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Preparation and thermal properties of epoxy-silica nanocomposites from nanoscale colloidal silica

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Abstract

Epoxy-silica nanocomposites were obtained from directly blending diglycidylether of bisphenol-A and nanoscale colloidal silica and then curing with 4,4-diaminodiphenylmethane. The epoxy-silica nanocompoites showed good transparency and miscibility observed with AFM, SEM, and TEM. The thermal stability of the epoxy resins was improved with the incorporation of the colloidal silica. However, a depression on the glass transition temperature of the resins was observed, owing to the plasticizing effect of the colloidal silica. Moreover, the nanoscale colloidal silica did not show effectively synergistic effect on char formation and flame retardance with phosphorus.
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1. Introduction

Recently the research efforts on epoxy resins have been focused on improving their thermal stability, leveling up glass transition temperatures, increasing dimensional stability, lowering dielectric constant, enhancing flame retardance, and satisfying halogen-free criterion. An approach of simultaneously achieving the above-mentioned objectives is reasonably attractive especially for epoxy resins used in modern electronic and electrical products. Formation of organic–inorganic nanocomposites, i.e. blending inorganic fillers and organic polymeric materials in molecular scale, have shown ability of providing a feasible approach of simultaneously improving the thermal, mechanical, and flame retardant properties as well as dimensional stability of polymeric materials [1–10]. The prominent properties of nanocomposites encourage the increasing investigations of the relative fields.

There are four major materials used to prepare inorganic–organic nanocomposties: (a) layered clay [11–15], (b) alkoxysilane compounds as precursors and performing through a sol–gel technique [16–19], (c) polyhedral oligomeric silsesquioxane (POSS) molecules [20,21], and (d) nanoparticles [22–28], nanofibers [29], and other synthetic materials [30,31]. However, owing to the poor compatibility between the organic matrix and inorganic fillers, some efforts are necessary to enhance the compatibility between the fillers and the hydrophobic polymer matrix during the preparation of nanocomposites. For examples, alkylammonium salts and silane coupling agents are widely used in layered clay and silica based nanocomposites, respectively.

Nanoscale colloidal silica, in addition to layer clay, has been considered as inorganic fillers for the preparation of nanocomposites associating with the sol–gel process [22–25] or in situ polymerization technique [28]. While sol–gel technique was utilized, silane coupling agents were usually employed in the preparation formulation, to enhance the inorganic–organic interfacial compatibility [22–25]. Meanwhile, during the heating period, the evaporation of solvent, the curing reaction of epoxy compound, and the gelation reaction of the hydrolyzed alkoxysilane occurred simultaneously. Moreover, the solution process of sol–gel technique was not practical in the manufacturing processes of epoxy molding compounds. The simultaneously released volatiles from the gelation of alkoxysilane sol would certainly bring about undesirable effects to the resin, and difficulties in processing during the epoxy curing reaction. Another drawback of using sol–gel process in the

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preparation of polymer–silica nanocomposites is its harm to the initial thermal stability of the resulting nanocomposites. This effect is mainly due to the residual of the silanoxy groups in the formed polymer–silica nanocomposites, and these silanoxy groups might perform dehydration reaction under high temperatures in the processing and using period of the nanocomposites.

Preformed nanoscale colloidal silica has been reported to form homogeneous PMMA–silica nanocomposites with in situ PMMA polymerization and without using any coupling agents [28]. To overcome the above-mentioned problems associated with sol–gel process, in this study, nanoscale colloidal silica was used in the preparation of epoxy-silica nanocomposites. Without employing silane coupling agents, epoxy-silica nanocomposites were obtained with high silica loadings of 70 wt%. Moreover, as nanoscale silica has been observed to show synergism on enhancing flame retardance of polymers with phosphorus [8,32–34], a phosphorus-containing epoxy and a curing agent [35] were also utilized in the formulation of preparing epoxy-silica nanocomposite to examine the reported Si/P synergism on flame retardance.

2. Experimental section

2.1. Materials

Diglycidylether of bisphenol-A (BE188) having an epoxy equivalent weight (EEW) of 188 was from Chang Chun Plastics Co. (Taiwan). The phosphorus-containing epoxy resin PE530 (EEW = 530) was prepared according to the literature [36] in our laboratory. Nanoscale silica particle was purchased from Nissan Chemical Co., Japan. The commercial product of MIBK-ST, in which 30–31 wt% of silica (particle size: 10–20 nm) was dispersed in methylisobutylketone (MIBK), was used as received. 4,4-Diaminodipheylmethane (DDM) and diethylphosphite (DEP) from Fluka Chemie AG were used as curing agents for epoxy compounds (Fig. 1).

