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Preparation and characterization of high refractive index silicone/TiO_2 nanocomposites for LED encapsulants

Jui-Hsiung Huang [a], Chiu-Ping Li [a], Cai-Wan Chang-Jian [b],*, Kuen-Chan Lee [c],**, Jen-Hsien Huang [a],*

[a] Department of Green Material Technology, Green Technology Research Institute, Chinese Petroleum Corporation(CPC Corporation), Kaohsiung, Taiwan
[b] Department of Mechanical and Automation Engineering, I-Shou University, Kaohsiung, Taiwan
[c] Department of Fragrance and Cosmetic Science, Kaohsiung Medical University, Kaohsiung, Taiwan

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ABSTRACT

In this study, a uniform dispersion of TiO_2 nanoparticles (NPs) in silicone for light-emitting diode (LED) encapsulation is demonstrated prepared through high-energy grinding method. Through interaction with surfactant, large clumps of the TiO_2 underwent de-aggregation to form a stable dispersed solution, during the grinding process. The silicone/TiO_2 composites were prepared by the blending of silicone resin with grinding TiO_2 fillers in isopropyl alcohol solvent, which was removed before curing. The refractive index (RI) of surfactant-coated TiO_2 NPs loaded silicone is 1.63 at 550 nm, significantly higher than that of conventional silicone ($n = 1.50$). The barrier properties and thermal conductivity (from 0.9 to 1.32 W/mK) of the silicone/TiO_2 composites also can be enhanced, significantly. As a result, a high-power LED encapsulated with this composite showed more than 7.3% increase in the light output and better stability compared to that with the conventional silicone resin.

1. Introduction

Although significant progress in LEDs has been made, higher light output is necessary to penetrate the general illumination market. In order to increase the light output to meet the demand for general illumination, high power LEDs have been developed. However, the LED efficiency generally is higher at relative low currents and as the injection current increases, the efficiency decreases gradually [1–3]. Moreover, high power LEDs generally generate much heat leading to higher junction temperatures. The increase in junction temperature has a dramatic effect on the chip's lifetime.

Another method to enhance the light output is to solve the light-trapping issue occurred at the encapsulant (low-n)-LED chip (high-n) interface. The trapped light is originated from the total internal reflection (TIR) due to the high-refractive-index contrast between the encapsulant and LED chip. Based on Snell's law, light incident on a planar semiconductor-encapsulant interface is totally reflected if the angle of incidence is larger than critical angle. The TIR results in significant reduction in light extraction efficiency. In order to extract more light from LEDs, efforts have been made, including wet-chemical texturing of a LED surface [4–6], employing periodic photonic crystals [7,8], planar graded refractive-index antireflection coatings [9,10], patterning of sapphire substrates [11], and shaping of LED chips [12]. Nevertheless, the fundamental obstacle of light extraction still lies in the large refractive-index contrast between the encapsulant and LED chip.

The silicone based resins are the most common encapsulants used in high power LED package due to its excellent thermal stability, good insulation to moisture, strong adhesion to substrate and high transparency. However, silicone based encapsulants reveal low RI (about 1.4–1.5) which limits the light extraction efficiency. Many improvements have been made to address this issue such as adding inorganic NPs to form a composite [13–17] and synthesis of silicone/epoxy hybrid resins [18–21]. The enhancement in RI is not the only benefit for adding NPs. An increase on the thermal conductivity on the introduction of metal oxides is also important. An improvement on the thermal stability and the reduction of the thermal expansion coefficient, both are

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E-mail address: cwchangjian@mail.isu.edu.tw.
*Corresponding authors at: Chinese Petroleum Corporation(CPC Corporation), Green Technology Research Institute, No. 2 Zuonan Rd., Nanzi Dist., Kaohsiung City 81126, Taiwan. Tel.: +886 7 5824141x7331/+886 7 6577711x3231.
E-mail addresses: cwchangjian@mail.isu.edu.tw (C.-W. Chang-Jian), kclee@kmu.edu.tw (K.-C. Lee), 295604@cpc.com.tw, r91524047@ntu.edu.tw (J.-H. Huang).
** Corresponding author at: 100 Shih-Chuan 1st Road, Kaohsiung City 80708, Taiwan. Tel.: +886 7 3121101x2818.

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welcomed for encapsulant, might be achieved at the same time [22]. However, if the added NPs are too large or easily aggregative they would cause scattering effect leading to the reduction of transparency. Consequently, the added NPs with small, uniform particle size and good dispersibility are critical to obtain high transparency and RI silicone/nanoparticle composite. Recently, much works have been demonstrated that the RI of silicon or other LED encapsulants can be increased by adding NPs leading to better light output. Unfortunately, the particle size of the adding NPs is still too large (20–40 nm) [13–17] and the dispersability is poor. This causes the serious decrease in transparency of the NPs/encapsulant composite. According to the Rayleigh equation [23,24], the particle size of adding NPs should be smaller than 15 nm to avoid the decrease in transparency of encapsulant due to the scattering effect. Therefore, an efficient way to produce NPs with excellent dispersability and small diameter (~10 nm) is crucial.

