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Effect of P/Si polymeric silsesquioxane and the monomer compound on thermal properties of epoxy nanocomposite

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Abstract

The unique polymeric silsesquioxane/4,4′-diglycidyether bisphenol A (DGEBA) epoxy nanocomposites have been prepared by sol–gel method. The structure of nanocomposites was characterized by attenuated total reflectance (ATR) and solid state ^{29}Si NMR. The characteristic intensity of trisubstituted (T) structure was higher than that of tetrasubstituted (Q) structure from solid state ^{29}Si NMR spectra of 3-isocyanatopropyltriethoxysilane (IPTS) modified epoxy. The activation energies of curing reaction of epoxy system and IPTS modified epoxy system are 28–66 kJ/mol and 57–75 kJ/mol, respectively, by Ozawa's and Kissinger's methods. The triethyoxysilane side chain of IPTS modified epoxy might interfere the curing reaction of epoxy/amine and increase the activation energy of curing. The thermal degradation of nanocomposites was investigated by Thermogravimetric analysis (TGA). The char yield of nanocomposites was proportional to the 2-(diphenylphosphino)ethyltriethoxysilane (DPPETES) moiety content at high temperature. A higher char content could inhibit thermal decomposition dramatically and enhance the thermal stability. Moreover, the nanocomposites possess high optical transparency.

Keywords: Epoxy nanocomposite; Polysilsesquioxanes; Sol–gel method; Thermal properties

1. Introduction

Polysilsesquioxanes (PSSQ) have general formula such as $(RSiO_{1.5})_n$, where R is a hydrogen atom or an organic group. The unique compatibility and reactivity of PSSQ of the polymer nanocomposite resulting the specific structure and excellent properties [1,2]. The effect of polysilsesquioxanes on the thermal, optical, and mechanical properties of epoxy resin has been investigated [3–5]. Generally, the polysilsesquioxanes/epoxy hybrid materials can be prepared by in situ sol–gel method. The inorganic moiety may disperse uniformly in the hybrid nanocomposites. The architecture of the inorganic

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segment of the nanocomposite always formed three-dimensional bonding and further developed a high performance nanocomposite [4,6–9]. Recently, various nanocomposites have been investigated and widely used as surface coatings, adhesives, castings, etc. [10–13]. The composite materials reinforced by nano-fillers may enhance their thermal, optical, and electrical properties. Incorporating the nano-fillers will increase the interfacial area dramatically and improve the overall properties of the polymer [14–16].

Recently, the "environment-friendly" material is the most important concept for polymeric application. The bromine compounds have been widely used to improve the flame resistance of polymers in the past. However, the halogen compounds may generate toxic and smoke pollution during combustion. For health consideration, the green flame retardant have been studied to reduce the flammability of polymer. Consequently, green materials such as phosphorus- and silicon-containing compound have been investigated to substitute the halogen composition [17–19]. Introducing phosphorus and silicon compound into the polymer matrix can inhibit the thermal decomposition efficiently. The P/Si synergistic effect of the phosphorus and silicon moieties on the thermal degradation has been reported [20–24].

In this work, 2-(diphenylphosphino)ethyltriethoxysilane (DPPETES) polysilsesquioxane and its monomer compound were utilized, which combined the phosphorus and silicon moiety. The tetraethoxysilane (TEOS) was used, as coupling agent and the 4,4-methylenedianiline (DDM) was the curing agent to prepare the epoxy nanocomposites of this study. The chemical structure of the nanocomposites was studied by attenuated total reflectance (ATR) and solid-state ^{29}Si NMR. The thermal properties were determined from differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA). The curing kinetic values were evaluated by Ozawa's and Kissinger's equation. Moreover, the optical properties and morphological properties would be discussed.

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)ethyltriethoxysilane (DPPETES monomer) 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., Geel, Belgium. Isopropyl alcohol (IPA), tetrahydrofuran (THF), and triethylamine (TEA) were purchased from the Tedia Co., Inc., OH, USA.

