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Syntheses and characterization of novel P/Si polysilsesquioxanes/epoxy nanocomposites

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ABSTRACT

Phosphorus-containing polysilsesquioxane (PSSQ) was introduced into diglycidyl ether of bisphenol A epoxy (DGEBA) to generate a novel P/Si PSSQ nanocomposite. A series of nanocomposites was fabricated by changing the content of the 2-(diphenylphosphino)ethyltriethoxysilane (DPPETES) monomer or P/Si PSSQ cured with DGEBA epoxy and modified epoxy. The structure, thermal properties and flame-retardancy of the P/Si PSSQ nanocomposites were characterized by FT-IR, solid-state ^{29}Si NMR, thermogravimetric analysis (TGA) and limited oxygen index (LOI) instruments. The nano-sizes of the particles in P/Si PSSQ were approximately 30–50 nm, and the polarity of nanocomposites might generate the nanophase-separated structure from transmission electron microscopy (TEM). The urethane-like side group of the modified epoxy and the fabrication of oligomers in the curing reaction affected the T_{d5} values of nanocomposites. TGA and LOI results indicated that the char yield (29 wt%) increased and the nanocomposites were not very flammable (LOI = 30). The hybrid materials also exhibited high thermal stability, good flame-retardance and a lack of phase separation.

1. Introduction

The effect of polysilsesquioxanes on the thermal, optical and mechanical properties of epoxy resin has received considerable attention recently [1–3]. The composite material reinforced by nano-scale fillers exhibit unique thermal, optical and electrical properties. Introducing these nano-sized inorganic fillers significantly increases the interfacial area between the fillers and the matrix improving the overall properties of the polymer [4].

"Environmentally friendly" is an important target attributable to applications of the polymeric materials. Over recent years, much attention has been paid to controlling the inherent flammability of common organic polymers by incorporating halogen-free flame-retardant moieties [5]. To avoid the use of halogenated flame-retardants in the epoxy resin, some alternatives that contain phosphorus, silicon and nitrogen groups have been developed [6–10]. Silicone-containing epoxy resin exhibits good thermal resistance, dimensional stability and physical strength to satisfy the requirements of an electronic and electrical matrix, adhesive applications, and aerospace components, for example [7–10].

Most epoxy resins that are modified with functional groups, such as imide [11], melamine [12], silicones [8] and nano-fillers [5] exhibit favorable flame-retardance. Phosphorus, silicon and nitrogen compounds are the agents that mostly replace halogen compounds in flame-retarding epoxy resins. Incorporating silicon into a phosphorus flame-retardant system and silicon may reduce the surface energy. Therefore, silicon will be made to migrate to the surface of the epoxy matrix and, providing a shielding layer with high thermal resistance protecting the polymer residue against thermal degradation [13,14].

Based on the idea described above, P/Si-containing polysilsesquioxane (PSSQ) was synthesized; various P/Si PSSQ or monomer contents were incorporated into epoxy resins. The morphology of nanocomposites was investigated by Si-mapping and TEM. The nanocomposites thus obtained exhibit excellent thermal properties.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A (DGEBA) epoxy used in this work was supplied by the Nan Ya Plastics Co. Ltd., Taiwan, with an epoxide equivalent weight of 180 g/equiv. 2-(Diphenylphosphino)

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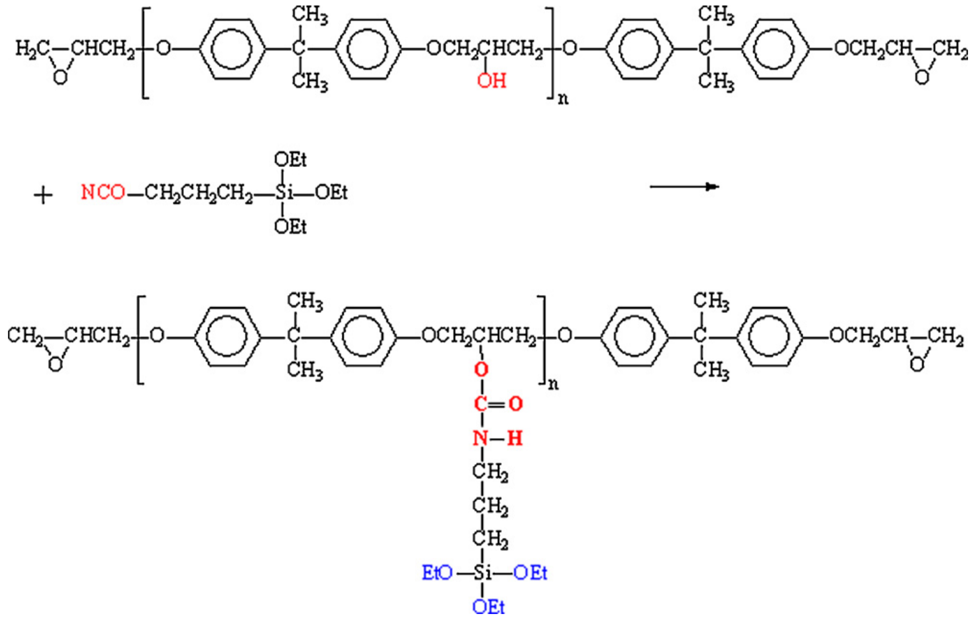


