



Organically modified clays as rheology modifiers and dispersing agents for epoxy packing of white LED



Yu-Ting Tsai, Jau-Yu Chiou, Chien-Yi Liao, Po-Yu Chen, Shih-Huang Tung^{*}, Jiang-Jen Lin^{**}

Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form

18 April 2016

Accepted 16 June 2016

Available online 18 June 2016

Keywords:

Nanoclays

Polymers

Curing

Rheology

ABSTRACT

We develop a new class of polyetheramine-modified organoclays that enable the homogenous dispersion of inorganic phosphorescent phosphor powder, yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG), in epoxy, which can then be used for packing of light-emitting diode (LED) devices. The organoclays are prepared from the ionic exchange reaction of sodium montmorillonite (Na^+ -MMT) with poly(oxypropylene) (POP) diamines of sufficiently high molecular weight, which are found to be effective for homogenizing YAG in the two-component epoxy system involving an anhydride curing agent and an aliphatic epoxy resin. By adding the POP-diamine-based organoclays, the viscosity of the anhydride/epoxy resins is greatly enhanced and the resin shows a non-Newtonian shear-thinning behavior. Because of the high viscosity that retards the molecular motion, the micrometer-scaled YAG particles can remain dispersed in the resins for a fairly long time without precipitation during the curing process. We investigate the rheological properties of the organoclays as the thickening agent and applied the organoclays to fabricate YAG particle-dispersed epoxy for packing of blue light LED that mixes the yellow light of the well-dispersed YAG particles to form uniform white illumination.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

White light-emitting diode (WLED) is an energy-efficient and environment-friendly light source that has been gradually used to replace conventional power-consuming lamps [1,2]. The recent developments in WLED have focused on the mixing of the emitting blue light and the yellow light of phosphorescent phosphor powders that are dispersed in packing material to generate pseudo white light. The size of the phosphorescent phosphor powders, such as yttrium aluminum garnet (YAG), $Y_3Al_5O_{12}$, is generally in micrometer scale [3]. It is known that large particles tend to aggregate and precipitate in liquid media, and thus achieving a uniform dispersion of the large particles in epoxy resins is challenging. Phosphorescent phosphor powders tend to settle at the bottom of the resins, which consequently results in an uneven illumination. In particular, the sedimentation problem becomes even more severe at elevated temperature due to a lower viscosity such that the curing process of resins may aggravate the particle

aggregation. The development of efficient methods to homogeneously disperse the large phosphorescent phosphor powders in epoxy is thus an important research topic.

Epoxy resins are widely used for the LED packing thanks to the advantages of workability, good adhesion, insulating, and excellent mechanical properties such as tensile strength and impact fracture resistance [4,5]. Among various commercially available epoxies, anhydride is generally selected as the curing agent to gain high transparency and luminous efficiency for LED packing. To fabricate the packing that can produce uniform yellow light, YAG particles have to be well dispersed in the anhydride/epoxy resins during the curing process. It has been known that an efficient method to retard the aggregation of large particles in liquid is to increase the liquid viscosity. In order to solve the sedimentation problem of YAG particles in LED packing process, the viscosity of resins is often purposely increased by adding organic thickeners [6,7]. However, the organic thickeners may cause a reduction of thermal and mechanical properties of the cured resins.

Recently, the polymer/layered silicate nanocomposites formed by introducing various organoclays into hydrophobic polymers have been intensively studied [8–12]. The layered silicate clays are generally intercalated or exfoliated by ionic exchange reaction with organic intercalated agents. The modified clays can be finely

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: shtung@ntu.edu.tw (S.-H. Tung), jianglin@ntu.edu.tw (J.-J. Lin).

dispersed in the polymer matrices and consequently lead to good properties such as gas barrier [13], thermal stability [14], flame retardation [15,16], and mechanical strength [17]. Previous reports have demonstrated a great improvement of material properties by incorporating modified montmorillonite, a natural silicate clay, into polymers, such as epoxy, nylon, polyamide, polyimide, and polyurethane system [18–20]. In addition to the superior properties that can be brought by organoclays into the polymer composites, in this work, we further found that the intercalated organoclays can be dispersed in the uncured anhydride/epoxy resins and greatly increase the viscosity of the resins [21–23], which in turn retards the rate of YAG particle sedimentation in resins during curing process. In other words, after curing, evenly dispersed YAG particles and good thermal/mechanical properties can be simultaneously achieved in the cured epoxy by the use of the organoclays.

We prepared the organoclays by the ionic exchange reaction of sodium montmorillonite (Na^+ -MMT) with alkyl-amines (C_{12} , C_{14} and C_{18} fatty amine) and various polyether-amines including poly(oxypropylene) (POP) and poly(oxyethylene) (POE) diamines [24–27], and dispersed the organoclays into two-component anhydride/epoxy curing system. The effect of the organoclays on the rheology of the resins, the dispersion of YAG particles in resins, and the transparency of the cured epoxy were investigated. Among the organoclays, the one prepared from POP diamine with high molecular weight can most effectively enhance the viscosity of the resin and thus facilitates the dispersion of YAG particles in the cured epoxy without a significant sacrifice of transparency. This work demonstrates that the organoclays are a class of good candidates for the application in LED packing.

