Highly thermally conductive flame-retardant epoxy nanocomposites with reduced ignitability and excellent electrical conductivities

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Abstract

A highly efficient phenylphosphonate based flame retardant epoxy resin (FREP) was firstly prepared from phenylphosphonic dichloride (PPDCI) and allylamine (AA). Functionalized graphite nanoplatelets (fGNPs) fillers were then performed to fabricate the fGNPs/FREP nanocomposites via mixing followed by casting method. The thermally conductive coefficient (λ), thermal diffusivity (α), flame retardancy, electrical conductivities and thermal stabilities of the fGNPs/FREP nanocomposites were all enhanced with the increasing addition of fGNPs fillers. The λ and α value of the fGNPs/FREP nanocomposite with 30 wt% fGNPs fillers was increased to 1.487 W/mK and 0.990 mm²/s, about 7 times and 6 times for that of pure FREP matrix (0.234 W/mK and 0.170 mm²/s), respectively. And the corresponding electrical conductivity was also increased to 5.0×10^{-4} S/cm, far better than that of pure FREP matrix (1.0×10^{-12} S/cm). In comparison with that of pure FREP, the THR and TSP value of the fGNPs/FREP nanocomposite with 15 wt% fGNPs fillers was decreased by 37% and 32%, respectively, char yield was increased by 13%, and LOI value was increased from 31% to 37%. However, the peak of heat release rate of the fGNPs/FREP nanocomposite became worse due to its high thermal conductivity. Nanoindentation revealed that there was negligible influence of fGNPs fillers on the hardness values and Young's modulus of the fGNPs/FREP nanocomposites.

1. Introduction

As one of crucial thermosetting plastics, epoxy resins possess high tensile strength and Young's modulus, excellent dimensional & thermal stabilities, good solvent resistance, low cost and easy processing, etc., and have widely applied as the matrix of coatings, adhesives and composites [1-4]. However, the low thermal conductivity [5-7] and poor flame retardancy [8,9] of epoxy resins have limited their wider application in key fields.

To the best of our knowledge, the addition of single thermally conductive fillers (such as SiO₂ [6], Al₂O₃ [10], ZrB₂ [11], BN [12-14], AlN [15], SiC [16], Si₃N₄ [17], Si₃N₄ nanowire [18], silica nanofibers [19], CNTs [20,21], boron nitride nanotube [22], graphite [23], graphite nanoplatelets [24,25], graphene oxide [26], graphene [27,28], etc.) or hybrid thermally conductive fillers (such as Al₂O₃/AlN [29], AlN/BN [30], AlN/MWCNTs [31,32], Cu/MWCNTs [33], SiO₂/graphene oxide [34,35], BN/graphene oxide [7], graphite nanoplatelets/SiC [36], graphite nanoplatelets/CNTs [37], nano silica/AgNWs [38], etc.) into epoxy matrix could enhance the thermal conductivities of the epoxy composites. Previous researches mainly pay more attention on the category, shape, size, volume & mass fraction, and the surface functionalization of the single and/or hybrid thermally conductive fillers on the thermal conductivities of the epoxy composites [17]. However, the improvement of the thermal conductivities of the epoxy composites is often less than expected from previous design [39].

Furthermore, relatively high loading of thermally conductive fillers results in an adverse impact on the processing behavior and mechanical properties of the epoxy resins [30].

With regard to the flame retardancy of the epoxy composites, phosphorous containing flame retardants are considered to be promising to reduce flammability of epoxy resins because most halogenated flame retardants are banned owing to their serious hazards for environment and human health [40–44]. In our previous work, a highly efficient phenylphosphonate based flame retardant epoxy resin (FREP) was developed. The LOI of FREP was increased from 22% to 31% at 5 wt% addition of flame retardant. And the corresponding heat and smoke release were both suppressed significantly in the cone calorimeter test [40]. Additionally, nano indentation [45] is proved to be an effective method of probing site specific mechanical properties at a very fine scale. During measurement, load displacement profiles are continuously recorded and then used to calculate Young's (elastic) modulus and hardness [46,47].