Scheme 1. Preparation of IPTS-modified epoxy.

ethyltriethoxysilane (DPPETES) and 3-isocyanatopropyltriethoxysilane (IPTS) were obtained from the United Chemical Technologies Inc., Bristol, PA, USA. Tetraethoxysilane (TEOS) and 4,4-methylenedianiline (DDM) were supplied by the Acros Organic Co., Belgium. HCl was obtained from the Union Chemical Works Ltd., Taiwan. Isopropyl alcohol (IPA), tetrahydrofuran (THF) and triethylamine (TEA) were received from the Tedia Co. Inc., USA.

2.2. Preparation of IPTS-modified epoxy (ME) precursor

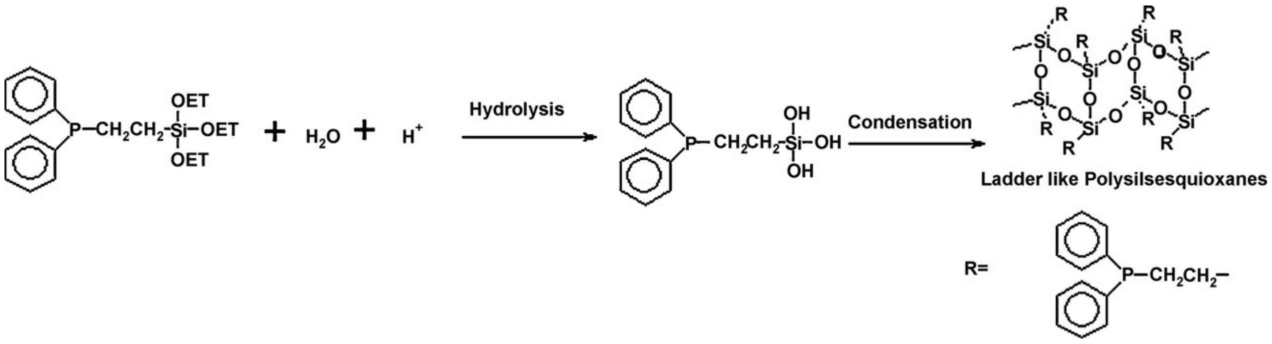
DGEBA resin (10 g) and THF (10 g) were stirred in a 250-ml round-bottom flask at room temperature to obtain DGEBA solution. After adding 3-isocyanatopropyltriethoxysilane (4 g, 16.19 mmol IPTS) and optimum concentration of triethylamine (TEA, about 0.2 g), the mixture was allowed to reflux at 60 °C and stirred until the characteristic peak of the NCO group disappeared from the FT-IR spectra. Then, the IPTS-modified epoxy (ME) precursor was obtained. The preparation method of the precursor has been described in our previous investigation [15]. The preparation of ME was shown as Scheme 1.

2.3. Preparation of P/Si polysilsesquioxanes (P/Si PSSQ)

2-(Diphenylphosphino)ethyltriethoxysilane (5 g, 13.263 mmol) was placed in a 100-ml glass bottle. The H_2O/DPPETES mixture with a molar ratio of 3:1 was prepared. The DPPETES/IPA/THF with a molar ratio of 1:6.23:1.67 was poured into the reaction system. HCl was added until the pH value was 2. The mixture was stirred at room temperature until the solution was clear. The wet gel was aged at room temperature for 48 h and dried at 80 °C for 24 h, and finally was kept in a vacuum oven at 200 °C for 24 h [16]. The preparation of ME was shown as Scheme 2.

