Influence of nano-AlN particles on thermal conductivity, thermal stability and cure behavior of cycloaliphatic epoxy/trimethacrylate system

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Abstract. We have prepared a series of nano-sized aluminium nitride (nano-AlN)/cycloaliphatic epoxy/trimethacrylate (TMPTMA) systems and investigated their morphology, thermal conductivity, thermal stability and curing behavior. Experimental results show that the thermal conductivity of composites increases with the nano-AlN filler content, the maximum value is up to 0.47 W/(m·K). Incorporation of a small amount of the nano-AlN filler into the epoxy/TMPTMA system improves the thermal stability. For instance, the thermal degradation temperature at 5% weight loss of nano-AlN/epoxy/TMPTMA system with only 1 wt% nano-AlN was improved by $\sim 8^{\circ}\text{C}$ over the neat epoxy/TMPTMA system. The effect of nano-AlN particles on the cure behavior of epoxy/TMPTMA systems was studied by dynamic differential scanning calorimetry. The results showed that the addition of silane treated nano-AlN particles does not change the curing reaction mechanism and silane treated nano-AlN particles could bring positive effect on the processing of composite since it needs shorter pre-cure time and lower pre-temperature, meanwhile the increase of glass transition temperature of the nanocomposite improves the heat resistance.

Keywords: polymer composites, epoxy, nano-AlN

1. Introduction

In recent years, polymer composite materials with excellent thermal conductivity have attracted increasing attention because the amount of heat generated in electronic devices is getting larger and larger, leading manufactures to seek for new composites that can remove the heat efficiently from the devices [1, 2]. Epoxy resins are widely used as matrices in the manufacturing process of reinforced composites, adhesives and surface coatings, high voltage electrical insulation materials, electronic components and packaging because of their high strength, stiffness, good thermal stability, and excellent adhesion and electrical insulating properties [3–5]. As the thermal conductivity of epoxy systems is very

low (about 0.2 W/(m·K)), thermally conductive fillers are added to these composites in order to dissipate the heat generated in electronic devices [6]. Various kinds of fillers, such as metals and metal oxides [7, 8], aluminum nitride (AlN) [9–11], boron nitride (BN) [12], and silicon carbide (SiC) [13] have been applied to prepare thermally conductive polymer composites. Among them, AlN is a non-toxic, low cost substance, readily available as high purity powder. On the one hand, because of the low coefficient of thermal expansion (CTE) and the high thermal conductivity (150–300 W/(m·K)) of AlN, AlN filled composite materials have attracted much attention in an attempt to reduce the CTE and thermal resistivity of polymer composites [14].

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In a previous paper, our research group have reported the preparation and characterization of epoxy/trimethylol-1,1,1-propane trimethacrylate (TMPTMA) system [15, 16]. In this study, nano-AIN particles with an average particle size of 50 nm were used with epoxy/TMPTMA system as the base system. Nano-AIN particles were pretreated with a silane coupling agent, which was employed to enhance the compatibility between the nano-AIN particles and the epoxy/TMPTMA system, as well as to prevent the agglomeration of the nano-AIN particles. By studying thermal conductivity, thermal stability, and curing behavior of nano-AIN/epoxy/TMPTMA system, we expect to learn comprehensive and in-depth understanding of the thermophysical properties and curing behavior of this system.

2. Experimental

2.1. Materials

The raw materials and corresponding specifications of epoxy resin, curing agent, latent accelerator, modifier agent, initiator and filler are given in Table 1.

2.2. Surface modification of nano-AIN particles

The nano-AIN particles were dried in a vacuum oven at 180°C for 24 h and appropriate amount of the silane (0.5–1 wt% based on the weight of AIN

particles) was added into a 500 ml three-necked flask, equipped with a mechanical stirrer and a reflux condenser, and mixed in high purity acetone (5 wt% based on the weight of silane) by stirring at 110–120°C for at least 4 h. After filtration, the silane treated powders were dried in a vacuum oven at 120°C for 2 h to remove the solvent and the silane molecules that were not well bonded and thus would not significantly contribute to the joint strength. The probable schematic reaction between nano-AIN particles and GPTMS is indicated in Figure 1.