In our present work, to further broaden the application of the epoxy resins in the high tech fields of the microelectronics (electronic packing), electronic information and electronic shielding, we developed a novel highly thermally conductive epoxy resins nanocomposites with reduced ignitability and excellent electrical conductivities. Phenylphosphonic dichloride (PPDCl) and allyl amine (AA) were firstly performed to synthesize reactive phenylphosphonate based flame retardant FP1, which were then introduced into epoxy matrix to fabricate the flame retardant epoxy resin (FREP). And the surface functionalized graphite nanoplatelets (fGNPs) fillers were then performed to fabricate the fGNPs/FREP nanocomposites via mixing followed by casting method. Herein, the "two step" method of methanesulfonic acid/ γ glycidyloxypropyltrimethoxysilane (MSA/KH 560) was performed to functionalize the surface of GNPs (fGNPs). The mass fraction of fGNPs fillers influencing on the thermal conductivities, flame retardancy, electrical conductivities, thermal stabilities and strength of the fGNPs/FREP nanocomposites was discussed and investigated in detail. In addition, the relationship between experimental thermal conductivities of the fGNPs/FREP nanocomposites and fGNPs fillers concentration was also compared with the predictions of theoretical models.

2. Experimental section

2.1. Materials

Epoxy resin (EPC), with epoxy equivalent of 0.54, was supplied from Faserverbundwerkstoffe® Composite Technology (Waldenbuch, Germany); Phenylphosphonic dichloride (PPDCl, 90%), allyl amine (AA, 98%) and curing agent of 4, 4 diaminodiphenylsulfone (DDS) were all purchased from Sigma Aldrich Corporation (Saint Louis, USA); Graphite nanoplatelets (GNPs), KNG 180, with diameter of 40 μm , super diameter/thickness ratio of 250, were received from Xiamen Knano Graphene Technology Co. Ltd. (Fujian, China); Methanesulfonic acid (MSA) was received from Chengdu Kelong Chemical Co. Ltd. (Sichuan, China); γ glycidyloxypropyltrimethoxysilane (KH 560) was supplied by Nanjing Shuguang Chemical Group Co., Ltd. (Jiangsu, China); Ethanol (EtOH) and tetrahydrofuran (THF) were all supplied by Tianjin Fu Yu Fine Chemical Co., Ltd. (Tianjin, China).

2.2. Preparation of the fGNPs/FREP nanocomposites

Surface functionalization of GNPs (fGNPs) was carried out by the "two step" method of MSA/KH 560 [25]. FREP was also prepared according to our previous work [40]. The synthesized flame

retardant N, N' diallyl P phenylphosphonicdiamide (FP1) was mixed with EPC at 100 °C for 5 min. Then the stoichiometric amount of DDS was added slowly into the FREP mixture at 130 °C. After DDS was totally dissolved, a certain amount of fGNPs fillers were added into the mixture and stirred uniformly, degassed in a vacuum oven. Finally, the obtained mixture was poured into the preheated moulds and then cured according to the following technology: 160 °C/1 h + 180 °C/2 h, followed by post curing at 200 °C for another 1 h.

2.3. Characterization

Thermally conductive coefficient (λ) and thermal diffusivity (α) [48] of the samples were measured using a Hot Disk instrument (AB Corporation, Sweden) according to standard ISO 22007 2: 2008; The electrical conductivities of the samples were measured by Agilent 4155C semiconductor parameter analyzer (Agilent, China); Thermal gravimetric (TG) analysis of the samples were carried out at 10 °C/min (argon atmosphere) by STA 449F3 (NETZSCH, Germany); Scanning electron microscopy (SEM) morphologies of the samples were analyzed by VEGA3 LMH (TESCAN Corporation, Czech Republic); Dynamic mechanical analyses (DMA) were performed using DMA/SDTA 861 e (Mettler Toledo Co. Switzerland) in the bending mode, at a heating rate of 5 °C/min from 25 °C to 200 °C at 1 Hz; Limiting oxygen index (LOI) of the samples was tested on oxygen index meter (FTT, UK) according to ASTM D2863 97 standard; Cone calorimeter test of the samples was performed on a cone calorimeter (FTT, UK) according to ISO 5660 1 standard. The heat flux was set as 50 kW/m²; The specimens for instrumented nanoindentation were metallurgically prepared with a great caution to minimize the influence of residual stresses and plastic deformation of surface. With an extremely low load, the samples were finished with a final polish using colloidal silica (0.05 μm). A Hysitron TI 950 nanoindenter equipped with a Berkovich diamond indenter was well calibrated by fused silica before testing. The peak indentation load was set as 9 mN with the fixed loading and unloading rates of 300 and 450 $\mu\text{N/s}$, respectively [49]. The dwell time at the maximum load was 5 s. To avoid the interference among the different indents, the intervals among any neighboring indents were greater than 100 μm . To get statistically significant results, at least 36 indents were conducted on each sample.