2.4. Preparation of hybrid nanocomposites

The hybrid nanocomposites were obtained by reacting DGEBA epoxy (EP) system and IPTS-epoxy (ME) system with various feeding ratios of DPPETES monomer and P/Si polysilsesquioxane (0, 3, 6, 9 and 12 wt%). For DGEBA epoxy and DPPETES monomer system, the abbreviations EP-DDM, EP-3M, EP-6M, EP-9M and EP-12M were assigned, respectively, for instance, EP-3M represents the DGEBA epoxy with 3 wt% DPPETES monomer and L represented P/Si polysilsesquioxanes. The coupling agent of the 9 wt% tetraethoxysilane was added to all of the reaction systems. HCl was used as catalyst, which has been described in our previous study [2]. All mixtures were stirred for 1 h, and via sol–gel process for 24 h at room temperature. In this study, 4,4-methylenedianiline (DDM) was used as the curing agent of various nanocomposites at 80 °C for 12 h and at 160 °C for 12 h.



Scheme 2. Preparation of P/Si ladder-like polysilsesquioxane.

2.5. Statistic heat-resistant index temperature

The statistic heat-resistant index temperature (T_s) was determined with the temperature of 5% weight loss (T_{d5}) and of 30% weight loss (T_{d30}) of the sample by the thermogravimetric analysis. The statistic heat-resistant index temperature (T_s) was calculated as shown below [17,18]:

$$T_s = 0.49[T_{d5} + 0.6(T_{d30} - T_{d5})]$$

2.6. Instrumental analysis

Liquid samples were cast onto the KBr pellet and the cured resins were measured with a PerkinElmer Spectrum One FT-IR equipped with an attenuated total reflectance (ATR) accessory. Solid-state ^{29}Si NMR analysis was performed with a Bruker DSX 400WB (400 MHz) NMR spectrometer. Nano-structures of epoxy nanocomposites were analyzed by a transmission electron microscopy, JEOL JEM-1230 and its accelerated voltage is 100 kV. The films of cured nanocomposites were microtomed by Ultracut Uct, which possessed 100 nm thickness size. Differential scanning calorimetry (DSC) thermograms were recorded with a Thermal Analysis DSC-Q10 differential scanning calorimetry. The testing temperature was from 30 to 250 °C, under a nitrogen gas flow of 40 ml/min. Thermogravimetric analysis was performed with a Thermal Analysis TGA-951 thermogravimetric analyzer, at a heating rate of 10 °C/min, under nitrogen atmosphere. The nitrogen gas flow rate was 100 ml/min. Limited oxygen index (LOI) values were measured with ATLAS Fire Science Products Co., New York, USA. The LOI test was performed according to the testing procedure of ASTM D2836 oxygen index method. The LOI represented the lowest oxygen content for sustaining the flame.

3. Results and discussion

3.1. Preparation and characterization of nanocomposites

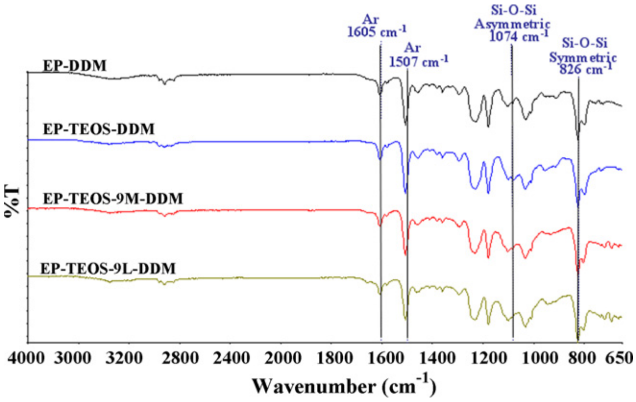


Fig. 1. The FT-IR spectra of nanocomposite of EP system (M, DPPETES monomer; L, DPPETES polysilsesquioxanes (P/Si PSSQ)).

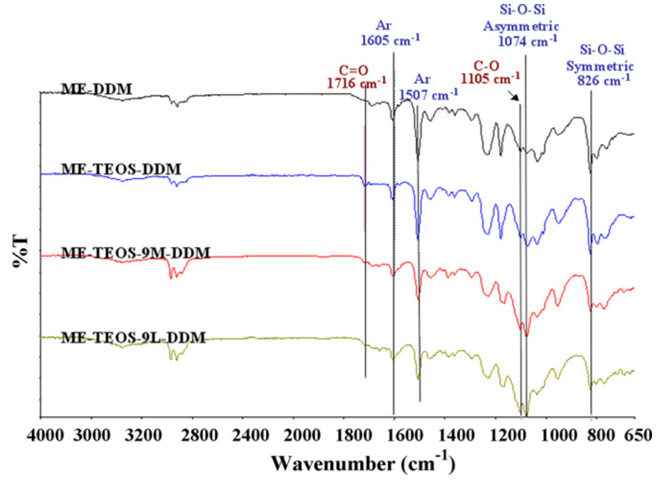


Fig. 2. The FT-IR spectra of nanocomposite of ME system (M, DPPETES monomer; L, DPPETES polysilsesquioxanes (P/Si PSSQ)).