2.3. Sample preparation

Firstly, epoxy resin (100 parts by weight [pbw]) and latent accelerator (0.5 pbw) were weighing and mixed vigorously at 160°C for about 10 min until the latent accelerator was dissolved completely in the epoxy resin. Then, the blends of epoxy resin and accelerator were rapidly cooled to the ambient temperature; this was followed by the addition of 90 pbw curing agent and suitable amounts of the initiator and modifier agent mixing for about 30 min. At last a specified quantity of silane treated nano-AIN particles were added into the blend and the mixture was dispersed by sonication for 1 hour at ambient temperature. The specimens with the compositions listed in Table 2 in detail.

Figure 1. The schematic reactions of AIN particles and GPTMS

Table 1. The detailed raw materials

Materials	Abbreviation	Purity	Supplier
3, 4-epoxycyclohexylmethy-(3', 4'-epoxy)cyclohexane carboxylate	CER	>98%	DOW Chemical, USA
methyl-hexahydrophthalic anhydride	MeHHPA	>98%	Shanghai Li Yi Science & Technology Development Co. Ltd., China
neodymium (III) acetylacetonate	Nd(III)acac	>99%	Qinyang Tianyi Chemical Co., Ltd., China
trimethylolpropane trimethacrylate	TMPTMA	>98%	Jinshi Tech-development Co., Ltd., China
dicumyl peroxide	DCP	>99%	Qinyang Tianyi Chemical Co., Ltd., China
3-glycidoxypropyltrimethoxy silane	GPTMS	>98%	Dow Corning Company, USA
aluminum nitride	AIN	>99%	Hefei Kaier Nanometer Technology Development Co., Ltd., China

Table 2. Formulation of experiment (parts by weight [pbw])

System	CER	MeHHPA	Nd(III)AcAc	TMPTMA	DCP	nano-AlN
A1	100	90	0.5	20	0.2	0
A2	100	90	0.5	20	0.2	1
A3	100	90	0.5	20	0.2	3
A4	100	90	0.5	20	0.2	5
A5	100	90	0.5	20	0.2	10
A6	100	90	0.5	20	0.2	15
A7	100	90	0.5	20	0.2	20

2.4. Characterizations and measurements

Field emission scanning electron microscope (FE-SEM, JEOL JEM-7401, Tokyo, Japan) was used to observe the dispersion of the nanoparticles in the composite samples. Samples were sputtered with thin layers of gold to avoid the accumulation of charge.

Transmission electron microscopy (TEM, JEOL JEM-2100, Tokyo, Japan) was utilized to analyze the morphology of the silane treated AlN particles at 120 kV under low-dose conditions. The AlN/acetone solution was dropped on a copper grid and subsequently the solvent was evaporated in an oven.

FTIR spectrum was recorded in KBr pellets on a Paragon 1000 (Perkin Elmer, Inc., USA) using a resolution of 4 cm⁻¹, and transmission measurements was employed.

LFA 447 Nanoflash (NETZSCH, Germany) was employed to automatically determine the thermal conductivity according to ASTM E1461, using the measured heat capacity and thermal diffusivity, with separately entered density data. Samples were prepared in cylindrical shape of 12.7 mm in diameter and 1.0–2.0 mm in thickness.

TGA (NETZSCH TG 209 F3, Germany) was used to investigate the thermal stability of the composites. The weight samples was approximately 10 mg and all the measurements were carried out under nitrogen atmosphere. Dynamic runs were carried out from 50 to 700°C at a heating rate of 10°C/min. Dynamic DSC (NETZSCH DSC 200 F3, Germany) measurements were performed at different heating rates of 5, 10, 15, and 20 K/min over a temperature range of 30–300°C. The reaction was considered to be complete when the rate curve leveled off to a baseline. The exotherm was measured under a nitrogen flow rate of 10 ml/min. The exotherm baseline was corrected via data in chamber. The cured sample was left in the DSC cell and cooled to 30°C, and then the cured sample was scanned at 20 K/min to

determine the glass transition temperature (T_g) of the reacted product. The initial temperature of the heat flow step of the second diagram was taken to be the T_g . The total area under the exotherm curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the heat of reaction, ΔH [J/g].

