased by increased particle concentration,

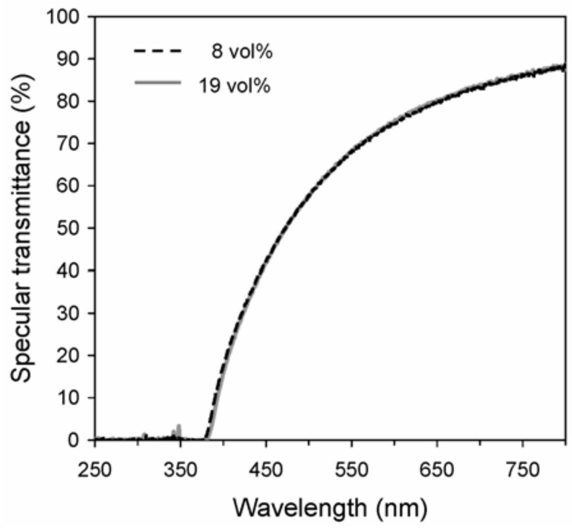

Figure 7. Specular transmittance spectra of ZnO / caprylic capric triglyceride hybrid films at the particle volume fraction of 0.08 and 0.19.

will decrease the relative refractive index and hence increase the optical transmittance in (3). In Fig. 5, the specular transmittance values thus calculated using the effective medium approximation is shown as a grey solid line. It was found that the experimental values were still much higher than the theoretical values. Hence the Rayleigh scattering model still cannot explain the abnormally high transmittance at the high particle concentration range even using the effective medium approximation.

A similar relationship between the refractive index and optical transmittance was found in ZnO /caprylic capric triglyceride hybrid systems. Fig. 6 shows the specular transmittance and refractive indices of the ZnO /caprylic capric triglyceride (n_m ~ 1.44) at 550 nm. It is evident that, when the volume fraction of particles was above 0.08 (~ 34 wt%), the transmittance values became almost constant. On the other hand, the refractive index increased linearly as the particle volume concentration increased. Fig. 7 shows the specular transmittance spectra at f_V = 0.08 and 0.19. The spectra were nearly identical to each other despite the large difference in particle concentration.

IV. Conclusion

The refractive index and visible-light transmittance of ZnO / organic hybrid films were investigated in the wide particle concentration range from 0 to 60 wt%. The refractive index of the hybrid systems was modified from 1.44 to 1.55 in a linear manner as the particle concentration increased. The optical transmittance initially decreased as the particle volume fraction increased. However, it reached a near constant value above the particle concentration of ~ 34 wt%. The effective medium approximation explained the change in refractive index as a function of particle concentration, however, it failed to explain the abnormally high transmittance at high particle concentration levels using the single-scattering approximation. A multiple scattering model may be required to describe the optical transmission of nanocomposite materials having a high particle concentration [16,17]. The results indicate the possibility of controlling refractive indices in nanocomposite films without altering their optical transmittance.

Acknowledgment

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