2.2. Preparation of IPTS modified epoxy precursor (ME) [25]

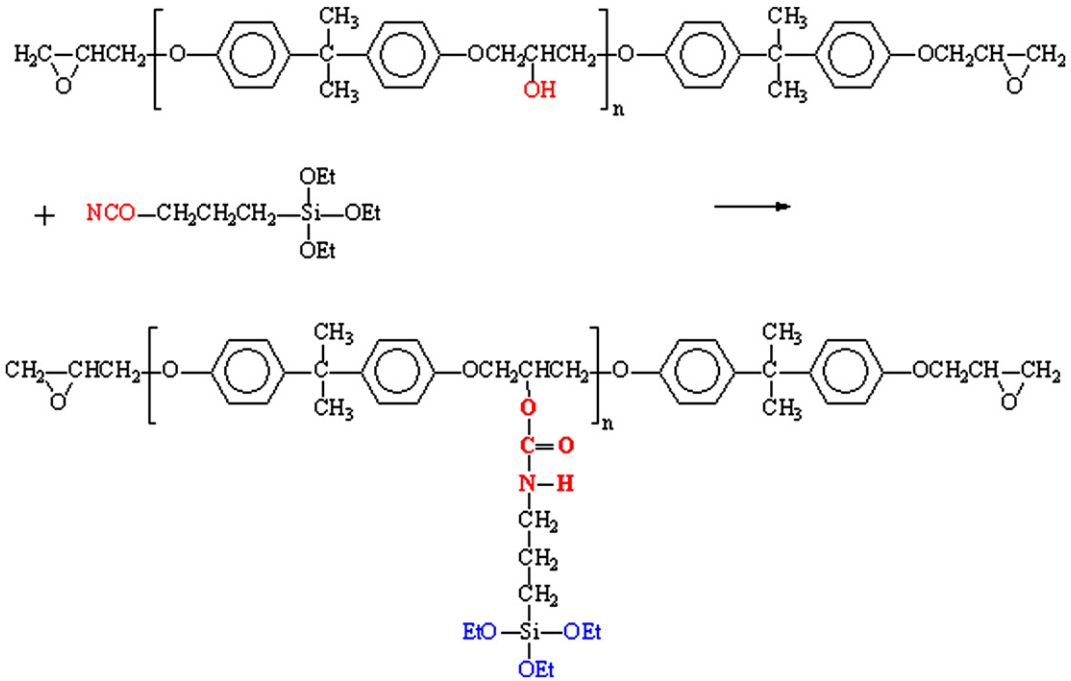
DGEBA resin (10 g) and THF (10 ml) were stirred in a 100 ml round-bottle flask at room temperature to obtain the DGEBA solution. Then, added the IPTS (4 g, 16.19 mmol) and the TEA (0.2 g, 1.98 mmol) into the DGEBA solution. All of the reactants were homogeneous and stirred at 60 °C until the characteristic peak of the NCO group (2270 cm^{-1}) in the FT-IR spectra disappeared. The reaction time was about 6–8 h. The IPTS modified epoxy (ME) removed THF by vacuum oven and obtained the clear viscosity product, which reaction described in Scheme 1.

2.3. Preparation of DPPETES polymeric silsesquioxane [2]

The DPPETES monomer (5 g, 13.263 mmol) was placed in a 100 ml round-bottle flask. Meanwhile, the H_2O (0.176 g, 39.789 mmol), the IPA (4.58 g, 76.23 mmol) and the THF (1.597 g, 22.149 mmol) were homogeneously mixed. Then, the mixture was added into the 100 ml round-bottle flask (the DPPETES monomer system). All of the reactants were stirred at room temperature for 48 h. The homogeneous mixture dried at 80 °C for 24 h and then was kept in a vacuum oven at 200 °C for 24 h. The DPPETES polymeric silsesquioxane was white powder.

2.4. Preparation of epoxy nanocomposites

The various epoxy nanocomposites were prepared from the DGEBA epoxy and IPTS modified epoxy (ME), which with different ratios of the DPPETES monomer and the DPPETES polymeric silsesquioxane (0, 3, 6, 9 and 12 wt%) to epoxy. For DGEBA epoxy reacted with 3 wt% DPPETES monomer, which abbreviated as the EP-3M. For



Scheme 1. Preparation of IPTS modified epoxy (ME).

DGEBA epoxy reacted with 3 wt% DPPETES polymeric silsesquioxane, the abbreviation of the epoxy nanocomposite was EP-3L. Additionally, the ME-3M was the abbreviation of the IPTS modified epoxy (ME) reacted with 3 wt% DPPETES monomer. The sol–gel reaction possessed 9 wt% TEOS and the optimum HCl concentration used as catalyst, which catalyst have been described in our previous study [4]. All mixtures were stirred for 1 h via the sol–gel process for 24 h at room temperature. All of the nanocomposites were heated at 80 °C for 12 h and then at 160 °C for 12 h.