3. Results and discussion

3.1. AlN characterization

In this study, to enhance the dispersion and interfacial adhesion between the AlN nanoparticles and epoxy matrix, a silane monomer, 3-glycidoxypopyl trimethoxy silane (GPTMS) has been chosen as a coupling agent to functionalize AlN nanoparticles. The chosen silane has two different functional groups, one of which is reactive with the epoxy resin and the other reacts with the surface of AlN nanoparticles. GPTMS can hydrolyze in aqueous solution (e.g. the acetone as used in the present study, where a small amount of water is present) and its methoxy groups will transform into hydroxyl groups. Afterwards these hydroxyl groups react with those on the surface of AlN nanoparticles, then the active coating of nano-AlN particles are obtained. The possible reaction scheme between GPTMS and nano-AlN particles can be seen in Figure 1. The epoxide groups at the other ends of silane can react with the epoxy during the curing process. The dispersion of AlN nanoparticles is thus enhanced by the silane coating. Thus, the interacting force between the AlN nanoparticles and epoxy matrix is improved because the chemical bonding between the AlN nanofillers and the epoxy matrix is enhanced.

Microscopy is very useful for the characterization of generated filler structures. The TEM images obtained for the as received nano-AlN and silane treated nano-AlN powders are compared in Figure 2. Comparison of TEM images (a) and (b) shows that silane treated nano-AlN particles display that

Figure 2. TEM micrograph and corresponding SAED patterns (insets) of (a) as received nano-AlN and (b) silane treated nano-AlN

the surface modification dramatically affects the aggregate particle size. The inset in Figure 2 illustrates the identical selected area electron diffraction (SAED) patterns for both AlN powders, which indicates that the silane treatment has modified only the nano-AlN particle surface leaving the particle core structure intact.

As shown in Figure 3a, the as received nano-AlN particles show a much strong absorption at $\nu = 3200\text{--}3500\text{ cm}^{-1}$, which may be attributed to hydroxyl group ($-\text{OH}$) peak stretching. The band at $\nu = 1641\text{ cm}^{-1}$ is attributed to $-\text{NH}-$ group vibration, which indicates that nano-AlN particles have the higher affinity and reactivity to moisture and water. Therefore, the surface treatment has been undertaken to prevent the nano-AlN particles from hydrolyzing. The spectra of silane-modified AlN nanoparticles are very similar to those of raw nano-

AlN particles, but some differences can still be detected. From Figure 3b, the stretching vibration band of ether group is found in the region $1050\text{--}1150\text{ cm}^{-1}$. The band at 2990 cm^{-1} , attributed to methylene groups, is stronger than that of the raw nano-AlN particles. The absorption bands of epoxy groups at $\nu_{\text{as}}(\text{CH}_2) = 3003\text{ cm}^{-1}$, $\nu_{\text{s}}(\text{CH}_2) = 1479\text{ cm}^{-1}$, $\nu(\text{C}-\text{O}) = 1225\text{ cm}^{-1}$ can be also observed. In addition, the absorption intensity of the bands at $\nu = 3200\text{--}3500\text{ cm}^{-1}$ and $\nu = 1641\text{ cm}^{-1}$, which are assigned to hydroxyl group and amine group, respectively, can be found to apparently decrease. These changes of characteristic peaks indicate that GPTMS has already been grafted successfully on the surface of nano-AlN particles.

The morphology of the fractured surfaces for A1 and A4 are shown in Figures 4a and 4b, respectively. In the case of the neat epoxy/TMPTMA system, the fractured paths of river-like patterns can be observed, indicating brittle fracture. The nanocomposite fails in brittle manner and silane treated nano-AlN particles are seen to be separated and uniformly embedded in the matrix. The inset in Figure 4b shows that no obvious naked particles and inorganic clusters are present, indicating good interfacial adhesion between the particles and polymer matrix after silane pretreatment. The scheme for epoxy/TMPTMA system filled with silane treated nano-AlN is shown in Figure 4c. It represents that the covalent bridge bonds are formed between silane treated nano-AlN fillers and the epoxy resin.