Table 1
Infrared absorbency of epoxy and modified epoxy system

Wave number (cm^{-1})	EP-DDM-system	ME-DDM system
	Function type	Function type
2972	—CH$_3$	—CH$_3$
2922	—CH$_2$— asymmetric	—CH$_2$— asymmetric
2876	—CH$_2$— symmetric	—CH$_2$— symmetric
1716	[a]	C=O
1605	C=C, aromatic ring	C=C, Aromatic ring
1507	Aromatic ring	Aromatic ring
1459	Aromatic ring	Aromatic ring
1388	—CH$_3$ umbrella	—CH$_3$ umbrella
1295	N—Ar	N—Ar
1231	Si—CH$_2$	Si—CH$_2$
1178	C—N	C—N
1105	[a]	C—O bonding of saturated ester —COO—
1074	Si—O—Si asymmetric	Si—O—Si asymmetric
953	Si—O	Si—O

[a] Not determinated.

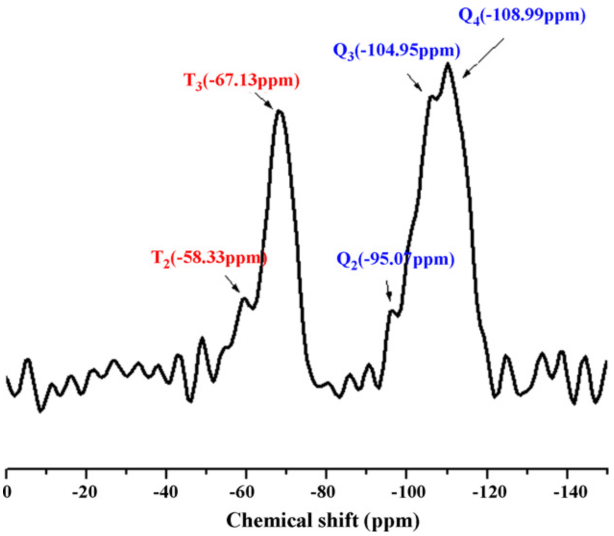
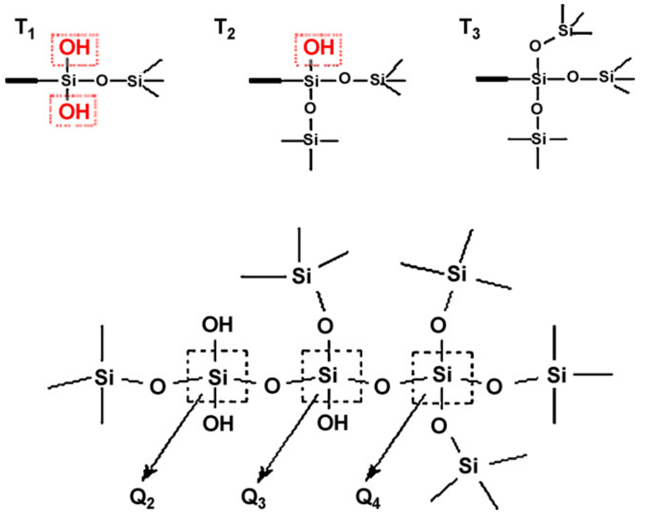


Fig. 3. The solid-state ^{29}Si NMR of EP/9 wt% DPPETES polysilsesquioxanes.

Figs. 1 and 2 were the FT-IR spectra illustrate and Table 1 summarized the FT-IR spectra peaks. The FT-IR peaks of 1716 cm^{-1} and 1105 cm^{-1} of IPTS-epoxy were corresponded to —C=O of side chain and the C—O bonding of saturated —COO— groups. The absorption peaks from —Si—O—R group appeared at 1074 cm^{-1} (broad). Fig. 3 shows the solid-state ^{29}Si NMR spectra of nanocomposite epoxy system possessing several major peaks at about −58.3, −67.1, −95, −105 and −110 ppm ***that were observed and assigned to the corresponding silsesquioxane absorption of disubstituted



Scheme 3. The T and Q structures of polysilsesquioxane.