2.5. Characterizations

The chemical structure of nanocomposite was characterized by the Perkin Elmer spectrum one FT-IR equipped with an attenuated total reflectance (ATR) accessory. The siloxane structure properties were investigated by solid-state ^{29}Si NMR analysis, which was performed with a Bruker DSX 400WB (400 MHz) NMR spectrometer. Differential scanning calorimetric (DSC) thermograms were recorded with a thermal analysis DSC-Q10 differential scanning calorimeter. The testing condition was from 30 to 230 °C, under a nitrogen gas flow of 40 ml/min and heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed with a thermal analysis TGA-951 thermogravimetric analyzer, at a heating rate of 5, 10, 15, 20, 30 °C/min, under nitrogen atmosphere, and the gas flow rate was 100 ml/min. UV–Vis spectra were measured by a Hitachi U-3300 spectrophotometer. Energy dispersive X-ray (EDX) measurements were conducted with a JEOL JSM 840A microanalyzer. The morphology of nano-structures of epoxy-nanocomposites was investigated by a transmission electron microscope (TEM), JEOL JEM-1230 and its accelerated voltage is 100 kV. The nanocomposites were microtomed with Reichert-Jung ULTRACUTE into 100 nm thick slices in a direction normal to the plane of the films.

2.6. Kinetic studies of curing reaction

2.6.1. Ozawa's method [26,27]

The Ozawa's method was expressed as Eq. (1)

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

where E_a is the activation energy of curing, R is the ideal gas constant, β is the heating rate, T_p is the maximal temperature of exothermic peak. The activation energy of curing can be obtained by plotting $\ln\beta$ vs. $1/T_p$.

2.6.2. Kissinger's method [28,29]

The Kissinger's method was used to calculate the activation energy of curing (E_a) by Eq. (2)

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{E_a}{R} \quad (2)$$

where β is the heating rate, T_p is the maximum temperature and R is the ideal gas constant. Therefore, the activation energy of curing can be determined from a plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$.

3. Results and discussion

3.1. Preparation and characterization of epoxy nanocomposites

Table 1 summarizes the characteristic peaks of the FT-IR spectra of IPTS modified epoxy and DGEBA epoxy nanocomposites. The wavenumber at 1716 cm^{-1} and 1105 cm^{-1} are the characteristic peaks of –C=O and saturated –COO– groups of IPTS modified epoxy. The absorption peaks at 1074 cm^{-1} (broad) attributed to the –Si–O–Si– group. The solid-state ^{29}Si NMR spectra are shown in Figs. 1 and 2. Fig. 1 illustrates the nanocomposite of DGEBA epoxy system, the peaks at −67.2 ppm, −93.6 ppm, −104 ppm and −110 ppm were observed and are assigned to the corresponded silsesquioxanes absorption of trisubstituted (T_3) of DPPETES compound and disubstituted (Q_2), trisubstituted (Q_3) and tetrasubstituted (Q_4) of siloxane bonding between TEOS and DPPETES segments,

Table 1
Characteristic peaks of DGEBA epoxy and IPTS modified epoxy (ME) nanocomposites of FT-IR spectra

Wave number (cm^{-1})	EP-DDM-system function type	ME-DDM system (ME) function type
1716	[a]	C=O
1605	C=C	C=C
1507	Ar	Ar
1459	Ar	Ar
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]	Saturated ester C–O
1074	Si–O–Si Asymmetric	Si–O–Si Asymmetric
953	Si–O	Si–O
826	Si–O–Si Symmetric	Si–O–Si Symmetric

[a] No functional group.

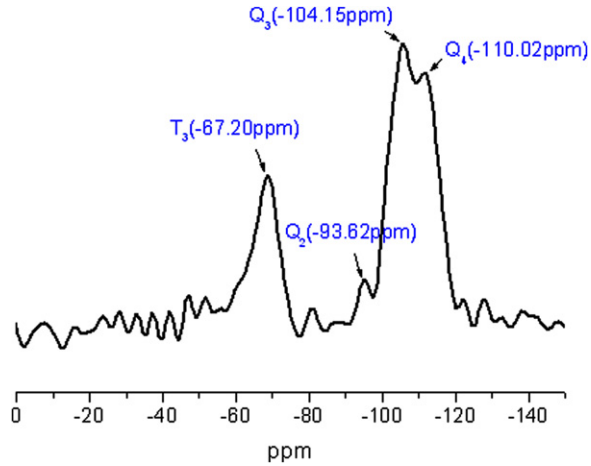


Fig. 1. The solid-state ^{29}Si NMR spectrum of DGEBA epoxy with 9wt% DPPETES monomer (EP-9M).