2.2. Equipment

Infrared spectra (FTIR) were obtained with a Perkin–Elmer 2000 FTIR. Atomic force microscope (AFM) measurement was carried out with an AFM of Seiko SPI3800N, Series SPA-400. Scanning electron micrograph and transmission electron micrograph were observed with a JEOL JSM 840A SEM and a JEOL JEM 1200EX TEM, respectively. Differential scanning calorimetry thermograms were recorded with a Thermal Analysis (TA) DSC-2900 in a nitrogen gas flow of 40 ml/min. TGA was performed by a TA TGA-2050 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere. The gas flow rate was 100 ml/min. The values of the limited oxygen index (LOI) were measured on a

Stanton Redcraft flame meter. The percentage in the O_2–N_2 (under a gas flow rate of 17 l/min) mixture deemed sufficient to sustain the flame was taken as the LOI.

3. Results and discussion

3.1. Epoxide-silica hybrid materials

The compatibility between the epoxide compounds and colloidal silica was first examined by mixing BE188 together with MIBK-ST. BE188 was observed to dissolve in MIBK-ST to result in a clear and transparent solution. After removing the solvent, the products were kept clear and transparent. The BE188-silica hybrid materials containing various silica contents from 10 to 70% were obtained (BE-10 to BE-70). These products demonstrated that the commercial colloidal silica MIBK-ST can be directly used as inorganic fillers in the preparation of epoxy-silica hybrid materials. The high loading of the colloidal silica in the resulting hybrid materials was noteworthy, especially without employing any coupling agents and surfactants. The obtained epoxy-silica hybrid materials were then cured with curing agents to prepare epoxy resin–silica nanocomposites. The reactivity of the BE188-silica hybrids toward the amine curing agent DDM was first examined by DSC. Fig. 2 showed the DSC thermograms of monitoring the curing reactions of BE188-silica hybrid materials (BE-10 to BE-70) with DDM. For all of the thermograms, both the onset point and the peak of the exothermic curve did not show obvious shift. This result indicated that the curing reaction of BE188 and DDM was not significantly altered by the addition of nanoscale colloidal silica. As a reasonable inference, the BE188-silica hybrid materials (BE-10 to BE-70) can therefore be purchased and fabricated like the commercial bisphenol-A type epoxy resins without altering the current processing conditions of the commercial epoxy resins. On the other hand, the thermal stability of the epoxy compounds was also enhanced with the introduction of the nanoscale silica. Fig. 3 showed the TGA thermograms of the BE188-silica hybrid materials being heated under air atmosphere. Both the temperatures of the onset weight loss and maximum weight loss rate shifted to high temperature region, and the degree of shift increased by increasing the amounts of silica loadings. Moreover, the char yields at 800 °C of the epoxy hybrid materials were almost equal to the weight fractions of the loading silica. Since pure BE188 exhibit no residuals at 800 °C, it can be reasonably interfered that the nanoscale silica might not be able to act as a catcher of polymeric char.

3.2. Morphology of cured epoxy-silica hybrids

The epoxy-silica hybrid materials with various silica contents (BE-10 to BE-70) were cured with the amine curing agent of DDM. The transparency of the cured epoxy-