3. Results and discussion

3.1. Thermal conductivities of the fGNPs/FREP nanocomposites

The mass fraction of fGNPs fillers affecting on the thermal conductivities of the fGNPs/FREP nanocomposites was shown in Fig. 1.

Both the λ and α values of the fGNPs/FREP nanocomposites were improved with increasing addition of fGNPs fillers. The λ value of the fGNPs/FREP nanocomposite with 30 wt% fGNPs fillers was improved to 1.487 W/mK, about 7 times for that of pure FREP matrix (0.234 W/mK). And the corresponding α value was also improved to 0.990 mm²/s, about 6 times for that of pure FREP matrix (0.170 mm²/s).

With an appropriate addition of fGNPs fillers (5 wt% and 10 wt%), there was some connectivity of fGNPs in some regions (Fig. 2b–c), presenting relatively smaller increment for the λ and α values of the fGNPs/FREP nanocomposites. Then the effective thermally conductive channels of fGNPs could be formed with relatively highly filled fGNPs fillers (>10 wt%), resulting from the effective connection of fGNPs to fGNPs (Fig. 2d–f). Therefore, the λ and α values of the fGNPs/FREP nanocomposites were both

Fig. 1. The mass fraction of fGNPs fillers affecting on the thermal conductivities of the fGNPs/FREP nanocomposites.

improved obviously. From Fig. 2, it was noted that the fGNPs fillers had relatively better interfacial compatibility with FREP matrix, which was also benefit for decreasing the interfacial thermal barrier of the fGNPs/FREP, finally to further increase the thermal conductivities of the fGNPs/FREP nanocomposites.

Experimentally and theoretical λ values from correlative models of the fGNPs/FREP nanocomposites [51–56] were also shown in Fig. 3.

The obtained experimental λ values of the fGNPs/FREP nanocomposites were in good agreement with the results from the series conduction, lower bound of Maxwell and EMT models, but far

Fig. 3. Experimentally and theoretical λ values from correlative models of the fGNPs/FREP nanocomposites.

from those for parallel conduction and upper bound of Maxwell models. It revealed that the fGNPs fillers possessed relatively uniform dispersion inner the FREP matrix with an appropriate addition of fGNPs fillers. However, the holes, cavities and/or bubbles might be introduced into the nanocomposites with highly filled fGNPs fillers, resulting in the enormous deviations between experimental and theoretical values.

Fig. 2. SEM morphologies of impact fractures for pure FREP matrix and fGNPs/FREP nanocomposites.

3.2. Flame retardancy of the fGNPs/FREP nanocomposites

In cone calorimeter test, the characteristic curves of heat release rate (HRR), total heat release (THR), total smoke production (TSP) and mass loss (ML) were shown in Fig. 4. Table 1 collected the data of time to ignition (TTI), peak of HRR (pHRR), THR, TSP and char residue after test. Moreover, the corresponding LOI values of pure FREP and 15 wt% fGNPs/FREP nanocomposite were also shown in Table 1.

From Fig. 4 and Table 1, the TTI of the 15 wt% fGNPs/FREP nanocomposite was 63 ± 3 s, which was longer than that of pure FREP (55 ± 3 s), indicated that the addition of fGNPs fillers reduced the ignitability of the FREP. HRR curves of FREP and 15 wt% fGNPs/FREP nanocomposite showed significantly different. In details, HRR peak of pure FREP was broad and low (pHRR was 419 ± 47 kW/m²), whereas HRR peak of the 15 wt% fGNPs/FREP nanocomposite was high and sharp (pHRR was 858 ± 38 kW/m²). However, THR of the 15 wt% fGNPs/FREP nanocomposite (59 ± 2 MJ/m²) was lower by 37% in comparison with that of FREP (82 ± 4 MJ/m²).

The addition of fGNPs fillers increased the fire propagation (increased HRR) of FREP, though the THR value of the fGNPs/FREP nanocomposite was decreased. This phenomenon on the heat release rate in the cone calorimeter test was different from other nanofillers filled polymers nanocomposites, such as layered double hydroxide (LDH) [57], zirconium phosphate (ZrP) [58] and talc [59], etc., based polymer nanocomposites, because usually these polymer nanocomposites would show lower heat release rate after introducing nanofillers into the polymers matrix. In the 15 wt% fGNPs/FREP nanocomposite, the increased fire propagation

(increased HRR) was induced by the accelerated thermal decomposition of FREP owing to the addition of fGNPs fillers.