In this study, we used a wet grinding method to disperse pure TiO_2 NPs. During the grinding process, large clumps of the TiO_2 NPs underwent de-aggregation to form a stable dispersed solution. The TiO_2 NPs with sizes around 10 nm can be blended into a silicone resin to formulate a transparent high RI composite. Moreover, the silicone/TiO_2 nanocomposites reveal better water vapor transmission rate (WVTR), oxygen transmission rate (OTR) and thermal conductivity compared with that of pure silicone resin. These enhanced properties are believed to have positive impact on the durability of LEDs. We have further tested the composites as encapsulant for high power LED packages and compared its performance with that using the pure silicone. This high-throughput, simple and cheap technology can offer an approach to be easily applied for industrial application.

2. Experimental

2.1. Materials

High-purity anatase TiO_2 powder (99.7%, Nanostructure & Amorphous Materials), sodium dodecyl sulfate (SDS) and isopropyl alcohol were used as the starting material, surfactant and solvent, respectively. Transparent silicone resin was purchased from Dow Chemical (OE-6550A and OE-6550AB).

2.2. Preparation of the TiO_2 dispersion and silicone/TiO_2 composite

High-energy ball milling was performed at a speed of 2000 rpm at room temperature using a batch-type grinder (JBM-B035) [25]. The milling duration was typically between 30 and 360 min; the concentration of TiO_2 and SDS were 10 wt% and 0.1 M, respectively. After high-energy grinding, the TiO_2 suspensions can be diluted to any concentration without precipitation. The as-prepared TiO_2 suspension was added directly into the OE-6550A under stirring for 30 min. Then, a rotary evaporator was used to remove the solvent within OE-6550A. Consequently, the mixture was blended with OE-6550B until a homogeneous mixture was obtained. The mixture was vacuum vented until the bubbles exploded and the mixture was clear and transparent. The mixture was poured into a stainless steel mold and heated in an oven for 2 h at 150 °C. After this curing process, the mold was taken out of the oven and the sample was removed from the mold.

2.3. Characterizations

Particle sizes and zeta potentials were measured using a particle size analyzer (Brookhaven 90 Plus Sn11408). X-ray diffraction (XRD) studies were performed using a Philips X'Pert/MPD apparatus. The surface morphologies of the polymer films were investigated using atomic force microscope (AFM, Digital Instrument NS 3a controller equipped with a D3100 stage) and scanning electron microscope (SEM, Hitachi S-4700). The transmittance spectra were obtained using a Jasco-V-670 UV–vis spectrophotometer. The RI of the hybrid materials was determined by an Abbe-refractormeter (model:WAY). The WVTR and OTR were obtained from a commercial PERME-W3/330 instrument. The barrier property was measured under 40 °C and the relative humidity was controlled at 90%.

3. Results and discussion

Fig. 1A shows the average particle sizes of the TiO_2 powder as a function of grinding time. The average particle size of TiO_2 decreased rapidly upon grinding for up to 180 min. With increasing grinding time, the TiO_2 particles were deaggregated and broken into smaller particles due to the plastic deformation that consequently led to the reduction of particle size. The images of the TiO_2 solutions with various grinding times are also shown in the inset of Fig. 1A. These images were got from the as-prepared solutions after 72 h on standing. It can be found that the TiO_2 can be fully dispersed after grinding for 240 min, suggesting that the smaller particle size leads to higher charges and therefore enhances the dispersibility. In order to investigate the correlation between surface charge of the NPs and the grinding time, the zeta potential versus PH for the TiO_2 solution with different grinding times was measured as shown in Fig. 1B. The isoelectric point (IEP) of TiO_2 solution was found to be a function of particle size (grinding time). When the grinding times increased

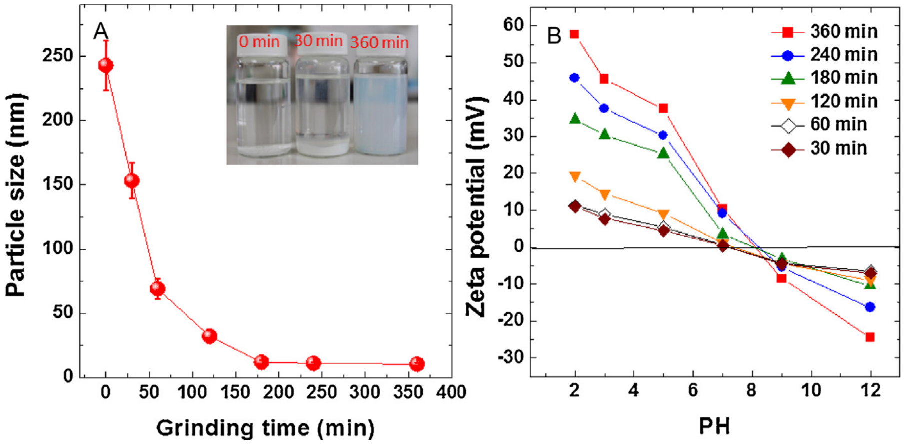

Fig. 1. *The relationship between particle size and grinding times.* Plots of the (A) average particle size in the TiO_2 powder with respect to the grinding time (inset: photograph of the TiO_2 solutions obtained after different grinding times) and (B) zeta potentials of the TiO_2 solutions with respect to pH.

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