(T_2), trisubstituted (T_3), disubstituted (Q_2), trisubstituted (Q_3) and tetrasubstituted (Q_4) of the Si—O—Si bonding of the silsesquioxane [19,20]. The T and Q architectures were illustrated as Scheme 3.

3.2. Thermal properties of PSSQ nanocomposites

Fig. 4 presents the DSC analytic trace of various nanocomposites of the EP and ME system. Table 2 summarizes the glass transition temperatures (T_g) of nanocomposites. The decline in T_g as the P/Si PSSQ content increases is significant. Since the increase of P/Si PSSQ content may reduce the cross-linking density, and P/Si PSSQ compounds may increase the steric hindrance of such nanocomposites. However, different T_g varied with the free volume of PSSQ [21].

Tables 3 and 4 summarize the TGA results, including the 5 wt% weight loss temperature (T_{d5}), limited oxygen index values, the statistic heat-resistant index temperature (T_s), and the char yield at 800 °C in an atmosphere of nitrogen. Fig. 5 displays TGA decomposition trace of various nanocomposites in the EP and ME system. The T_{d5} values of various nanocomposites were not proportional to the P/Si polysilsesquioxanes content, perhaps because of the degradation of the urethane-like group of the modified epoxy system and the consequently lower molecular weight oligomer of the cured epoxy. The flammability of various nanocomposites was determined from LOI. A material with an LOI of higher than 26 will exhibit self-extinguishing behavior and may be regarded as a low flammability material. The LOI values of the EP system were higher than those of the ME system, because the latter system contained a urethane-like side group, which increases flammability.

The char yield was proportional to the P/Si polysilsesquioxanes content. The P/Si PSSQ contained phosphorous, and phosphorous groups were degraded at a relatively low temperature, determining the char yield; meanwhile, a protective layer was formed to prevent further thermal degradation. The Si—O—Si segments form thermally stable silicate structures. Furthermore, silicon migration may be caused by inorganic silica elements, which not only have P/Si synergistic effects but also prevent thermal degradation [5,7,12,20]. The additions of P/Si PSSQ compound to the EP or ME epoxy nanocomposites increases char yields. Higher char yields correspond to the evolution of lower amounts of volatile organic moieties and combustible compounds during thermal degradation. For neat nanocomposites, the T_{d5} of the EP system was higher than that of the ME system. Since the bonding force between the NCO

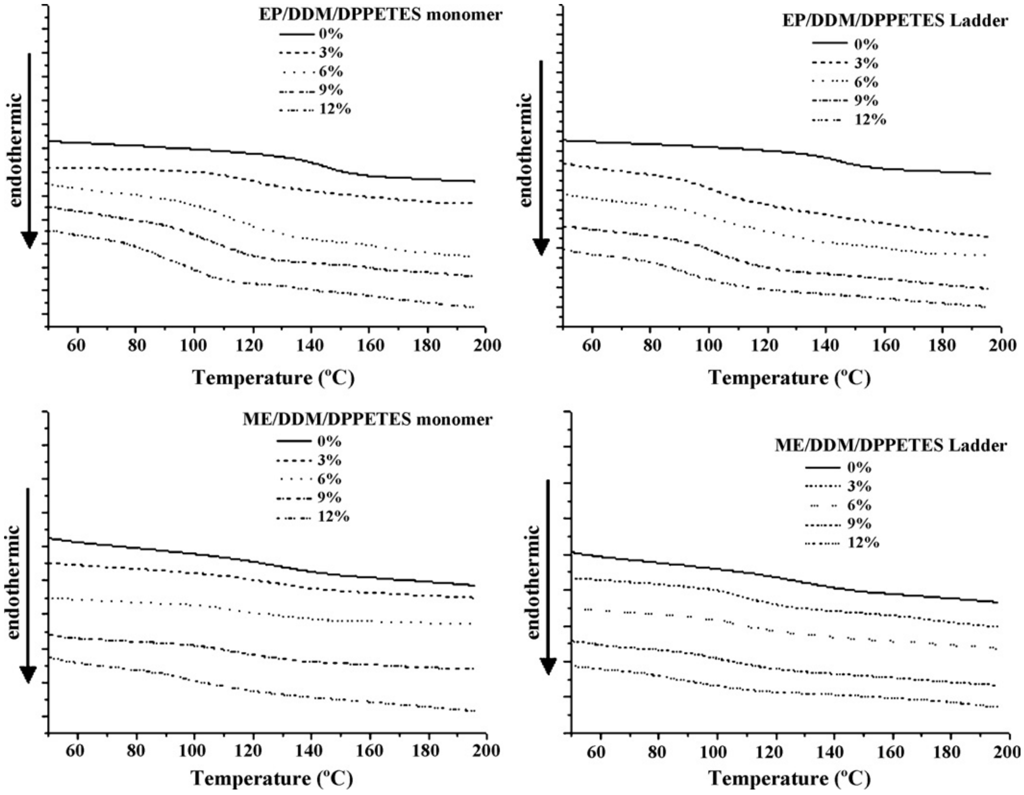


Fig. 4. The DSC curves of various EP and ME nanocomposites.