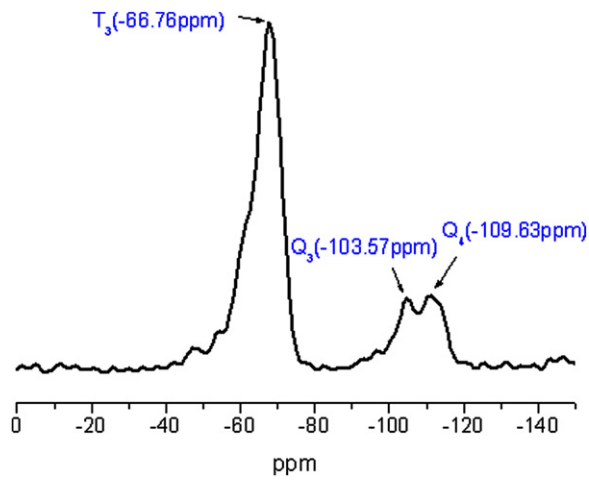


Fig. 2. The solid-state ^{29}Si NMR spectrum of IPTS modified epoxy (ME) with 9 wt% DPPETES monomer (ME-9M).

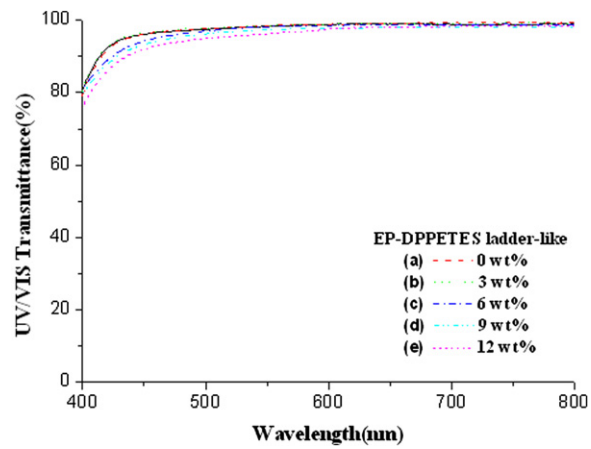


Fig. 3. UV/Vis spectra of DGEBA epoxy system with different DPPETES polymeric silsesquioxane contents.

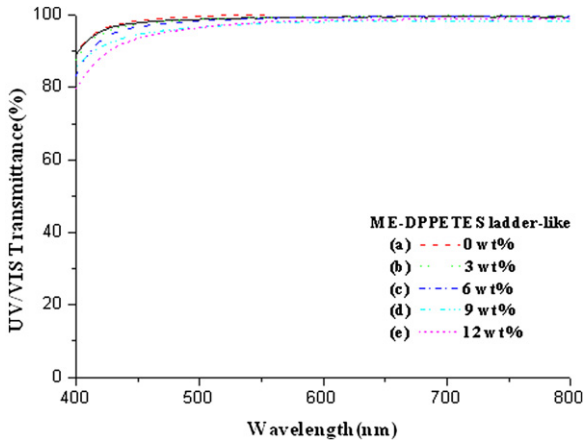


Fig. 4. UV/Vis spectra of IPTS modified epoxy (ME) system with different DPPETES polymeric silsesquioxane contents.

respectively. Fig. 2 exhibits the solid-state ^{29}Si NMR spectrum of the nanocomposite of IPTS modified epoxy system three major peaks appeared at −66.7 ppm, −103.6 ppm and −110 ppm indicated the T_3, Q_3 and Q_4 structures, respectively [30,31]. Additionally, Figs. 1 and 2 showed the shoulder peak at –60 ppm, which was the disubstituted (T_2) of siloxane bonding. The phenomenon resulted from the sol–gel was the random chemical reaction and the siloxane bonding was irregular architecture. Consequently, there was a shoulder peak at −60 ppm neighbor on trisubstituted (T_3) of siloxane bonding (−66 to −68 ppm). It was notably that the Q and T peaks intensity in the DGEBA epoxy and IPTS modified epoxy system showed quite different. The DGEBA epoxy possesses higher Q peaks intensity as shown in Fig. 1. In the DGEBA epoxy system, TEOS can react with DPPETES monomer or DPPETES polymeric silsesquioxane easier than IPTS modified epoxy. Meanwhile, the ratio of T structures to Q structures was significantly different,