2. Experimental

2.1. Materials

The natural aluminosilicate clays, sodium montmorillonite (Na^+ -MMT), with a cationic exchange capacity (CEC) of 120 mequiv/100 g was obtained from Nanocor Co., USA. The aluminosilicate platelets are the fundamental units in the multilayered structure. Each primary stack is structured of 8–10 edge-sharing octahedral platelets with the average dimensions of $400 \times 400 \times 1 \text{ nm}^3$. Poly(oxyalkylene)-backboned diamines, including poly(oxypropylene) (POP) and poly(oxyethylene) (POE) diamines, are commercially available under the trade name Jeffamine[®] amines and were purchased from Huntsman Chemical Co. POP- and POE-diamines of different molecular weight, $M_w = 400$ or 2000 (POP400, POP2000 and POE2000), were used. The shorter segment amines, including fatty amine series, 1-dodecylamine (C_{12} -amine), 1-tetradecylamine (C_{14} -amine), and 1-octadecylamine (C_{18} -amine), were purchased from Alfa Co. Commercially available cerium doped yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$, YAG) is a synthetic crystalline material with a particle size of 13–14 μm . The aliphatic epoxy resin, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (Union Carbide ERL-4221, abbreviated as 4221) with an epoxide equivalent weight of 137, was purchased from Aldrich Chemical Co. The anhydride-type curing agent, methyl hexahydrophthalic anhydride (MHHPA) with an equivalent weight of 168, was purchased from Huntsman Chemical Co. The catalyst, 1,8-diazabicyclo-(5,4,0)-undecene-7-octanoic acid salt (code U-CAT SA102, abbreviated as SA102), was purchased from San Apro Co., Japan.

2.2. Preparation of organoclays

The preparation of the POP2000-modified organoclays with an equivalent molar ratio of organic agent to CEC of Na^+ -MMT equal to

one (CEC ratio = 1) is taken as an example as follows. Na^+ -MMT (10 g, 120 mequiv/100 g) was swelled in 1 L of deionized water and stirred vigorously at 80 °C for 1 h. The amine-salt, prepared from POP2000 (24 g, 12 mmol) and equivalents of hydrochloric acid (35 wt %, 0.876 g, 24 mmol) in water, was added to the slurry. The inorganic/organic weight ratio ($R_{i/o}$) of this organoclay is 30/70. After stirring at 80 °C for 1 h, the precipitates were collected at ambient temperature, washed with deionized water, and dried under vacuum at ambient temperature. According to the CEC of Na^+ -MMT, varying CEC ratios, from 0.43 to 8.2, were prepared and all the samples used in this study are listed in Table 1.

2.3. Preparation of YAG-dispersed epoxy with organoclays

Taking MMT-POP2000-70 organoclay as an example, the procedure for preparation of YAG-dispersed anhydride/epoxy with organoclays is described below. MMT-POP2000-70 (0.250 g, 1 phr) was dispersed in anhydride-type curing agent MHHPA (11.2 g, 66.6 mmol) by mechanical stirring at room temperature. Subsequently, epoxy resin 4221 (13.8, 54.7 mmol) and catalyst SA102 (0.125 g, 0.5 phr) were added. The YAG particles (2.50 g, 10 phr) were then added, followed by mechanical stirring until complete homogeneity. The anhydride/epoxy resins were cast on a flat aluminum-foil mold in the form of films or plates, and were cured under a programmed heating at 80 °C for 1 h and 120 °C for 1 h in a vacuum oven. The composites with varying amount of organoclays and desired amount of YAG particles could be obtained through the above procedure.

2.4. Characterization

X-ray diffraction (XRD) was performed on a Schimadzu SD-D1 diffractometer with a Cu target at a scanning rate of 2°/min. The generator voltage was 45 kV and the current was 40 mA, which produces X-ray with a wavelength of 1.5405 Å. Thermogravimetric analysis (TGA) was conducted on a TA instrument Q50 analyzer. The rheological experiments of uncured resins were performed on an AR2000EX stress controlled rheometer (TA Instruments). Cone-and-plate geometry (40 mm diameter with 4° cone angle) was used. The plate was equipped with Peltier-based temperature control, and the samples were studied at 25 or 80 ± 0.1 °C. For the steady-shear experiments, sufficient time was allowed at each shear rate to ensure that the viscosity reached its steady-state value. For transmission electron microscopy (TEM) imaging, the cured anhydride/epoxy samples were microtomed to ~ 80 nm thickness at room temperature with a diamond knife. TEM images were collected on a JEOL JEM-1230 transmission electron

Table 1
Properties of organoclays.

Sample	CEC ratio ^a	$R_{i/o}$ ^b	d-spacing (Å) ^c	η_{YAG} ^d
MMT-POP400	1	68/32	17	0
MMT-POP2000-95	8.2	5/95	26	0
MMT-POP2000-90	3.9	10/90	57	0
MMT-POP2000-80	1.7	20/80	51	4
MMT-POP2000-70	1	30/70	52	10
MMT-POP2000-60	0.64	40/60	48	8
MMT-POP2000-50	0.43	50/50	45	1
MMT-POE2000	1	29/71	18	0
MMT- C_{12} -amine	1	79/21	21	0
MMT- C_{14} -amine	1	73/27	20	0
MMT- C_{18} -amine	1	73/27	18	0

^a Equivalent molar ratio of organic agent/CEC of Na^+ -MMT.

^b Inorganic/organic weight ratio.

^c Determined by X-ray diffraction.

^d Capability of dispersing YAG, defined as phr ratio of YAG/organoclay.

microscope at an accelerating voltage of 100 kV. Scanning electron microscopy (SEM) was performed on a JEOL JSM-5600 SEM system operated at 15 kV. The samples were coated with Pt before imaging. The transparency test was conducted on an UV-vis spectroscope (Perkin-Elmer Lambda 20 UV-vis spectrophotometer) and determined by the absorbance at the wavelength of 550 nm. The thickness of the samples was 20 μm .