Table 2
The T_g values of epoxy and modified epoxy system

Epoxy system				Modified-epoxy system			
Monomer (wt%)	T_g (°C)	Polysilsesquioxane (wt%)	T_g (°C)	Monomer (wt%)	T_g (°C)	Polysilsesquioxane (wt%)	T_g (°C)
0	145.3	0	145.3	0	126.4	0	126.4
3	118.6	3	103.7	3	123.1	3	109.4
6	109.6	6	102.6	6	114.8	6	107.3
9	102.3	9	101.6	9	112.4	9	100.2
12	84.7	12	93.2	12	97.9	12	82.9

Table 3
Thermal decomposition characteristics of the epoxy of DPPETES monomer and DPPETES polysilsesquioxanes system

DGEBA epoxy DPPETES monomer system					DGEBA epoxy DPPETES polysilsesquioxanes system				
wt%	T_{d5} (°C)	LOI	T_s (°C)	$\text{Char}_{800\,°C}$ (%)	wt%	T_{d5} (°C)	LOI	T_s (°C)	$\text{Char}_{800\,°C}$ (%)
0	343.90	26	186.97	17.10	0	343.90	26	186.77	17.10
3	325.90	27	183.53	19.50	3	311.30	28	179.35	18.60
6	311.30	29	180.76	20.30	6	284.60	29	176.29	21.00
9	295.70	29	178.50	21.20	9	334.00	30	185.12	22.00
12	314.80	28	183.42	21.30	12	324.30	29	185.43	22.80

Table 4
Thermal decomposition characteristics of modified epoxy of DPPETES monomer and DPPETES polysilsesquioxanes system

Modified epoxy DPPETES monomer system					Modified epoxy DPPETES polysilsesquioxanes system				
wt%	T_{d5} (°C)	LOI	T_s (°C)	$\text{Char}_{800\,°C}$ (%)	wt%	T_{d5} (°C)	LOI	T_s (°C)	$\text{Char}_{800\,°C}$ (%)
0	310.20	23	186.19	24.00	0	310.20	23	186.19	24.00
3	319.10	24	187.46	25.50	3	321.40	24	186.56	26.10
6	325.00	25	188.56	26.50	6	333.90	24	189.48	27.40
9	335.40	26	190.92	27.50	9	323.40	26	189.10	28.40
12	329.00	25	190.90	27.80	12	309.00	26	185.93	29.20