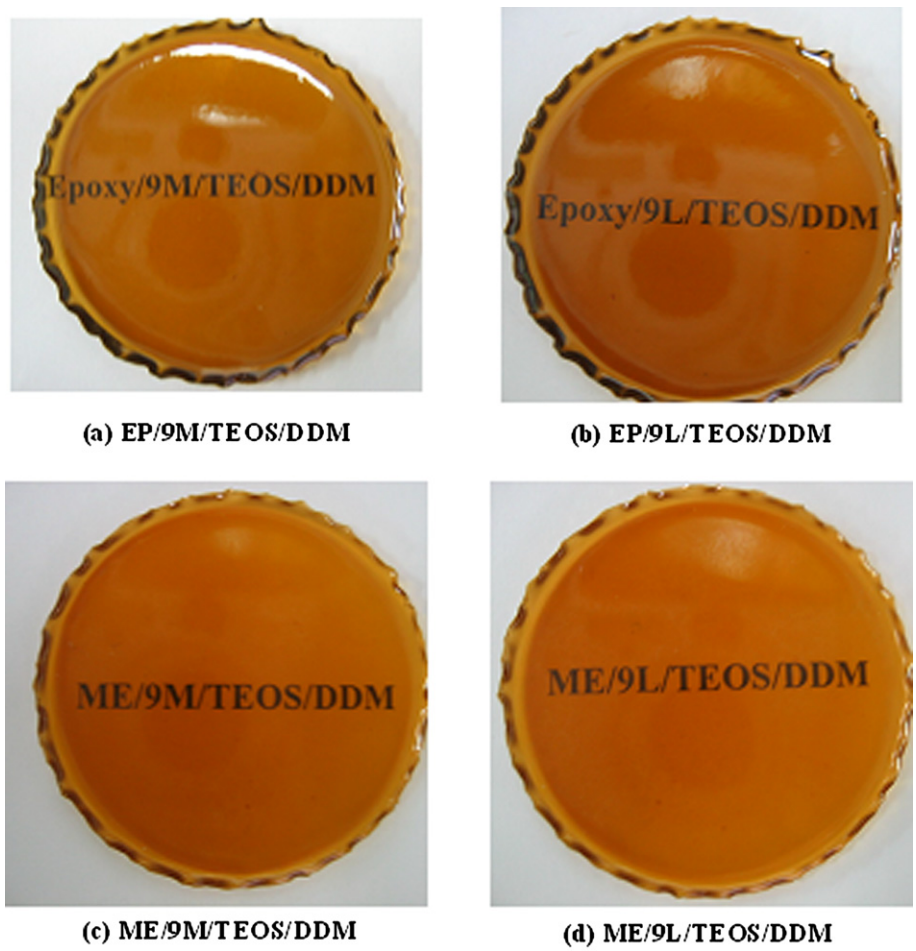


Fig. 5. Transparency of (a) EP-9M, (b) EP-9L, (c) ME-9M, (d) ME-9L.

Fig. 2 (IPTS modified epoxy system) possessed higher T structure moiety. The IPTS modified epoxy containing triethoxysilane group side chain. The IPTS modified epoxy possessed more T repeating units than the DGEBA epoxy system and exhibited higher ratio of T structures moiety to Q structures moiety as shown in Fig. 2.

3.2. Optical properties of nanocomposites

Figs. 3 and 4 are the UV/Vis spectra of various nanocomposites. The nanocomposites show high transmittance in 450–800 nm region. All of the nanocomposite exhibited excellent optical transparency. The good transmittance may result from the formation of a homogeneous phase of nanocomposites. The nanocomposites resulted in transparent samples as shown in Fig. 5. The phase-separation does not occur for all silica containing nanocomposites after curing and via sol–gel reaction. It may confirm that the inorganic segments were miscible with epoxy materials [10].

3.3. Morphological properties of nanocomposites

The silicon elements are distributed evenly in the nanocomposites as can be observed from the Si-mapping micrographs by SEM-EDX analyses (small white spots as shown in Fig. 6). This phenomenon confirmed that these nanocomposites are extremely miscible without aggregation. The nanoscale polymeric silsesquioxane domains were further studied by TEM analysis. The TEM microphotograph is shown in Fig. 7. The particles were dispersed uniformly throughout the epoxy matrix with sizes below 50 nm. This phenomenon reveals that the nanocomposites exhibit good miscibility between organic and inorganic phases.