3. Results and discussion

3.1. Structure and properties of intercalated silicate clays

Fig. 1 illustrates the preparation of organoclays by the intercalation of various poly(oxyalkylene) amine salts and fatty amine salts into sodium montmorillonite (Na^+ -MMT). The intercalated agents, including hydrophobic poly(oxypropylene) (POP) diamines, fatty amine (C_{12} -, C_{14} - and C_{18} -amine), and hydrophilic poly(oxyethylene) (POE) diamines, were treated with hydrochloric acid, which allows the ionic exchange reaction with the silicate clays to form the organoclays as listed in Table 1. The pristine clays are hydrophilic in nature and tend to swell in water. After the modification by the intercalated agents, all the organoclays became dispersible in organic solvents, such as toluene, methanol, and isopropanol.

We used X-ray diffraction (XRD) to determine the interlayer d-spacing of the clays with and without the intercalation of organic agents. The XRD data are shown in Fig. 2. The d-spacing of pristine Na^+ -MMT is ~ 12 Å estimated from the diffraction peak. Since POP2000 alone does not reveal any diffraction peak, the diffraction peaks of the representative organoclay MMT-POP2000-70 should result from the layer structure of the organoclay, and the d-spacing, determined from the first order peak, is expanded to 52 Å, indicative of the successful intercalation of POP2000 agent into the clay. Furthermore, the data show clear high order Bragg's peak up to $n = 4$, implying a highly regular stacking of the POP2000-intercalated silicate clays. The d-spacings of all the organoclays are listed in Table 1. All the intercalated agents can expand the d-spacing, among which POP2000 is the most efficient one. The thermogravimetric analysis (TGA) profile of the representative organoclay MMT-POP2000-70 is shown in Fig. 3. The 5% weigh loss

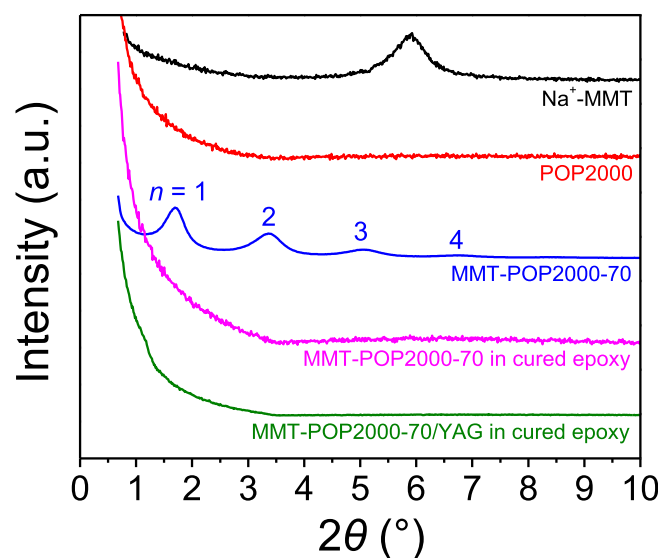


Fig. 2. XRD data of Na^+ -MMT, POP2000, MMT-POP2000-70 organoclay, MMT-POP2000-70 in cured anhydride/epoxy (1:100 phr), and MMT-POP2000-70/YAG in cured anhydride/epoxy (1:5:100 phr).

occurs at 234 °C, much higher than the curing temperature of the resins at 120 °C, and thus can ensure that the organoclays are thermally stable during the fabrication process.

3.2. Rheological properties of MMT-POP2000-dispersed resins

We have examined the rheology of all the intercalated agents and found that only the POP2000-modified organoclays, MMT-POP2000, can significantly enhance the viscosity of anhydride/epoxy resins and transform the resins from Newtonian to non-Newtonian fluid. The efficiency of the MMT-POP2000-based dispersants to enhance the viscosity is dependent on the inorganic/organic weight ratio ($R_{i/o}$). Fig. 4 shows the viscosity data as a function of shear rate for the resins with 1 phr MMT-POP2000 at different $R_{i/o}$. Among the MMT-POP2000 dispersants, the most efficient one to increase viscosity is the organoclay at $R_{i/o} = 30/70$

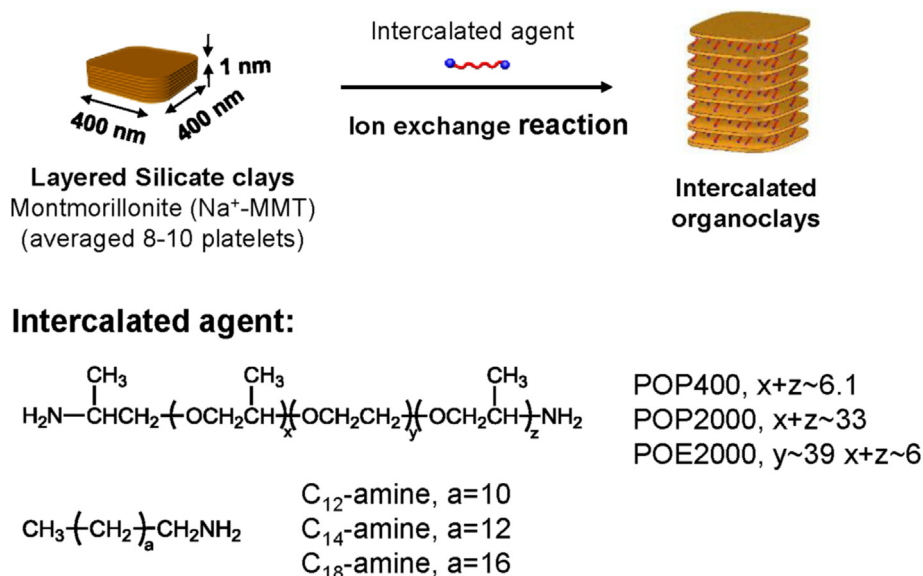


Fig. 1. Intercalation of organic agents into Na^+ -MMT through ionic exchange reaction.