Figure 3. FT-IR spectrum of as received nano-AlN (a) and silane treated nano-AlN (b)

Figure 4. FE-SEM micrograph of fracture surface of (a) A1, (b) A4, and (c) scheme for epoxy/TMPTMA system filled with silane treated nano-AlN. The inset in (b) is a magnified view showing the draw part.

3.2. Thermal conductivity

Figure 5a shows the variation of thermal conductivity of nano-AlN/epoxy/TMPTMA system as a func-

Figure 5. (a) thermal conductivity of nano-AlN/epoxy/TMPTMA system. (b) thermal conductivity enhancement of nano-AlN/epoxy/TMPTMA system comparison with neat epoxy/TMPTMA system at 25°C. (c) thermal conductivity of silane treated nano-AlN/epoxy/TMPTMA system and as received nano-AlN/epoxy/TMPTMA system with 5 wt% AlN loading.

tion of temperature. In the range from 25 to 100°C, the absolute thermal conductivity of the nano-AlN/epoxy/TMPTMA system increases, which is similar to the conclusion of Timofeeva *et al.* [8]. The experimental data also display that the thermal conductivity of nano-AlN/epoxy/TMPTMA system increased

with increasing the nano-AlN filler loading. The thermal conductivity enhancement for nano-AlN/epoxy/TMPTMA system containing different content nano-AlN filler is presented in Figure 5b. Here, λ enhancement (%) = $(\lambda_1 - \lambda_0)/\lambda_0$, where λ_0 is the thermal conductivity of the neat epoxy/TMPTMA system (0.18 W/(m·K)) and λ_1 is the thermal conductivity of the nanocomposites due to the addition of nano-AlN filler at 25°C. The results show that there is a 161% enhancement in thermal conductivity for A7. For the lower nano-AlN filler content (less than the percolation threshold), the main reason is attributed to that the covalent bridges minimize the interfacial phonon scattering and decrease the interface heat resistance by surface modification particles/epoxy resin. Various mechanisms have been presented to explain the increase of the effective thermal conductivity of composites containing different nanoparticles, such as interface interaction at the particle/resin interface [17], the nature of heat transport in the nanoparticles and the effects of nanoparticle clustering [18]. Based on our experimental results, it was concluded that the three dimensional network formed by the silane treated nano-AlN/epoxy dominates the thermal conduction mechanism, which leads to the nanocomposite with excellent thermal conductivity. Meanwhile, thermal conduction chains, the prevailing means to conduct thermal diffusion in the large-size filler/resin, are the secondary means to conduct thermal diffusion in the nanocomposites [13]. Figure 5c shows the detailed information for comparing the thermal conductivity of as received nano-AlN/epoxy/TMPTMA system and silane treated nano-AlN/epoxy/TMPTMA system with 5 wt% AlN loading. We can see that the thermal conductivity of silane treated

nano-AlN/epoxy/TMPTMA system is higher than that of as received nano-AlN/epoxy/TMPTMA system. It can be inferred that silane treatment is an effective approach to increase the thermal conductivity of nano-AlN/epoxy/TMPTMA system. The understanding of interface structure between nano-AlN fillers and the resin enables us to understand the thermal conduction mechanisms, therefore guides us to choose proper filler surface treatment approaches to gain excellent thermal conductivity. Furthermore, it also leads us to design the novel nanocomposites with high thermal conductivity.

3.3. Thermal stability

Thermal stability is very important for polymeric materials. In present study, the thermal stability of epoxy/TMPTMA system incorporated with the silane treated nano-AlN filler has been investigated by TGA by using heating rate of 10°C/min. Figure 6 shows the TG and DTG thermograms of the nano-AlN/epoxy/TMPTMA system. The weight loss of the system due to degradation is monitored as a function of temperature. The characteristic thermal parameters selected were the temperature for 5% and 10% weight loss and maximum degradation temperature, which is the highest thermal degradation rate temperature. The results are summarized in the Table 3. In case of neat epoxy/TMPTMA system, there is almost no weight loss up to 250°C, but the degradation rate becomes very quick beyond that temperature, the main decomposition is degraded abruptly between 250°C and 410°C. There exists a second decomposition reaction between 410 and 500°C, which could be assigned to the decomposition reaction of TMPTMA network. The first decomposition reaction could be attributed to the decom-