BE188

PE530

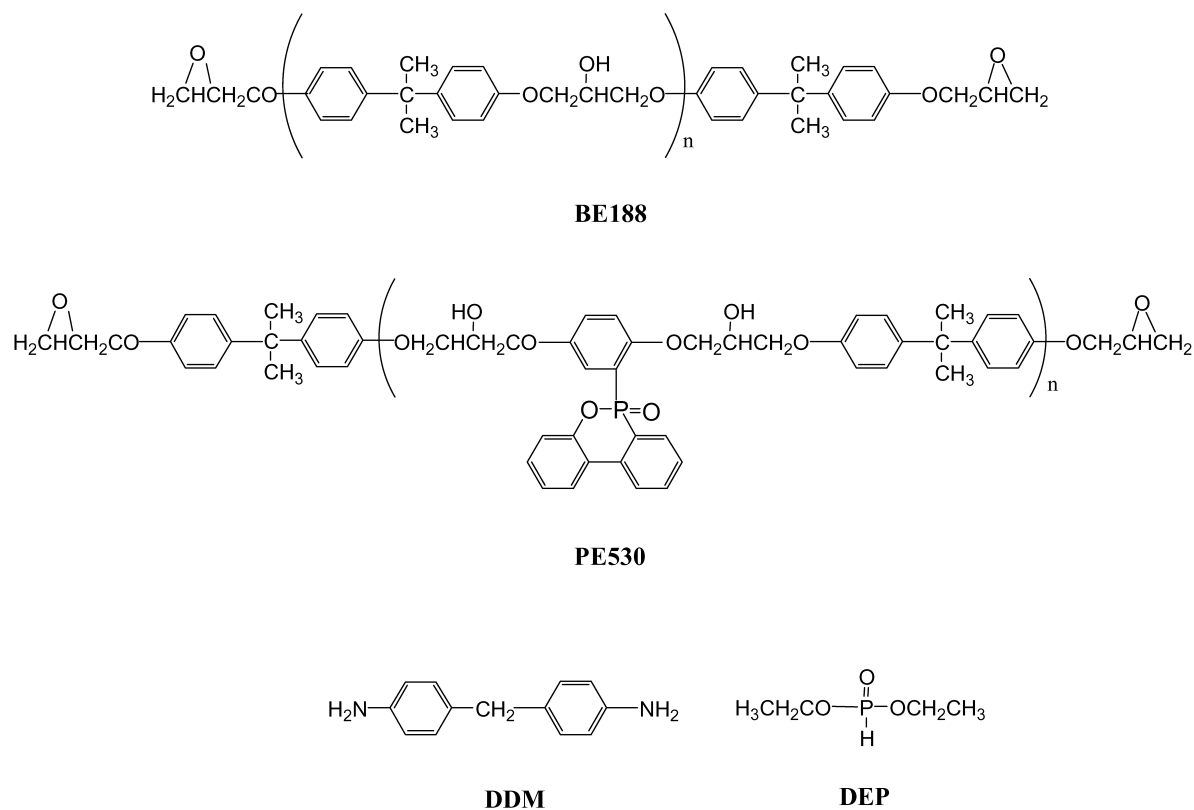**DDM**   **DEP**

Fig. 1. The chemical structures of the used epoxy compounds and curing agents.

silica hybrid resins (ESHR) was noteworthy (Fig. 4). It was implied there was no macroscopic phase-separation in the ESHR resins. That is to say, during the formation of the ESHR resins the nanoscale silica particles do not aggregate together to form silica domains greater than wavelengths of the visible lights. The good miscibility between the silica particles and the cured epoxy resins was therefore demonstrated. The homogeneity of the cured ESHR was studied using the tapping mode AFM [35]. Fig. 5 showed the AFM topography images and phase images of the cured ESHR.
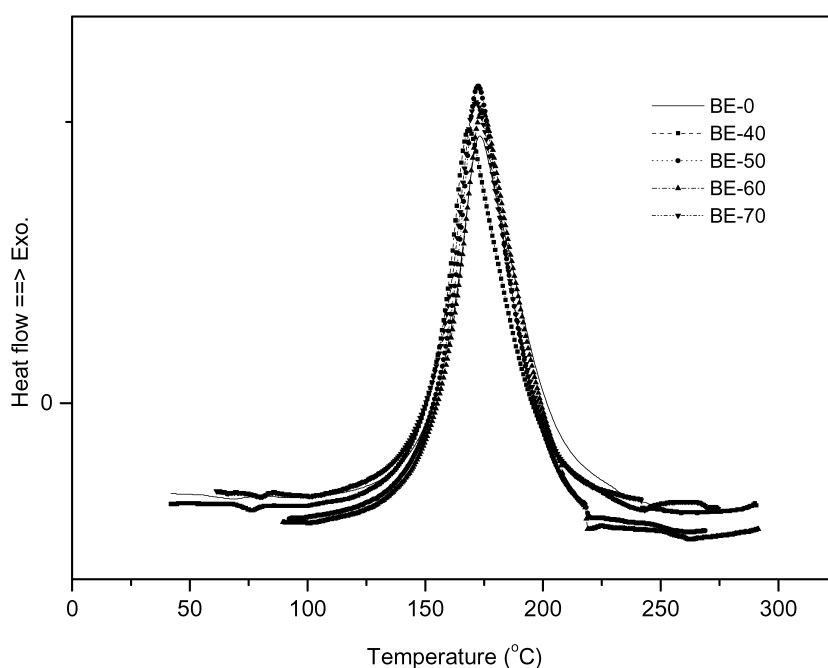

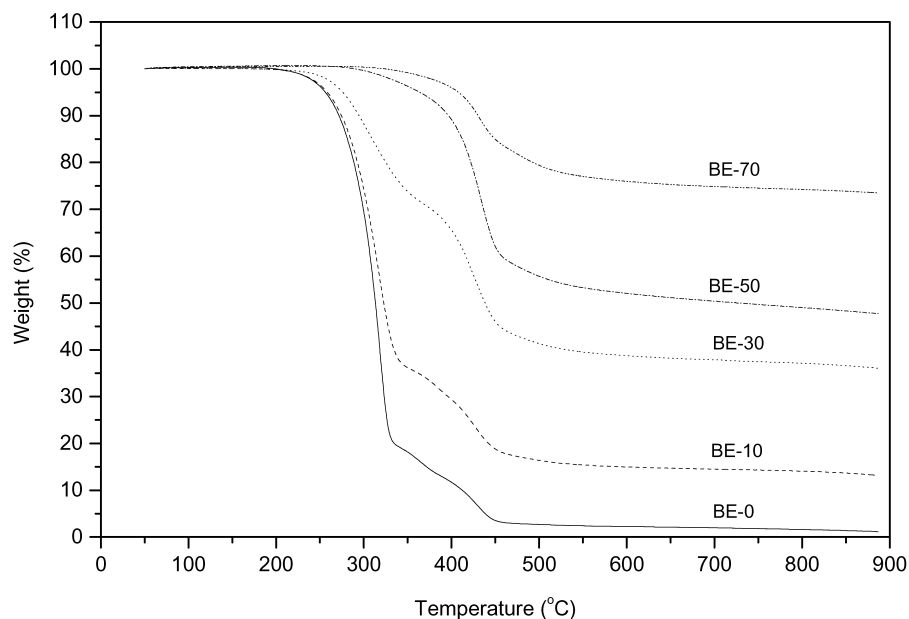Fig. 2. DSC thermograms of epoxy-silica compounds cured with DDM.