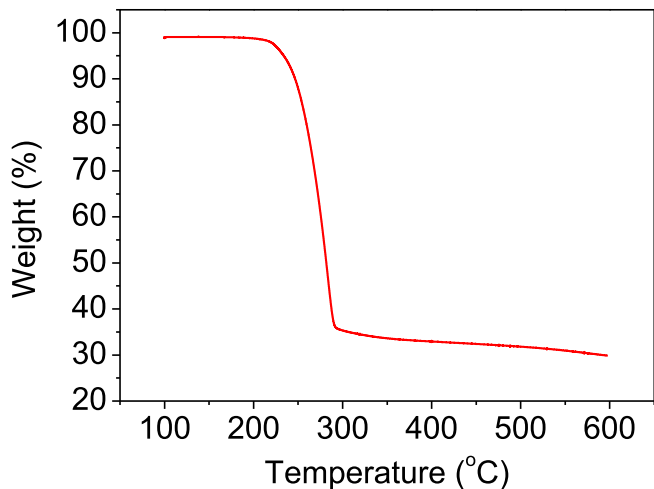


Fig. 3. Thermogravimetric analysis (TGA) of MMT-POP2000-70 organoclay.

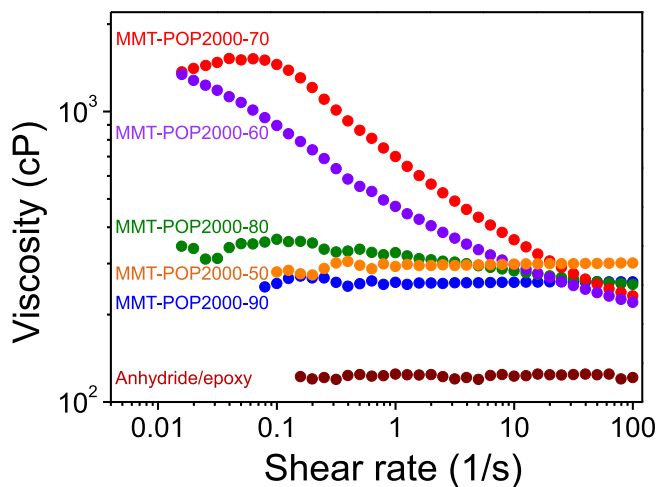


Fig. 4. Viscosity of anhydride/epoxy resins with 1 phr MMT-POP2000 organoclay of varying inorganic/organic weight ratio ($R_{i/o}$) as a function of shear rate.

(CEC ratio = 1), MMT-POP2000-70, followed by the one at $R_{i/o} = 40/60$, MMT-POP2000-60, especially in the range of low shear rate where the viscosity is increased by more than one order of magnitude. Other MMT-POP2000 organoclay can also enhance the viscosity, but not as much as the above two organoclay can. Since YAG particles are so large that tend to agglomerate or precipitate in low-viscous liquid media, MMT-POP2000 organoclay that can work as efficient thickening agents are capable of lowering the mobility of YAG particles to maintain a fine dispersion of YAG in the resin for a sufficiently long time. In the following results and discussion, we will focus the influence of MMT-POP2000-70 organoclay on the rheological properties of the anhydride/epoxy resin.

The dependence of the viscosity on shear force in anhydride/epoxy system with and without the addition of the MMT-POP2000-70 organoclay are compared in Fig. 5. The normal formulation of anhydride/epoxy at 1/1 equivalent ratio exhibits a low viscosity and a Newtonian behavior at 25 °C, i.e. a viscosity independent of shear rate. The viscosity of the anhydride/epoxy resin with 0.5 phr of MMT-POP2000-70 is slightly increased and the resin remains Newtonian. By adding 1.0 phr MMT-POP2000-70 organoclay into the resin, the viscosity is drastically increased from 120 cP to 1500 cP at low shear rate between $10^{-2} \sim 10^{-1}$ 1/s. When the shear

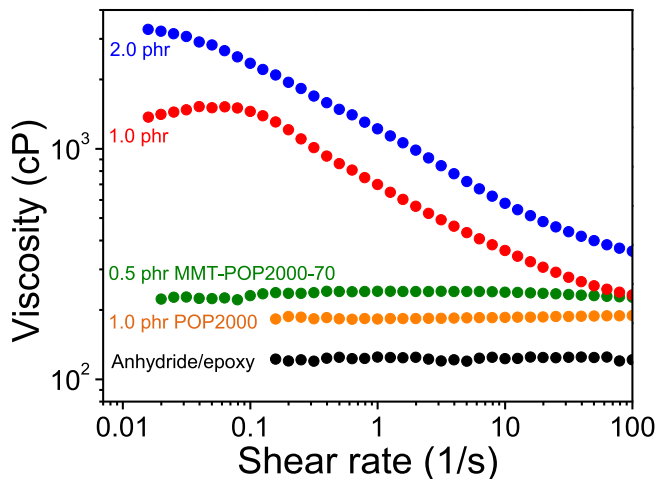


Fig. 5. Viscosity of anhydride/epoxy resin, and the resin with 1 phr POP2000 and 0.5, 1.0, and 2.0 phr MMT-POP2000-70 organoclay as a function of shear rate at 25 °C.

rate is increased to 100 1/s, the viscosity is greatly decreased to 200 cP, i.e. a typical non-Newtonian shear thinning behavior. By adding more organoclay with 2.0 phr, the viscosity is further enhanced to 3000 cP at low shear rate. The addition of more organoclay can further increase the viscosity but more organoclay lowers the transparency of the cured epoxy, which is unfavorable for the LED packing application. The control experiment in Fig. 5 shows that 1 phr POP2000 agent is unable to significantly affect the viscosity of the anhydride/epoxy resin.