Figure 6. TGA (a) and DTG (b) curves of the nano-AlN/epoxy/TMPTMA system

Table 3. Degradation properties of nano-AlN/epoxy/TMPTMA system

Sample	Weight loss temperature [°C]			Residue [%]
	T _{5%}	T _{10%}	T _{max}	
A1	326	336	340	0.9
A2	334	340	349	1.5
A3	334	340	349	3.4
A4	331	339	350	4.1
A5	331	339	348	5.7
A6	328	337	348	8.3
A7	329	337	349	10.5

position reaction of epoxy network. This was in good agreement with the results from our previous study [15, 16]. In the case of A2, incorporation of this small amount of the nano-AlN filler into the epoxy/TMPTMA system slightly improves the thermal stability because it increase the temperature at 5% weight loss by about 8°C. The maximum degradation temperature (T_{max}) also increased by addition of the nano-AlN filler. However, higher loading of the nano-AlN filler does not lead to any further improvement of the thermal stability. The experimental results also show that the residual weight percent at 700°C of the nano-AlN/epoxy/TMPTMA system increases upon addition of increasing amount of nano-AlN filler.

3.4. Curing behavior

In order to understand the influence of the silane treated nano-AlN filler on the epoxy/TMPTMA system in-depth, the curing behavior of all systems were investigated. The curing curves of A1 and A4 systems are shown in Figure 7. Shift of the DSC exothermic peaks to lower temperatures is observed in the presence of silane treated nano-AlN particles, illuminating that silane treated nano-AlN particles filled epoxy is obviously faster in reaching the

exothermic peak than neat epoxy/TMPTMA system. The curing mechanism of epoxy/TMPTMA system involves three stages consisting of radical reaction of TMPTMA, the adduct, and etherification reactions of epoxy/MeHHPA. The third stage (i.e., the etherification reaction) dominates the cure process and is discussed mainly in this study.

The exothermic peak temperatures (T_p) and the heats of the reaction (ΔH) for A1-A7 systems are summarized in Table 4. From Table 4, it is clear that silane treated nano-AlN particles act as catalyst and facilitate the curing at the initial curing stage by lowering T_p . For the development of the composites, the cure acceleration effect caused by silane treated nano-AlN particles could bring positive effect on the processing of composite since it needs shorter pre-cure time or lower pre-temperature. In this study, this accelerating effect might also be partially attributed to the remaining hydroxyl groups (–OH) and amino groups (–NH₂) on the surface of nano-AlN particles since the epoxy/TMPTMA system was used as the martrix. The total heats of reaction (ΔH) of all the studies systems which are calculated by the total area under the exothermic peaks are reported in Table 4. The result indicate that the inclusion of silane treated nano-AlN parti-

Table 4. Curing kinetic parameters of the nano-AlN/epoxy/TMPTMA system and glass transition temperatures (T_g) of the cured systems

System	T_p [°C]	ΔH [J/g]	E_a [kJ/mol]	T_g [°C]
A1	249.8	130.4	83.28	176.4
A2	227.6	137.3	71.27	180.0
A3	222.7	139.9	53.13	180.1
A4	222.7	139.6	68.85	181.4
A5	216.2	154.0	64.54	177.9
A6	222.3	132.1	77.20	181.8
A7	222.0	137.8	73.81	186.7

Figure 7. Dynamic DSC curves with different heating rates of (a) A1 and (b) A4

cles increases the ΔH , possibly due to the addition of epoxy concentration in the composite.