Fig. 3. TGA thermograms of BE188-silica hybrid materials in air.

From the micrographs it can be seen that the silica particles were homogeneously dispersed in the hybrid material matrix [35–39]. For ESHR-70, the high silica content led this hybrid material being silica-rich. Therefore, the silica particles might approach together to exhibit silica grains having sizes greater than the size of the original colloidal silica (20 nm). The homogeneity of the cured ESHR resins was further characterized with SEM-EDS Si-mapping (Fig. 6). Homogeneous distributions of silicon on the surface of the fracture sections of the ESHR resins were observed for all samples [40]. There was no aggregation of the silica being observed from the SEM-EDS Si-mapping photograph. Moreover, TEM micrographs of the ESHR resins provided another direct observation of the silica dispersion in the hybrid materials (Fig. 7). Silica particles were clearly observed homogeneously dispersing in the matrix.

3.3. Thermal properties of ESHR

The cured ESHR samples were characterized with DSC and TGA to evaluate their thermal properties. The glass transition temperatures of the ESHR resins read from DSC heating scans were collected in Table 1. While with low loadings of silica, the ESHR resins exhibited glass transition temperatures lower than that of pristine epoxy resin. The decrease in T_gs of the ESHR resins might be due to the plasticizing effect of the silica particles in the epoxy domains. Introduction of silica particles might also increase
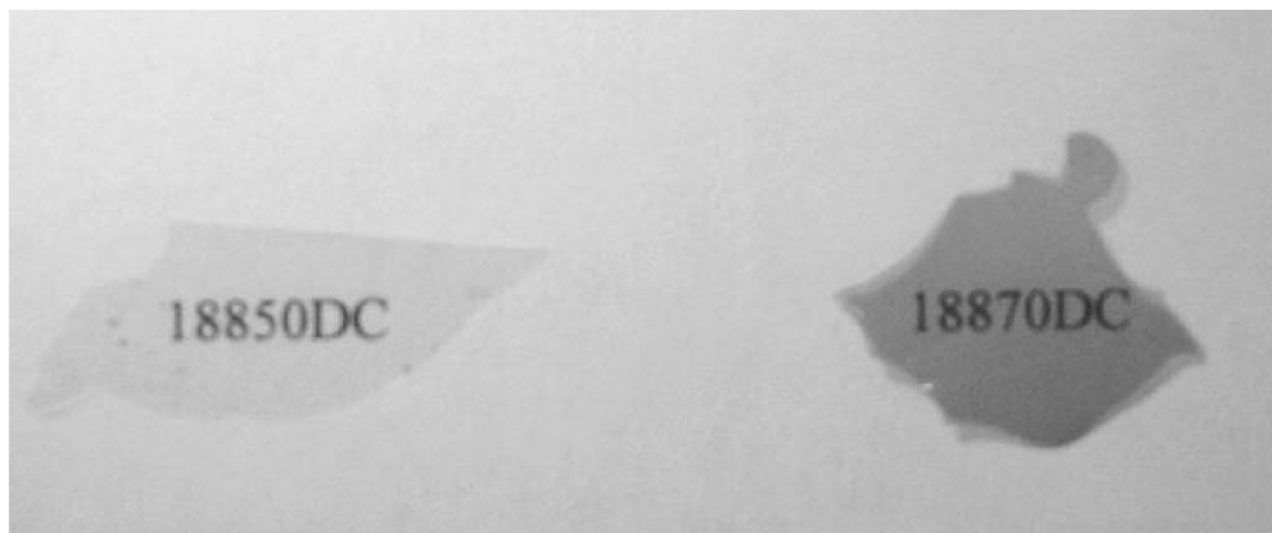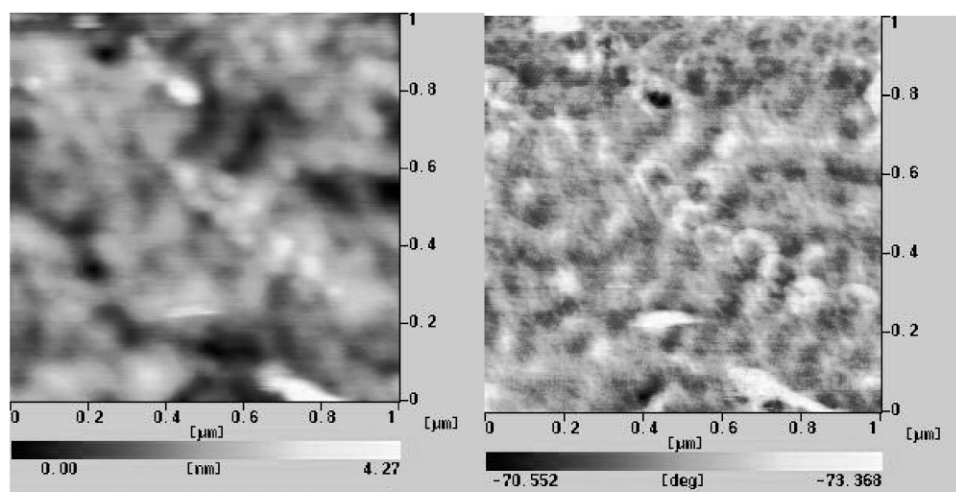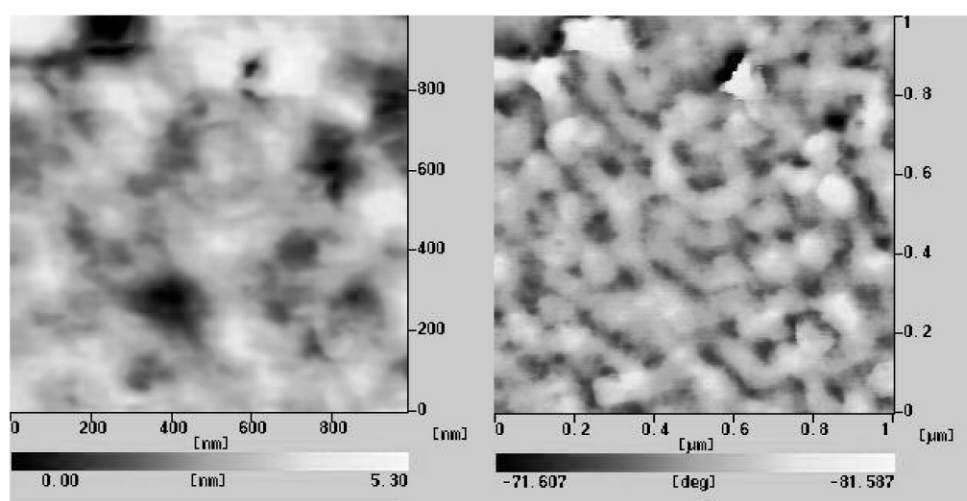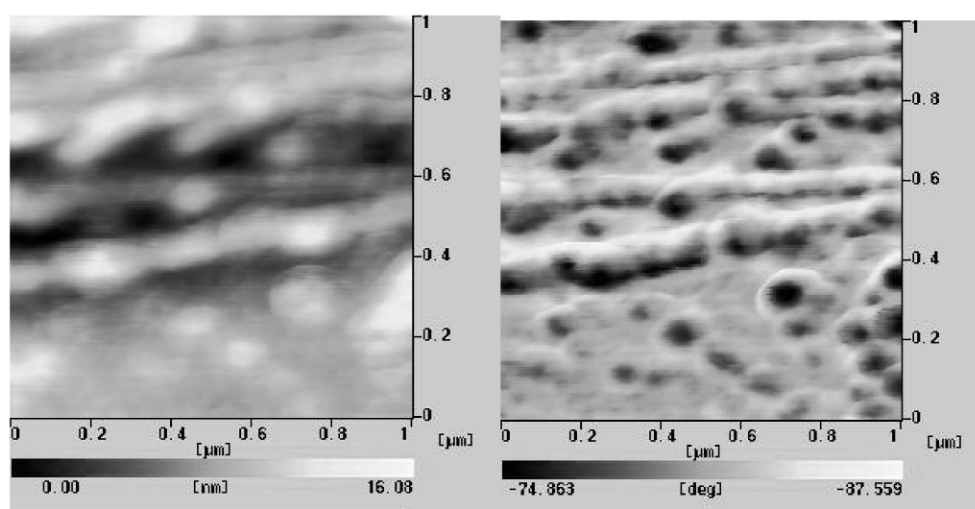

Fig. 4. The transparency of the cured epoxy-silica hybrid resins: ESHR–50 (left) and ESHR–70 (right).