MMT-POP2000-70 organoclay are found to be an efficient thickening agent in anhydride by itself without the epoxy, implying anhydride is the key component in the anhydride/epoxy resin responsible for the viscosity enhancement. In anhydride, the addition of organoclay increases the viscosity to 2000 cP at low shear rate, followed by a decrease to 100 cP at high shear rate at 25 °C as shown in Fig. 6. The trend is similar to that of the anhydride/epoxy resin. Since anhydride alone without organoclay exhibits a Newtonian behavior, it is apparent that the increase of viscosity and the shear thinning behavior result from the interaction between the organoclay and anhydride molecules. Note that the organoclay are unable to disperse in epoxy alone without

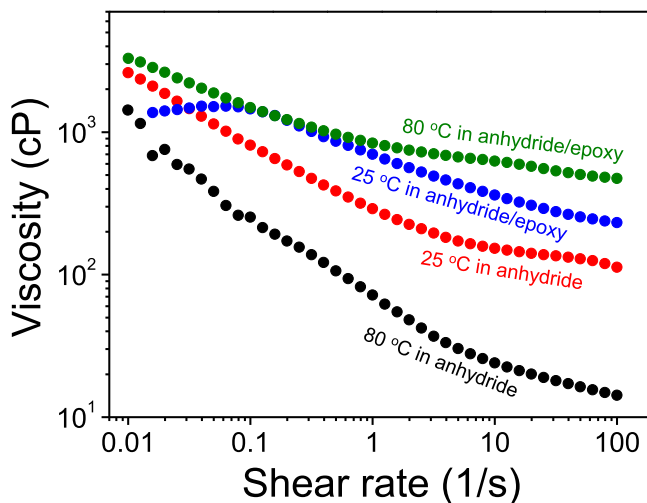


Fig. 6. Viscosity of anhydride alone and anhydride/epoxy resins with 1 phr MMT-POP2000-70 organoclay as a function of shear rate at 25 and 80 °C.

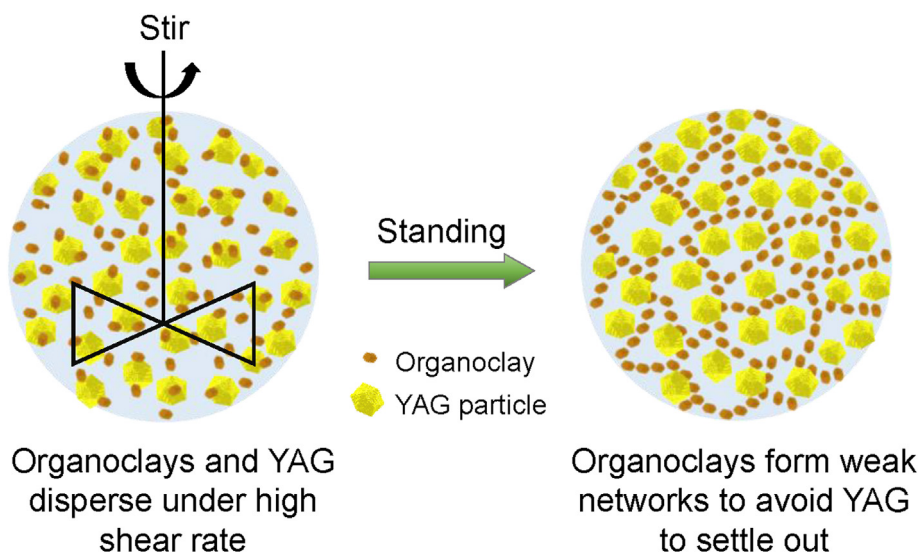


Fig. 7. Schematic of the processing and the homogenous dispersion of YAG in the presence of MMT-POP2000 organoclays.

anhydride possibly because the solvent quality of epoxy to POP2000 is not as good as that of anhydride due to the high molecular weight of epoxy that reduces the mixing entropy of POP2000 and epoxy.

The rheological thickening behavior caused by the organoclays is also seen at 80 °C both in anhydride and anhydride/epoxy system, as shown in Fig. 6. At 80 °C, the organoclays can still well disperse in the resins and the addition of organoclays brings about the same behavior of viscosity change at 25 °C. It is worth noting that at 80 °C, the viscosity in anhydride/epoxy system is higher than that at 25 °C in the whole shear rate range of measurement. This is unusual because viscosity generally decreases with increasing temperature. There are two possible factors that may give rise to the enhancement of the viscosity with increasing temperature in this system. One is that the anhydride/epoxy resin could have been partially crosslinked at 80 °C to form larger molecules that cause an irreversible viscosity increase. This argument, however, can be ruled out because the viscosity restores when the temperature is cooled down from 80 to 25 °C. The other is that the spatial distribution of organoclays in anhydride/epoxy resin is temperature-dependent and a high temperature leads to a structure that favors high viscosity, which we suggest to be the real factor responsible for this behavior. The detailed mechanism will be discussed later in this paper. This unusual rheological property is in fact advantageous for the dispersion of phosphorescent phosphor powders in cured epoxy because the powders can be more stably dispersed in the resin at curing temperature because of the higher viscosity.