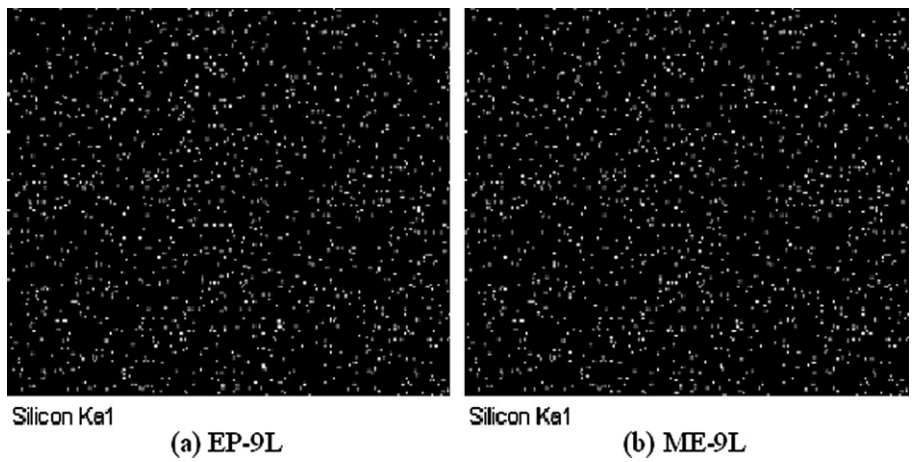


Fig. 6. THE Si-mapping photographies of (a) EP-9L, (b) ME-9L.

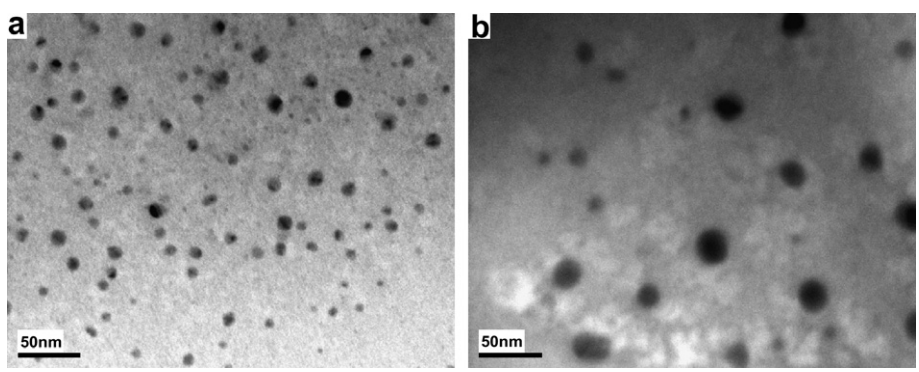


Fig. 7. The TEM microphotographs (a) EP-9L, (b) ME-9M (×300K).

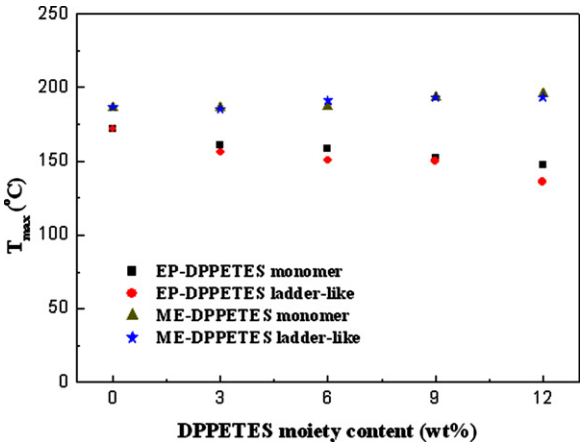


Fig. 8. The maximum temperature of exothermic peak (T_{max}) versus DPPETES moiety contents of DGEBA epoxy (EP) and IPTS modified epoxy (ME).