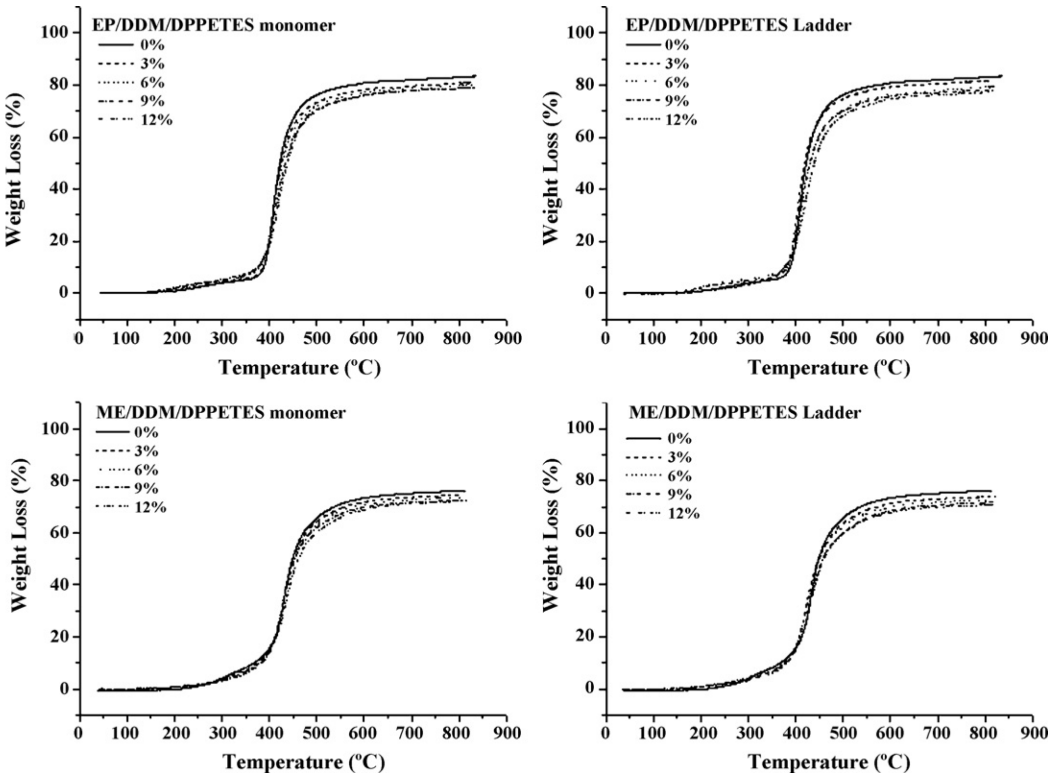


Fig. 5. The TGA curves of various EP and ME nanocomposites.

group and the hydroxyl group was very weak, decomposition proceeded easily at low temperature.

In Tables 3 and 4, the thermal degradation property index was newly calculated as the statistic heat-resistant index temperature (T_s) [17,18]. According to these tables, the DPPETES moiety nanocomposites have statistic heat-resistant index temperature values approximately 170–190 °C, suggesting that the nanocomposites have moderate heat-resistance and thermal sta-

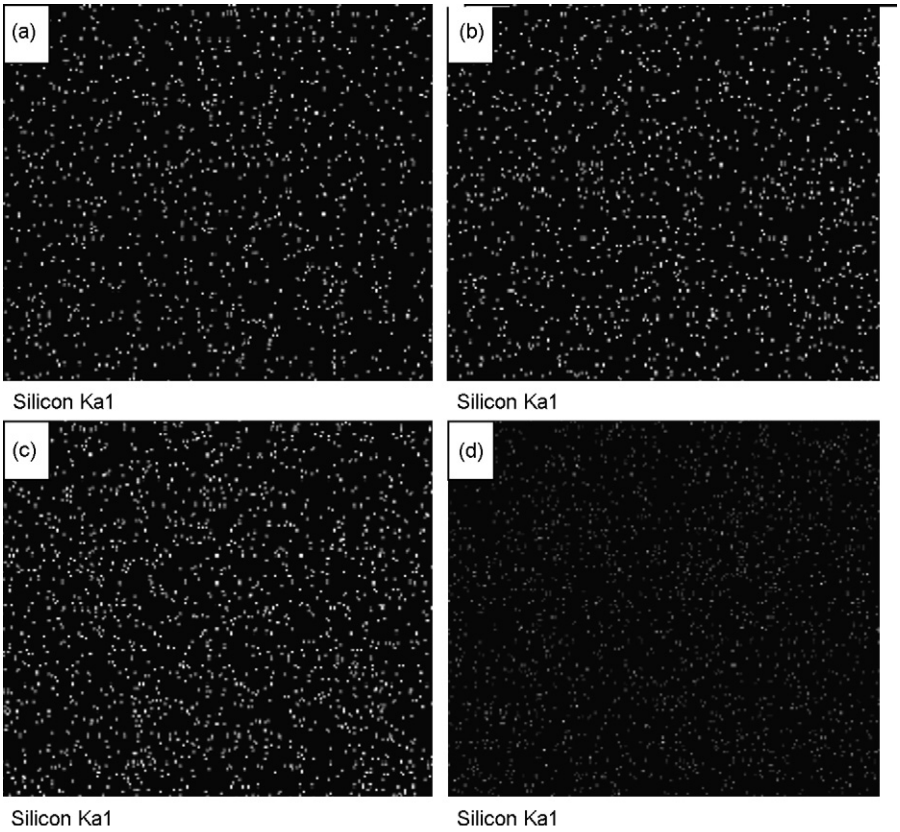


Fig. 6. The Si-mapping photographs: (a) EP-9M, (b) EP-9L, (c) ME-9M and (d) ME-9L.