Fig. 5. AFM microscopic photographs of (A) ESHR-30, (B) ESHR-50, and (C) ESHR-70. Left: topographic image and right: phase image.
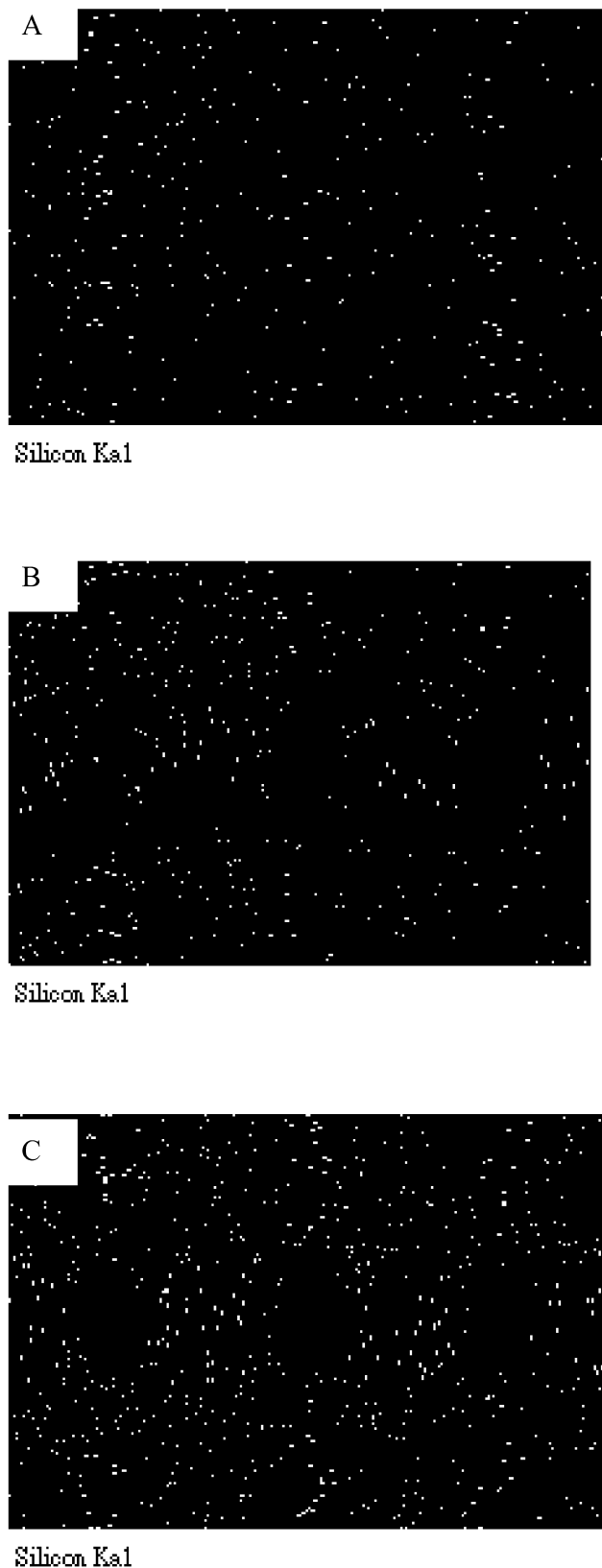
Silicon Ka1

Silicon Ka1

Silicon Ka1

Fig. 6. SEM-EDS Si-mapping microscopic micrographs. (A) ESHR-3-, (B) ESHR-50, and (C) ESHR-70.

Fig. 7. TEM microscopic micrograph of ESHR-70.

the free volume of the resins to reduce their T_gs. However, for ESHR resins with high silica contents, the motion of polymer chain was heavily inhibited by the silica domains. Therefore, ESHR-50 showed a relatively high T_g, and T_g was not detectable in the DSC measurements for the cured ESHR-70 resin due to their high silica contents.

Fig. 8 showed the typical TGA thermograms of the hybrid resins and the analyzed data were collected in Table 1. The temperatures of the onset weight loss and the maximum weight loss of the ESHR resins both increased by increasing the silica contents of ESHR resins. Therefore, it was demonstrated that the thermal stability of the epoxy resins improved with the formation of hybrid resins with silica and the amplitude of improvement increased by increasing the silica contents of the hybrid resins. The char residuals of the ESHR resins (800 °C, air atmosphere) were almost equal to their respective silica loading, to imply that the introduction of nanoscale colloidal silica into bisphenol-A type epoxy resins does not bring significant enhancement on char formation to the epoxy resins. Organosilicon compounds are considered to be used as flame retardants for polymeric materials [33,41,42]. The flame retarding