The mass loss rate of the 15 wt% fGNPs/FREP nanocomposite was faster than that of FREP during the developed fire zone as shown in Fig. 4. However, the char residue of the 15 wt% fGNPs/FREP nanocomposite was $37 \pm 1\%$, which was more than that of FREP ($24 \pm 2\%$). The increased residue amount showed that the addition of fGNPs fillers improved the charring ability of FREP. In addition, the smoke release of FREP was also suppressed. TSP of the 15 wt% fGNPs/FREP nanocomposite was 17 ± 1 m², which was 8 m² lower than that of FREP (25 ± 2 m²). The lowered TSP of the 15 wt% fGNPs/FREP nanocomposite was also conducive to lower the fire hazard of FREP.

In addition, the LOI value of the 15 wt% fGNPs/FREP nanocomposite increased from 31% to 37% compared with that of FREP. However, in the vertical burning test, the 15 wt% fGNPs/FREP nanocomposite did not pass the UL94 V 0 rating.

In this work, the impact of 15 wt% fGNPs on heat release was caused by the improved thermal conductivity of FREP. The heat transfer of the 15 wt% fGNPs/FREP nanocomposite was increased under cone heater, leading to the longer TTI, compared with that of FREP. However, the increased heat transfer also reduced the temperature gradient of sample. Meanwhile, the lowered TSP was correlating with the increased mass residue of the 15 wt% fGNPs/FREP nanocomposite compared with that of FREP.

3.3. Electrical conductivities of the fGNPs/FREP nanocomposites

Fig. 5 presented the mass fraction of the fGNPs fillers affecting

Fig. 4. Characteristic curves of heat release rate (HRR), total heat release (THR), total smoke production (TSP) and mass of the pure FREP matrix and fGNPs/FREP nanocomposite with 15 wt% fGNPs fillers. a: HRR; b: THR; c: TSP and d: mass loss.

Table 1

The burning data from cone calorimeter test and LOI values of pure FREP matrix and 15 wt% fGNPs/FREP nanocomposite.

Sample	TTI ^a (s)	pHRR ^b (kW/m ²)	THR ^c (MJ/m ²)	TSP ^d (m ²)	Residue (wt%)	LOI ^e (%)
FREP	55 ± 3	419 ± 47	82 ± 4	25 ± 2	24 ± 2	31
15 wt% fGNPs/FREP	63 ± 3	858 ± 38	59 ± 2	17 ± 1	37 ± 1	37

^a Meant time to ignition.

^b Meant peak of HRR.

^c Meant total heat release.

^d Meant total smoke production.

^e Meant limiting oxygen index.

Fig. 5. The mass fraction of the fGNPs fillers affecting on the electrical conductivities of the fGNPs/FREP nanocomposites.

on the electrical conductivities of the fGNPs/FREP nanocomposites. The electrical conductivities of the fGNPs/FREP nanocomposites were improved with increasing addition of fGNPs fillers. And the electrical conductivity of the fGNPs/FREP nanocomposite with 30 wt% fGNPs fillers was increased to 5.0×10^{-4} S/cm, far better than that of FREP (1.0×10^{-12} S/cm). An appropriate addition of fGNPs might be dispersed independently and isolated by FREP matrix, hardly to contact between each other. And the corresponding conductive paths could be formed with the increasing addition of fGNPs fillers, resulting in a rapid improvement of the electrical conductivities. With a further increasing addition of fGNPs (>15 wt%), the role of fGNPs fillers just perfected the network structure, resulting in the slight improvement of the electrical conductivities. Certainly, the active polar groups on the surface of fGNPs fillers could influence the intrinsic electrical conductivity of

fGNPs fillers, which could catch π electron and hinder the migration of the free electron, against the improvement of the electrical conductivities of the fGNPs/FREP nanocomposites.

3.4. Thermal properties of the fGNPs/FREP nanocomposites

TGA and DMA curves of FREP and the fGNPs/FREP nanocomposites were presented in Fig. 6, and the corresponding char asteristic data were presented in Table 2.