3.3. YAG dispersion in MMT-POP2000 resin

The capability of the organoclays for dispersing YAG particles, η_{YAG} , in the anhydride/epoxy resin is summarized in Table 1. η_{YAG} is defined as the maximum phr ratio of YAG to organoclay at which YAG particles can be homogeneously dispersed in cured epoxy. The dispersion capability of MMT-POP2000 increases with the efficiency of the organoclays to enhance the viscosity of the resins, as compared with the viscosity data shown in Fig. 4. Among these dispersants, the most capable one is MMT-POP2000-70 organoclay. Loading 1 phr of this organoclay to the resin can well disperse 10 phr YAG. As expected, MMT-POP2000-60 that can greatly thicken resins also performs well in dispersing YAG, $\eta_{YAG} \sim 8$. For

those unable to significantly increase the viscosity, YAG particles tend to precipitate after curing. This confirms that the viscosity is the key factor for dispersing YAG particles.

3.4. Mechanism

POP2000 alone can dissolve in the anhydride/epoxy resin but is unable to significantly increase the viscosity at 1 phr (Fig. 5). This is because the anhydride/epoxy resin is a good solvent for POP2000, and in a good solvent, polymer chains tend to repel one another due to the steric effect. The energy barrier for the POP2000 chains to diffuse in the resin is low in the presence of such a repulsive interaction between chains, and the enhancement of the viscosity is thus limited. Pure Na⁺-MMT is unable to disperse in the anhydride/epoxy resin and therefore large aggregates of Na⁺-MMT precipitate out from the resin without an influence on the viscosity. When POP2000 intercalates into Na⁺-MMT and modify the clay surface, the aggregation of the organoclays can then be prevented through the steric repulsion of the grafted POP2000 in the resin. However, since the organoclays are not fully exfoliated but each contains 8–10 sheets in average, the attraction force between the large organoclay stacks in the resin is considerable and should play a role on the rheological property of the resin. We suggest that for MMT-POP2000 organoclays at the inorganic/organic weight ratio of 30/70 and 40/60, the balance between the attraction force of MMT clays and the repulsion force of POP2000 chains leads to a weak attractive interaction between MMT-POP2000 organoclays in the resin. The attraction force is not strong enough to cause a severe aggregation of the organoclays but is able to allow the organoclays to form weak networks that increase the friction between organoclays. The viscosity is thus enhanced. The weak networks are rather stable at low shear rate but gradually disassemble when shear rate is increased, which explains the shear-thinning behavior observed for MMT-POP2000-70 and MMT-POP2000-60 organoclays (Fig. 4).

The organoclays cannot be dispersed in epoxy alone, implying that the epoxy in anhydride/epoxy resin plays an adverse role in dispersing MMT-POP2000 organoclays in the resin. At elevated temperature, this adverse effect is weakened because the increase of the entropic contribution promotes mixing. In other words, MMT-POP2000 organoclays can disperse more uniformly and form a denser network in anhydride/epoxy resin at high temperature,

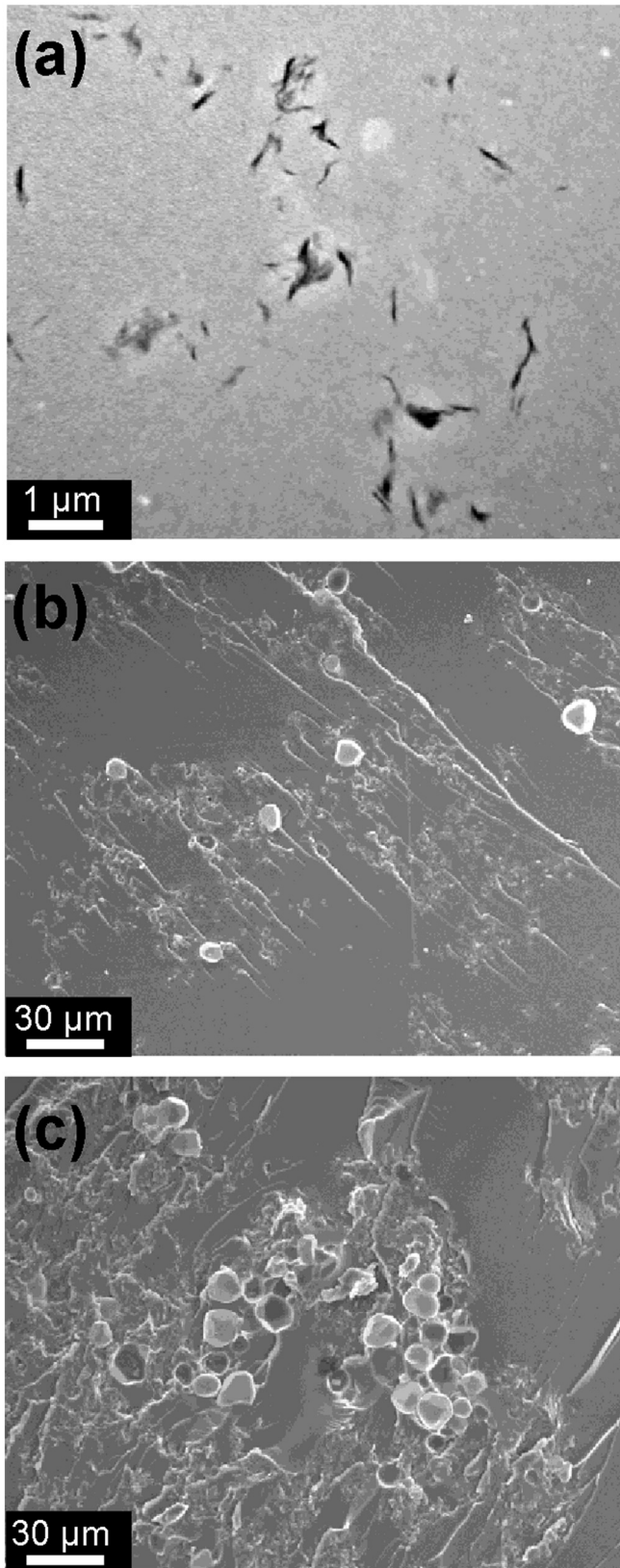


Fig. 8. (a) TEM image of the cured anhydride/epoxy with 1 phr of MMT-POP2000-70, and SEM images for YAG dispersion in the anhydride/epoxy cured sample at (b) MMT-POP2000-70:YAG:anhydride/epoxy = 1:5:100 and (c) MMT:YAG:anhydride/epoxy = 1:5:100 by weight.