Table 1
Thermal properties of ESHR resins

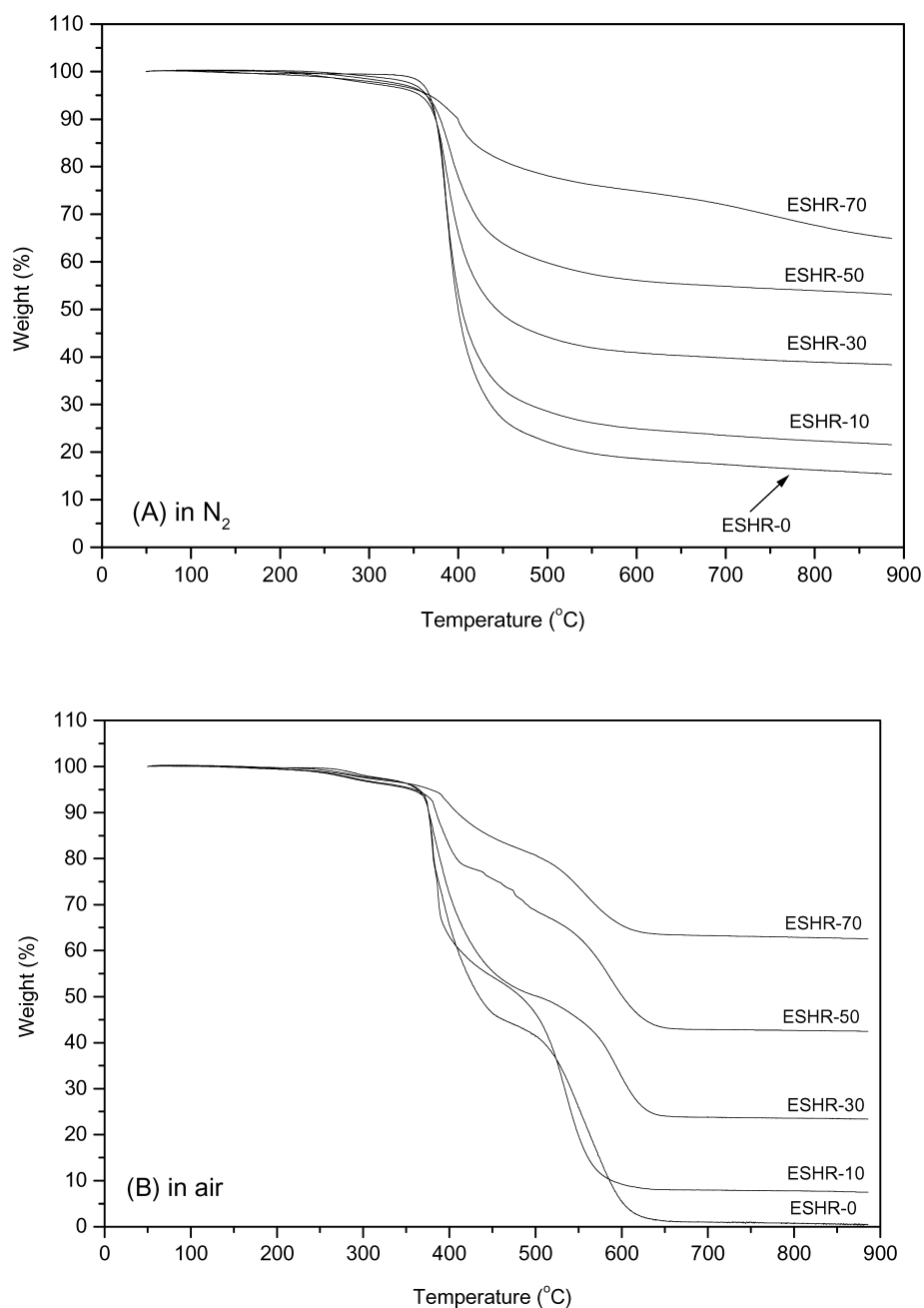| ESHR Samples	$T_{d_{10}}$[a] (°C)		Char residual at 800 °C (wt%)		T_g (°C)	LOI
	In air	In N$_2$	In air	In N$_2$		
ESHR-0	377	375	0	16.3	165	23.0
ESHR-10	377	375	7.8	22.4	147	23.0
ESHR-30	377	375	23.6	39.0	120	24.0
ESHR-50	386	380	42.7	54.0	153	25.0
ESHR-70	409	400	62.9	67.9	–	26.0

[a] Temperature at 10% weight loss.

Fig. 8. TGA thermograms of the ESHR resins in (A) nitrogen and (B) air atmosphere.

effect of organosilicon compounds performs through a condensed-phase mechanism. Two major actions were proposed in the condensed-phase mechanism: one was the formation of a silica layer on the surface of the polymeric materials, and the other was this formed silica serving as a protective layer to the char formed from polymeric materials [32]. However, this behavior was not observed for the ESHR resins since the added silica showed no effect on enriching char formation. Therefore, the added colloidal silica might not be so helpful to improve the flame retardance of the epoxy resins. The measured LOI values of the ESHR resins did not show significant change with the

loadings of the colloidal silica to further demonstrate the above inference (Table 1). However, ESHR-70 showed a relatively high LOI value of 26.0. This high LOI value of ESHR-70 might be due to the relatively small amount of combustible epoxy resin in the nanocomposites.

From the condensed-phase mechanism of flame retardation of silicon compounds [32], the poor flame-retardance of the ESHR resins might be referred to two factors: one is the poor char-formation of BE188/DDM resin and the other is the poor migration ability of the silica particles. The first factor could be compensated by introducing phosphorus element into the epoxy resin

compositions, since phosphorus is considered as another efficient element for improving polymeric materials' flame retardance through enriching char formation of polymers [33–36,43]. The results were discussed in Section 3.4.