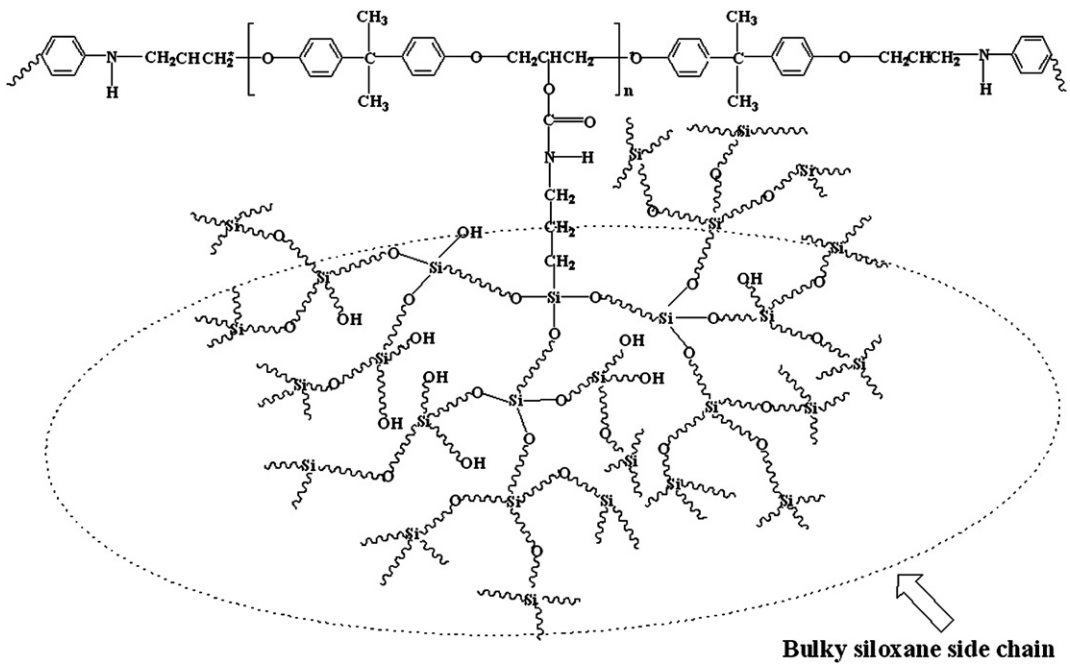
3.4. Thermal properties of nanocomposites

Fig. 8 explicates that introducing silicon group into the IPTS modified epoxy system may increase the maximum exothermic temperature (T_{max}). However, the reactivity of the DGEBA epoxy system was not increased. This result indicates that the triethoxysilane side group of IPTS modified epoxy could react with TEOS or DPPETES segments and generates the T architecture of siloxane side chain. The side chain in T siloxane may interfere the curing reaction of epoxy/amine (the siloxane side chain showed as Scheme 2). Consequently, the T_{max} of IPTS modified epoxy system will be higher than that of unmodified epoxy system.

The activation energies of curing of various nanocomposites are summarized in Tables 2 and 3. The activation energies of curing of DGEBA epoxy system were lower than that of IPTS modified epoxy system. The triethoxysilane side chain of IPTS modified epoxy was reacted with DPPETES segments or TEOS segments by sol–gel process. Meanwhile, the formation of the T architecture in siloxane side chain was promoted. This side chain

Table 2
The activation energies of curing of DGEBA epoxy/DPPETES moiety nanocomposites

Samples	Ozawa's method		Kissinger's method	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R
EP-DDM	43.26	0.98	52.88	0.98
EP-3M	52.22	0.98	62.37	0.99
EP-6M	37.88	0.98	47.40	0.98
EP-9M	51.66	0.99	61.88	0.99
EP-12M	49.02	0.95	58.88	0.96
EP-3L	42.74	0.97	52.43	0.98
EP-6L	28.61	0.96	37.58	0.98
EP-9L	39.68	0.95	49.11	0.96
EP-12L	56.05	0.99	66.39	0.99



Scheme 2. The bulky siloxane side chain of the epoxy (ME).

Table 3
The activation energies of curing of IPTS modified epoxy (ME)/DPPETES moiety nanocomposites

Samples	Ozawa's method		Kissinger's method	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R
ME-DDM	61.56	0.99	72.57	0.99
ME-3M	62.27	0.99	73.33	0.99
ME-6M	57.08	0.99	67.89	0.99
ME-9M	58.00	0.99	68.84	0.99
ME-12M	64.33	0.99	75.61	0.99
ME-3L	58.88	0.99	69.74	0.99
ME-6L	59.89	0.99	70.84	0.99
ME-9L	62.12	0.99	73.18	0.99
ME-12L	60.44	0.99	71.56	0.99

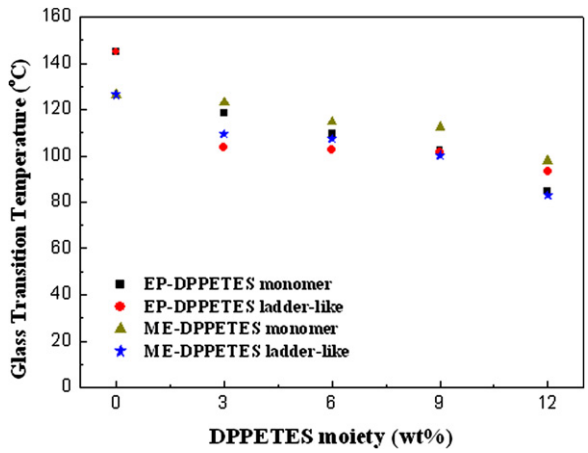


Fig. 9. The T_g versus DPPETES moiety contents of unmodified DGEBA epoxy (EP) and IPTS modified epoxy (ME).