From a dynamic DSC run, the total area S of the exothermal peak (the region between the exotherm and the baseline) is in direct proportion to the ΔH release during the whole cure reaction. The fraction extent of conversion α at any temperature T can be expressed by Equation (1):

$$\alpha = \frac{\Delta H_T}{\Delta H} = \frac{S_T}{S}, \quad 0 \leq \alpha \leq 1 \quad (1)$$

where ΔH_T is the heat of reaction of partially cured samples heated up to the temperature T . A comparison of the curing process, at 10°C/min heating rates, among the neat epoxy/TMPTMA system and the silane treated nano-AlN particles filled epoxy/TMPTMA systems is shown in Figure 8. It confirms that the silane treated nano-AlN particles act as catalyst at the initial curing stage again. Furthermore, a sigmoidal form of the curves, which is indicative of an autocatalytic kinetics of all the studies systems, is observed. That is to say, the addition of the silane treated nano-AlN particles does not change the autocatalytic cure reaction mechanism of the epoxy/TMPTMA system. It can be seen that all α values increased very slowly at the beginning. When the temperature is high enough, the α values are raised rapidly over 90%, and then they are leveled off.

Ozawa Equation (2), which was concluded to be independent of the order of reaction, is used to calculate the cure reaction activation energy E_a [19, 20].

$$\frac{d(-\ln\beta)}{d\left(\frac{1}{T_p}\right)} = 1.052 \frac{E_a}{R} \quad (2)$$

The value of E_a can be determined from the slope of the plot of $-\ln\beta$ versus $1/T_p$. Furthermore, the influence of the silane treated nano-AlN particles on the E_a parameters of A1–A7 systems was also studied. The calculated values of E_a of A1–A7 systems are reported in Table 4. The decreased values of E_a for the filled system also implied that the nano-AlN particles facilitate the curing process. Since the effect of increased concentration of the silane coupling agent was equal to the effect of increase the crosslinking density in the curing system, it is understandable of the decrease values of E_a when the

Figure 8. Conversion versus temperature plot at 10°C/min heating rates of the A1–A7 systems

nano-AlN particles coupled with higher concentration of the silane coupling agent. But the E_a does not show any trend on increasing the amount of the nano-AlN particles.

During the cure reaction, the system undergoes gelation (liquid-to-rubber) and vitrification (rubber-to-glass) transitions. As the cure reaction proceeds, it is possible that the glass transition temperature (T_g) increases over the curing temperature (T_c), this phenomenon is called vitrification. [21] From Table 4, the T_g s of the silane treated nano-AlN particles filled epoxy/TMPTMA systems are found to be higher than that of the neat epoxy/TMPTMA system. Meanwhile, the T_g s of the silane treated nano-AlN particles filled epoxy/TMPTMA systems were improved with increasing content of the silane treated nano-AlN particles, although A5 system deviates from this trend. The glass transition in polymers is a complex phenomenon that is influenced by many factors including free volume, molecular mobility, molecular weight, and crosslink density [22, 23]. When the silane treated nano-AlN particles are introduced into systems, there would result in increased T_g . There could be the main reason that the epoxide groups are the end groups of the silane coupling agent, which would result in a higher crosslinking density in the epoxy/TMPTMA system.

4. Conclusions

The influences of nano-AlN particles on the thermal conductivity, thermal stability and the curing reaction of CER/TMPTMA systems have been investigated. The thermal conductivity of A7 system was up to 0.47 W/(m·K), which is 161%

increase when compared with the neat epoxy/TMPTMA system. Incorporation of a small amount of the nano-AlN filler into the epoxy/TMPTMA system improves the thermal stability. However, higher loading of the nano-AlN filler does not lead to any further improvement of the thermal stability. For instance, the thermal degradation temperature at 5% weight loss for A2 system was improved by $\sim 8^{\circ}\text{C}$ over the neat epoxy/TMPTMA system. The resulting fractional extent of conversion versus temperature curves of all the systems considered present the same sigmoidal functional form which is indicative of an autocatalytic kinetics, that is to say, the addition of silane treated nano-AlN particles does not change the cure reaction mechanism. For the development of the nanocomposite, the cure acceleration effect caused by silane treated nano-AlN particles could bring positive effect on the processing of composite since it needs shorter pre-cure time and lower pre-temperature, meanwhile the increase of glass transition temperature of nanocomposite would bring the positive effect to improve the heat resistance.

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