3.4. Introduction phosphorus into the epoxy-silica nanocomposites

Phosphorus was introduced into the epoxy-silica nanocomposites by using the phosphorus-containing epoxy compound PE530 or curing agent DEP [35] (Fig. 1). The compositions for the preparation of nanocomposites were listed in Table 2. The cured resins were characterized with DSC and TGA and the analytical results were also collected in Table 2. The glass transition temperatures of all of the PESHR resins were lower than that for the silica-free resins owing to the plasticizing effect of the low contents of the colloidal silica. The depression in the PESHR resins' T_g was especially obvious for the DEP cured epoxy resins due to the flexible and soft P–C and P–O linkage [35]. Introduction of phosphorus into the ESHR resins significantly increased the char yields of the nanocomposites at high temperatures. The char yields of the PESHR resins were found to increase with increasing silica contents. However, the colloidal silica in the PESHR resins might be considered as inorganic parts, which did not show weight loss under the experimental temperature. Therefore, for the ESHR and PESHR resins containing the same colloidal silica contents, the increase in char yields observed for PESHR should be mainly due to the incorporation of phosphorus into the ESHR resins. On the other hand, the synergism effect of phosphorus and silicon on enhanced char formation of polymers was reported with our previous studies [8,32–34]. Especially, this synergism effect was observed with epoxy resins possessing phosphorus and nanoscale silica formed from in situ sol–gel reaction [8]. In the present work, this P–Si synergistic effect could still be considered being operative, although less obviously. The P–Si synergism effect of char formation is

due to the migration of silica to the surface of the formed char to form a protecting layer in order to prevent further thermal degradation of the char. The pre-formed colloidal silica, in spite having the size of 20 nm, is probably too big to migrate to the char surface under heating. The above results suggested that using pre-formed silica particles in the formulations of epoxy resins is not effective on char protection and enhancement.

The measured LOI values of the PESHR resins were shown in Table 2. The high LOI values of the PESHR resins were mainly contributed from phosphorus element. Loading colloidal silica into the P-containing epoxy resins, however, only can slightly level up the LOI values of the epoxy resins. The colloidal silica in the PESHR did not exhibit obvious synergistic effect on LOI enhancement with phosphorus. The results were coincident with the data of the char yield. Although nanoscale silica was observed to show synergism on enhancing flame retardance of polymers with phosphorus [8,32–34], however, the expected effect was not observed in this study. As being demonstrated, the P–Si synergistic effect on improving polymers' flame retardance could be obtained while using in situ formed silica from sol–gel process [8,44]. However, it was suggested that preformed nanoscale silica do not exhibit significantly synergistic effect with phosphorus on polymer's flame retardance improvement.

4. Conclusions

Nanoscale colloidal silica can be blended with commercial bisphenol-A type epoxy compounds to form organic–inorganic hybrid materials with loading as high as 70 wt% of colloidal silica. The hybrid materials can be cured with commercial curing agents without altering the curing conditions. The resulting cured ESHR showed good transparency and miscibility. The thermal stability of the epoxy resins was improved with the incorporation of the

Table 2
Thermal properties of phosphorus-containing ESHR resins

ESHR Samples	Epoxy	Curing agent	CS contents (wt%)	Phosphorus contents (wt%)	$T_{d_{10}}$[a] (°C)		Char residual at 800 °C (wt%)		T_g (°C)	LOI
					In air	In N$_2$	In air	In N$_2$		
PESHR-I-0	PE530	DDM	0	2.55	388	390	6.1	20.4	140	29.0
PESHR-I-3	PE530	DDM	3	2.47	347	382	9.7	24.1	137	29.0
PESHR-I-5	PE530	DDM	5	2.42	364	383	10.1	24.5	130	29.5
PESHR-I-10	PE530	DDM	10	2.30	339	382	14.9	28.1	131	30.0
PESHR-I-20	PE530	DDM	20	2.00	370	385	25.4	36.0	135	31.0
PESHR-II-0	BE188	DEP	0	4.42	328	333	4.3	2.7	138	29.5
PESHR-II-5	BE188	DEP	5	4.23	340	336	10.3	28.6	70	30.0
PESHR-II-10	BE188	DEP	10	3.99	338	331	16.4	35.4	70	30.5
PESHR-II-20	BE188	DEP	20	3.68	353	353	25.3	39.4	66	31.0
PESHR-II-30	BE188	DEP	30	3.28	355	355	33.8	50.6	62	31.0

[a] Temperature at 10% weight loss.

colloidal silica. However, a depression in the glass transition temperature of the resins was observed, owing to the plasticizing effect of the colloidal silica. Moreover, the nanoscale colloidal silica did not show effectively synergistic effect on char formation and flame retardance with phosphorus.

Acknowledgements

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