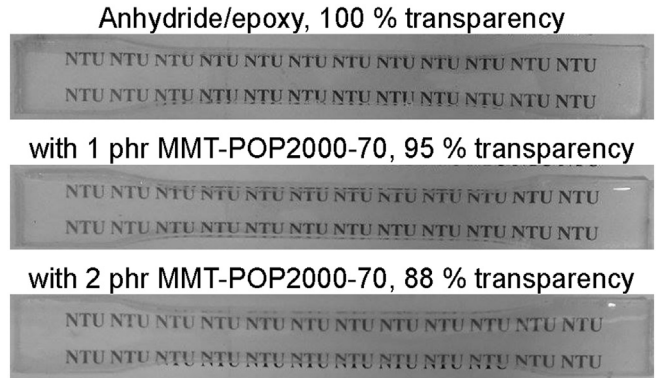


Fig. 9. Comparison of the transparency for the cured anhydride/epoxy films without and with 1 and 2 phr MMT-POP2000-70 organoclay.



Fig. 10. (a) Cured film at MMT-POP2000-70:YAG:anhydride/epoxy = 1:5:100 by weight and (b) light emitting test for the film.

which is why the viscosity at 80 °C is higher than that at 25 °C (Fig. 6). The high viscosity reduces the motion of YAG particles and the well-dispersed state can last longer than the time required for curing. YAG particles can therefore homogeneously distribute in the crosslinked epoxy after curing.

The shear-thinning behavior of the MMT-POP2000 organoclay-based resin provides another advantage for processing. Since the viscosity is low at high shear rate, the YAG particles can be easily dispersed in the resin under high-speed stirring with a low energy consumption. The well-dispersed YAG particles after vigorous stirring can be fixed at rest for curing due to the quick and pronounced enhancement of the viscosity, as illustrated in Fig. 7. As described in the preceding section, the viscosity at 80 °C can be further enhanced compared to that at 25 °C (Fig. 6). In other words, the dispersion of YAG particles can be even more stable at curing temperature, which further facilitates the epoxy packing of LED with uniform YAG particles.

3.5. Structure and properties of cured epoxy

The TEM image of the cured anhydride/epoxy with 1 phr of MMT-POP2000-70 is shown in Fig. 8(a). A locally dispersed organoclay without a large-scaled aggregation can be seen. Such a dispersion caused by the weak attractive interactions between the organoclays is suggested to be the origin for the thickening behavior of the resin. The homogeneity of YAG particles in the cured anhydride/epoxy resin was examined by SEM. Fig. 8(b) and (c) compare the distribution of 5.0 phr YAG in the cured samples in the presence of 1.0 phr MMT-POP2000-70 organoclay and pure

Na⁺-MMT. In Fig. 8(b), the YAG particles are uniformly distributed in the whole sample cured from the high viscosity resin caused by MMT-POP2000-70 organoclay as an efficient thickening agent, in contrast to the formation of YAG clusters in the control experiment shown in Fig. 8(c) where the resin is mixed with 1.0 phr pure Na⁺-MMT which has no significant effect on the rheological properties of the resin. The XRD profiles of MMT-POP2000-70 in cured anhydride/epoxy with and without YAG particles are shown in Fig. 2. No distinct diffraction peak is observed for both cases, which may be due to the low content of MMT-POP2000-70 in the samples.

There is a concern about losing transparency of cured epoxies after addition of organoclays into the resin. The maintenance of a high transparency in packing materials is necessary for LED light bulbs. The transparency was determined by UV-vis transmission at the wavelength of 550 nm and the transmission of pure anhydride/epoxy film is set to be 100%. After loading 1 and 2 phr of MMT-POP2000-70 in the resins, the transmission of the cured films slightly drops to 95% and 88%, respectively. The transparency of the two films with MMT-POP2000-70 is compared with that of pure anhydride/epoxy film in Fig. 9. Only a slight loss of transparency is observed for the films with organoclays. The anhydride/epoxy with 1 phr MMT-POP2000-70 can well disperse YAG particles and simultaneously maintains a high transparency of 95% without a serious interference of light, indicating that the organoclay is a good dispersant for LED packing.

Lastly, the cured anhydride/epoxy film containing 5.0 phr YGA and 1.0 phr MMT-POP2000-70 was used for light emitting test. The yellowish film with well-dispersed YGA particles is shown in Fig. 10(a). When a blue light irradiates through the film, the blue light mixes with the yellow light of YAG to generate pseudo white light, as displayed in Fig. 10(b). The test confirms the feasibility of this packing material for white LED illumination application.

4. Conclusions

We have developed a new class of POP-intercalated layered silicate clays capable of homogeneously dispersing phosphorescent phosphor powders in epoxy that provides the required properties for LED packing. The organoclays intercalated by poly(oxypropylene) diamines behave as a rheology modifier to enhance the viscosity of anhydride/epoxy resins and to cause a shear thinning behavior, which in turn facilitates the dispersion of YAG particles in resins. As a result, the inherent agglomeration of YAG particles in resins can be avoided during the curing process through the rheological control for the high viscosity and the shear thinning properties. A cured composite epoxy with homogeneously dispersed YAG particles can thus be obtained. Furthermore, the organoclays can impart good mechanical property and thermal stability to the epoxy without the deterioration of light transparency. The organoclays demonstrate an excellent capability to disperse yellowish YAG particles in the epoxy curing system and are promising for packing of blue LED aiming at the application of white LED illumination devices.