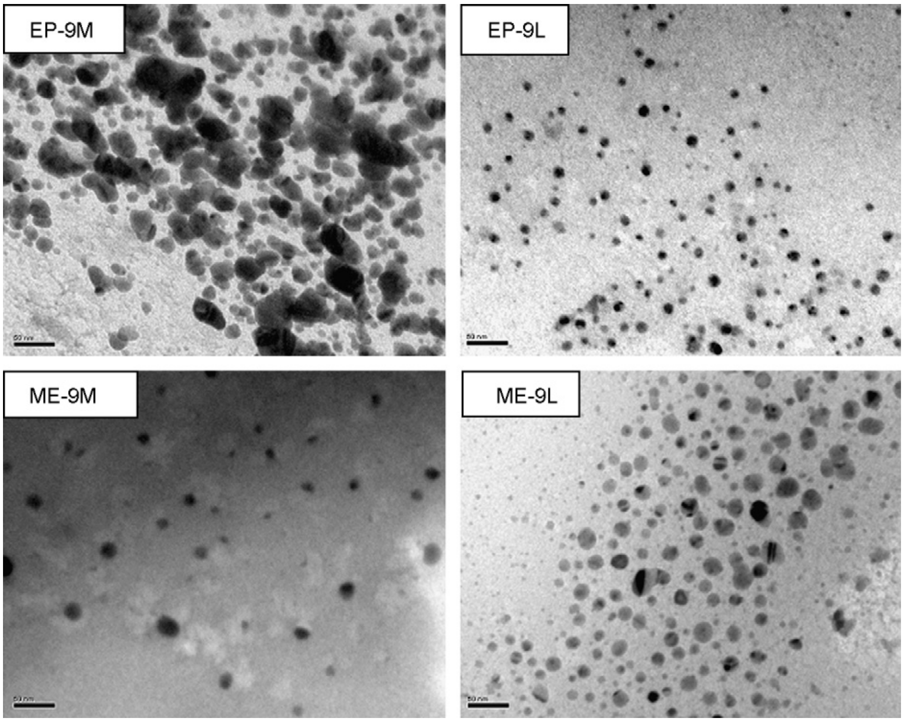


Fig. 7. The transmission electron microphotographs (TEM) of ME-9M, ME-9L, EP-9M and EP-9L (300 K, scale bar: 50 nm).

bility. However, the experimental results of Lehrle and coworkers [18] suggested that oligomers with low molecular weight could be produced during curing or a sol–gel reaction. This phenomenon indicates that the sol–gel reaction and epoxy curing reaction proceed by random reaction mechanisms and easily generate oligomers of low molecular weight causing thermal degradation in the early stages. Hence, the T_{d5} and LOI values of the nanocomposites did not increase in proportion to each other.

3.3. Morphological properties of PSSQ nanocomposites

Figs. 6 and 7 show the Si-mapping and TEM microphotographs, respectively. The PSSQ particles with sizes of approximately 30–50 nm were dispersed uniformly throughout the polymer matrix. The TEM microphotographs demonstrated that the nanocomposites exhibit good miscibility between organic (epoxy) and inorganic (P/Si PSSQ) phases. The sol–gel reaction changes the sizes of nano P/Si PSSQ particles. The reactions involve various degrees of hydrolysis and condensation yields nano P/Si PSSQ particles with various sizes. In the sol–gel reaction, the cluster segregation of DPPETES moiety might occur; meanwhile, most of the polar groups were on the cluster surface of DPPETES moieties [22]. Consequently, the difference of polarity between inorganic–organic materials might generate the nanophase-separated structure as illustrated from the TEM microphotographs. The Si-mapping microphotographs suggest that the inorganic silica nano-particles in the nanocomposites are distributed uniformly on the nanometer scale and their nano-architectures are well defined.

4. Conclusions

A novel P/Si PSSQ nanocomposite was successfully synthesized by the sol–gel process. The sizes of the particles in the P/Si PSSQ domain depend on the composition and are in the range 30–50 nm; the P/Si PSSQ particles were dispersed fairly homogeneously and the difference of polarity between inorganic–organic materials might generate the nanophase-separated structure, as revealed by Si-mapping and TEM. The nanocomposites exhibited high thermal stability and flame-retardance, based on TGA and LOI, respectively. The char yield and LOI were increased to 29 wt% and 30, respectively. Additionally, the thermal stability increased with the char yield and P/Si synergistic effect. The T_{d5} values of various nanocomposites were not proportional to DPPETES moiety, because of the urethane-like group of ME and the production of the oligomer in the nanocomposite curing reaction. The excellent thermal stability of P/Si nanocomposites is exploited in thermal protection applications.

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