The $T_{\text{Heat-resistance index}} (T_{\text{HRI}})$ and glass transition temperature (T_g) values of the fGNPs/FREP nanocomposites were increased with the increasing addition of fGNPs fillers. The T_{HRI} value of the fGNPs/FREP nanocomposite with 25 wt% fGNPs fillers was improved to 181.4 °C, higher than that of FREP (173.0 °C). It revealed that the thermal stabilities of the fGNPs/FREP nanocomposites were enhanced with the increasing addition of fGNPs fillers. It was mainly attributed that fGNPs fillers possessed relatively higher λ value than that of FREP. And relatively better interfacial compatibility of fGNPs/FREP could be favor of increasing the thermal stabilities of the fGNPs/FREP nanocomposites. In addition, the fGNPs fillers might occupy the space of the molecular chain for FREP matrix, to hinder the rotation of the FREP molecular chain, resulting in the increase of the T_g values of the nanocomposites.

3.5. Nanoindentation of the fGNPs/FREP nanocomposites

The mass fraction of fGNPs fillers affecting on the hardness and Young's modulus of the fGNPs/FREP nanocomposites was presented in Fig. 7. In Fig. 7a, three representative load displacement curves of pure FREP (different colors) were superimposed on each other, highlighting the excellent reproducibility and homogeneous (isotropic) properties of the samples. Fig. 7b revealed that there was negligible influence of fGNPs fillers on the hardness values and Young's modulus of the fGNPs/FREP nanocomposites. For thermo setting FREP, the corresponding strength of FREP was mainly

Fig. 6. TGA and DMA curves of FREP matrix and the fGNPs/FREP nanocomposites. (a)TGA; (b)DMA.

Table 2

Corresponding characteristic data of FREP matrix and the fGNPs/FREP nanocomposites.

Samples	Weight loss temperature/°C		$T_{Heat\ resistance\ index}^a/°C$	Residual/%	$T_g/°C$
	5%	30%			
Pure FREP	326	371	173.0	24.8	129.2
5 wt% fGNPs/FREP	324	381	175.8	28.0	140.7
10 wt% fGNPs/FREP	328	380	176.1	31.2	146.5
15 wt% fGNPs/FREP	329	387	178.3	32.4	148.9
20 wt% fGNPs/FREP	330	387	178.5	34.9	150.1
25 wt% fGNPs/FREP	330	397	181.4	39.4	152.8

^a The sample's heat-resistance index is calculated by Eq. (1) [12]. $T_{Heat\ resistance\ index} = 0.49 \times [T_5 + 0.6 \times (T_{30} - T_5)]$ (Eq. (1)). T_5 and T_{30} is corresponding decomposition temperature of 5% and 30% weight loss, respectively.

Fig. 7. The mass fraction of fGNPs fillers affecting on the hardness and Young's modulus of the fGNPs/FREP nanocomposites. (a) Three representative load-displacements of pure epoxy; (b) Hardness and Young's modulus of the fGNPs/FREP nanocomposites.

relying on the chain interaction and the rigidity of the units. Varying the amount of fGNPs fillers could not change such intrinsic behavior. As a result, there was a little influence on the hardness and Young's Modulus of the fGNPs/FREP nanocomposites.

4. Conclusions

Both λ and α values of the fGNPs/FREP nanocomposites were improved with the increasing addition of fGNPs fillers. The λ and α value of the fGNPs/FREP nanocomposite with 30 wt% fGNPs fillers was improved to 1.487 W/mK and 0.990 mm²/s, about 7 times and 6 times for that of FREP matrix (0.234 W/mK and 0.170 mm²/s), respectively. In comparison with that of FREP, the ignitability of 15 wt% fGNPs/FREP nanocomposite was decreased according to the time to ignition in the cone calorimeter test and improved LOI value (from 31% to 37%). The electrical conductivities of the fGNPs/FREP nanocomposites were improved with the increasing addition of fGNPs fillers. The corresponding electrical conductivity of the fGNPs/FREP nanocomposite with 30 wt% fGNPs fillers was increased to 5.0×10^{-4} S/cm, far better than that of FREP matrix (1.0×10^{-12} S/cm). TGA revealed that the thermal stabilities of the fGNPs/FREP nanocomposites were enhanced with the increasing addition of fGNPs fillers. Nanoindentation testing revealed that there was negligible influence of fGNPs fillers on the hardness values and Young's modulus of the fGNPs/FREP nanocomposites.

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