not only increases the steric hindrance of structure but also interferes the curing reaction of epoxy/amine. The bulky siloxane side chain was showed into Scheme 2. Consequently, the activation energies of curing will increase. The same tendency was also found from the T_{max} in Fig. 8. It is notably the activation energies of curing of DPPETES polymeric silsesquioxane system were slightly higher than that of DPPETES monomer system. The molecular weight and structure of the DPPETES polymeric silsesquioxane were higher than that of DPPETES monomer; hence, the thermal curing reaction might be inhibited by the macromolecule.

The glass transition temperatures (T_g) of nanocomposites are summarized in Fig. 9. Generally, polymers with nano-filler show higher T_gs, due to the nanosize effect. From the Fig. 6, the T_g values decreased proportionally to DPPETES moiety content. Introduction of DPPETES moiety may interfer the thermal curing of nanocomposite.

Tables 4 and 5 summarized the results of TGA of various nanocomposites at a heating rate of 10 °C/min under N_2. The Td_5s of IPTS and DGEBA nanocomposites were not proportional to the DPPETES segments content. The DPPETES moiety contains phosphorous functional group that may be degraded at relatively low temperature and improved the char formation. Meanwhile, the Si–O–Si segments formed thermally stable silica compound. Silica may migrate to the char surface serving as a protection layer to retard further degradation of char at

Table 4
Thermal decomposition characteristics of DGEBA epoxy/DPPETES moiety nanocomposites

DPPETES monomer (wt%)	Td_5 (°C)	$Char_{800\,°C}$ (%)	DPPETES polymeric silsesquioxane (wt%)	Td_5 (°C)	$Char_{800\,°C}$ (%)
DGEBA epoxy systems					
0	343.9	17.1	0	343.9	17.1
3	325.9	19.5	3	311.3	18.6
6	311.3	20.3	6	284.6	21.0
9	295.7	21.2	9	334.0	22.0
12	314.8	21.3	12	324.3	22.8

Table 5
Thermal decomposition characteristics of IPTS modified epoxy (ME)/DPPETES moiety nanocomposites

DPPETES monomer (wt%)	Td_5 (°C)	$Char_{800\,°C}$ (%)	DPPETES polymeric silsesquioxane (wt%)	Td_5 (°C)	$Char_{800\,°C}$ (%)
IPTS modified epoxy (ME) system					
0	310.2	24.0	0	310.2	24.0
3	319.1	25.5	3	321.4	26.1
6	325.0	26.5	6	333.9	27.4
9	335.4	27.5	9	323.4	28.4
12	329.0	27.8	12	309.0	29.2

higher temperature [17,31–36]. The Td_5 of DGEBA epoxy system was higher than that of IPTS modified epoxy system. The char yield of IPTS and DGEBA nanocomposites increased with DPPETES segments content. The char yield of IPTS nanocomposites was higher than that of DGEBA nanocomposites. Since the triethoxysilane side chain of IPTS nanocomposites promoted the formation of Si–O–Si network structure.

4. Conclusion

The unique polymeric silsesquioxane nanocomposites have been prepared from DPPETES compound and epoxy material. The silsesquioxane nano-filler affects the thermal properties of nanocomposites. The trisubstituted siloxane side chains of IPTS nanocomposite enhance the T_{max} temperature of curing reaction. The activation energy of curing of the IPTS modified epoxy and unmodified DGEBA epoxy system are 57–77 kJ/mol and 28–66 kJ/mol. The increasing activation energy of curing attributed to the triethyloxysilane group side chain of IPTS epoxy and the DPPETES polymeric silsesquioxane, which may enhance the steric hindrance. By introducing of DPPETES segments, the steric hindrance not only generates higher free volume but also decrease the T_g. TGA results indicated that the introduction of DPPETES compound may enhance the thermal stability of nanocomposites. The char yield increases with DPPETES segments content. The phosphorous functional group of DPPETES segments will degrade at lower temperature, hence, increases the formation of the thermal stable char. UV/Vis spectra show that the nanocomposites possess excellent optical transparency without phase separation. From Si-EDX analysis, and TEM microphotographs showed that the inorganic silica segments were well distributed in the matrix. The sizes of inorganic particles were below 50 nm.

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