Acknowledgments

We acknowledge financial supports from the Ministry of

Economic Affairs and the Ministry of Science and Technology of Taiwan.

References

- [1] N. Narendran, Y. Gu, Life of LED-based white light sources, *J. Disp. Technol.* 1 (2005) 167.
- [2] P. Schlotter, R. Schmidt, J. Schneider, Luminescence conversion of blue light emitting diodes, *Appl. Phys. A* 64 (1997) 417–418.
- [3] S. Fujita, S. Yoshihara, A. Sakamoto, S. Yamamoto, S. Tanabe, YAG glass-ceramic phosphor for white LED (I): background and development, *Proc. SPIE* 5941 (2005) 594111.
- [4] C. May, *Epoxy Resins: Chemistry and Technology*, second ed., Marcel Dekker, New York, 1988.
- [5] H. Lee, K. Neville, LETTERS—"Book review—handbook of epoxy resins", *Ind. Eng. Chem.* 59 (1967) 16–17.
- [6] Y.T. Lim, O.O. Park, Phase morphology and rheological behavior of polymer/layered silicate nanocomposites, *Rheol. Acta* 40 (2001) 220–229.
- [7] M.J. Solomon, A.S. Almusallam, K.F. Seefeldt, A. Somwangthanaroj, P. Varadan, Rheology of polypropylene/clay hybrid materials, *Macromolecules* 34 (2001) 1864–1872.
- [8] C.-W. Chiu, T.-K. Huang, Y.-C. Wang, B.G. Alamani, J.-J. Lin, Intercalation strategies in clay/polymer hybrids, *Prog. Polym. Sci.* 39 (2014) 443–485.
- [9] M.C. Woodle, P.Y. Lu, Nanoparticles deliver RNAi therapy, *Mater. Today* 8 (2005) 34–41.
- [10] S.S. Ray, M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, *Prog. Polym. Sci.* 28 (2003) 1539–1641.
- [11] M. Alexandre, P. Dubois, Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials, *Mater. Sci. Eng. R* 28 (2000) 1–63.
- [12] C.-W. Chiu, J.-J. Lin, Self-assembly behavior of polymer-assisted clays, *Prog. Polym. Sci.* 37 (2012) 406–444.
- [13] R.K. Bharadwaj, Modeling the barrier properties of polymer-layered silicate nanocomposites, *Macromolecules* 34 (2001) 9189–9192.
- [14] J.W. Gilman, Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites, *Appl. Clay Sci.* 15 (1999) 31–49.
- [15] A.B. Morgan, Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems, *Polym. Adv. Technol.* 17 (2006) 206–217.
- [16] J.W. Gilman, C.L. Jackson, A.B. Morgan, R. Harris, E. Manias, E.P. Giannelis, M. Wuthenow, D. Hilton, S.H. Phillips, Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites, *Chem. Mater.* 12 (2000) 1866–1873.
- [17] M.A. Osman, J.E. Rupp, U.W. Suter, Tensile properties of polyethylene-layered silicate nanocomposites, *Polymer* 46 (2005) 1653–1660.
- [18] A.N. Ajjou, D. Harouna, C. Detellier, H. Alper, Cation-exchanged montmorillonite catalyzed hydration of styrene derivatives, *J. Mol. Catal. A Chem.* 126 (1997) 55–60.
- [19] J.J. Lin, C.C. Chu, C.C. Chou, F.S. Shieu, Self-assembled nanofibers from random silicate platelets, *Adv. Mater.* 17 (2005) 301–304.
- [20] A. Usuki, N. Hasegawa, H. Kadoura, T. Okamoto, Three-dimensional observation of structure and morphology in nylon-6/clay nanocomposite, *Nano Lett.* 1 (2001) 271–272.
- [21] K. Haraguchi, T. Takehisa, S. Fan, Effects of clay content on the properties of nanocomposite hydrogels composed of poly(N-isopropylacrylamide) and clay, *Macromolecules* 35 (2002) 10162–10171.
- [22] C.-W. Chiu, W.-T. Cheng, Y.-P. Wang, J.-J. Lin, Fine dispersion of hydrophobic silicate platelets in anhydride-cured epoxy nanocomposites, *Ind. Eng. Chem. Res.* 46 (2007) 7384–7388.
- [23] H. Koerner, E. Hampton, D. Dean, Z. Turgut, L. Drummy, P. Mirau, R. Vaia, Generating triaxial reinforced epoxy/montmorillonite nanocomposites with uniaxial magnetic fields, *Chem. Mater.* 17 (2005) 1990–1996.
- [24] D. Porter, E. Metcalfe, M. Thomas, Nanocomposite fire retardants—a review, *Fire Mater.* 24 (2000) 45–52.
- [25] C.-C. Chou, F.-S. Shieu, J.-J. Lin, Preparation, organophilicity, and self-assembly of poly(oxypropylene) amine-clay hybrids, *Macromolecules* 36 (2003) 2187–2189.
- [26] K.M.A. El-Nour, A.a. Eftaiha, A. Al-Warthan, R.A. Ammar, Synthesis and applications of silver nanoparticles, *Arab. J. Chem.* 3 (2010) 135–140.
- [27] J.-J. Lin, I.-J. Cheng, R. Wang, R.-J. Lee, Tailoring basal spacings of montmorillonite by poly(oxyalkylene) diamine intercalation, *Macromolecules* 34 (2001) 8832–8834.