PREPARATION, CHARACTERIRATION AND PROPERTIES OF NOVEL ORGANIC/INORGANIC EPOXY HYBRID

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Abstract

Organic-inorganic hybrids were prepared using diglycidyl ether of bisphenol A (DGEBA) type epoxy and silane modified isocyanuric acid triglycidyl ester (SM-IATE) via the sol-gel process. The DGEBA type epoxy was modified by a coupling agent to improve the compatibility of the organic and inorganic phases. The sol-gel technique was used successfully to incorporate silicon and nitrogen into the network of hybrids increasing thermal stability.

FTIR and ^{29}Si NMR were used to characterize the structure of the hybrids. Results revealed that T^3 are the major environments forming a network structure. The morphology of the ceramer was examined by scanning electron microscopy (SEM), Si mapping and transmission electron microscope (TEM). Particles sizes were below 100nm. The hybrids were nanocomposites. UV/VIS spectrum of epoxy hybrid shows there is no obvious absorbance over a range of 400 ~ 800 nm. This phenomenon revealed the hybrids are transparent. TGA revealed the char yields of hybrids increased with the contents of inorganic components. The integral procedure decomposition temperatures (IPDT) of hybrids were higher than that of pure epoxy. The thermal stability of hybrids increased with the contents of inorganic components. The inorganic components can improve the thermal stability of pure epoxy.

1. Introduction

Epoxy resins have been commercially available for about 50 years and are widely used in modern industries. Up to now, research efforts on improving the properties of the epoxy resins, including their thermal stability, are under progress for meeting the requirements from the versatile and advanced applications. Formation of stable char is one of the desirable mechanisms of flame retardation in polymers, since the char layer acts both as a thermal insulator a barrier to oxygen diffusion. A good way to enhance char formation is by addition of inorganic fillers, since the presence of the inherently stable inorganic phase makes char more mechanically stronger, consequently improving its insulating and barrier properties. In recent times, nanocomposites have emerged as a promising class of materials with good fire resistance.

Organic-inorganic hybrid materials are nanophase separated metal oxide clusters connected to a continuous polymer network via a coupling agent [1, 2]. These materials have drawn considerable attention in recent years due to improvements in various properties including thermal stability, flame retardance, as well as mechanical properties [3-6].

An interesting method for obtaining these hybrids is the in situ sol-gel process, which allows obtaining silica domains into the polymer network. It involves a series of hydrolysis and condensation reactions starting from a hydrolysable multifunctional alkoxysilane as precursor for the inorganic domain formation. The advantages of sol-gel process over the traditional ceramic synthesis process are the abilities to form pure and homogeneous products at low temperature [7]. The use of suitable coupling agent permits to obtain an interconnected network preventing macroscopic phase separation. The coupling agent provides covalent bonding between the organic and inorganic phases, therefore, well-dispersed nanostructured phases may result [8].

` In this study, novel organic/inorganic epoxy hybrid containing nitrogen/silicon will be prepared via the sol-gel method. The structures of monomers and hybrids will be characterized by FTIR, ^{1}H-NMR and ^{29}Si-NMR. Thermal, morphological properties

will be discussed by TGA, DSC, SEM and TEM, respectively.

2. Experimental

2.1 Materials

The epoxy resin used was the diglycidyl ether of bisphenol A (DEGBA, NPEL-128) which was generously provided by Nan Ya Plastics Corporation, Taiwan. 3-Isocyanatopropyltriethoxysilane (IPTS) was purchased from United Chemical Technologies, Inc., U.S.A. Isocyanuric acid triglicidyl ester (IATE) was obtained from TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan. 3-Aminopropyltriethoxysilane (APTS) was supplied from ACROS Organics Co., Janssens Pharmaceuticalaan, 3A2440 Geel. Poly(oxypropylene) diamine (Jeffamine D400) was from the Huntsman Corporation, Salt Lake City,Utah 84108 USA. N,N-Dimethyl Acetamide (DMAc) was from TEDIA Co. Farfield, Ohio, U.S.A. Tetrahydrofuran (THF) was reagent grade and supplied by Echo Chemical Co. Ltd., Taiwan. Concentrated hydrochloric acid used was obtained from the Union Chemical Works Ltd, Taiwan. Isopropyl alcohol (IP) was purchased from the Tedia Company, Inc, Farfield, Ohio, and U.S.A.

2.2 Preparation of IPTS-Epoxy/SM-IATE hybrid materials

The hybrid ceramers were prepared by mixing two solutions, A and B. Solution A consisted of modified epoxy resin and THF solvent. The modified epoxy resin was synthesized as follows: 4g IPTS (equivalent weight 247g) was added to 10g DGEBA type epoxy resin(equivalent weight 180g) at 60℃, and was then stirred for 4 hours until the characteristic peak of the NCO group disappeared. IPTS reacted with epoxy to form IPTS-Epoxy【9】. Solution B was composed of IATE/APTS in a molar ratio 3:1. IATE was dissolved into DMAc and its solid content was 20 wt%. APTS was then slowly poured into IATE solution and mixed at 50℃ for 12 hours. APTS was incorporated into IATE to form silane modified IATE (SM-IATE). HCl was used as the catalyst for hydrolysis. D400 was used as the curing agent of the modified epoxy resin. The IPTS-Epoxy/SM-IATE hybrid materials were prepared with various SM-IATE feed ratios in Table 1. The mixtures were stirred until the solutions became clear. The solutions were cast into aluminum dishes to gel at room temperature. The wet gels w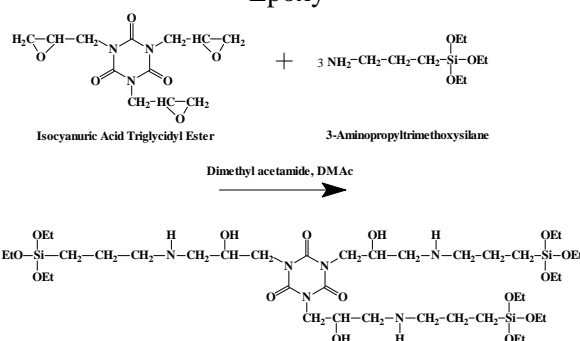ere aged at room temperature for 48 hours, and were then dried at 80℃ for 2 hours in a vacuum oven. The samples were placed in a vacuum oven at 150℃ for 4 hours, then was cured at 160℃ for 24 hours.
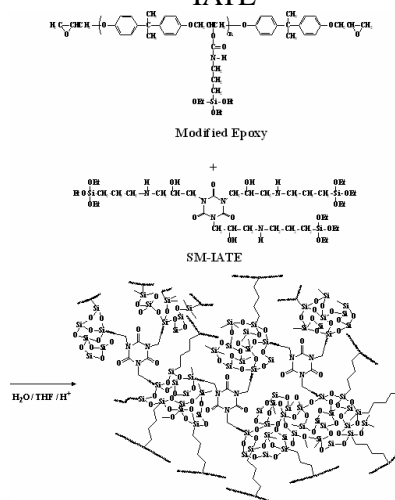
2.3 Reaction schemes

The novel hybrid materials were prepared as described in scheme 1-3 :
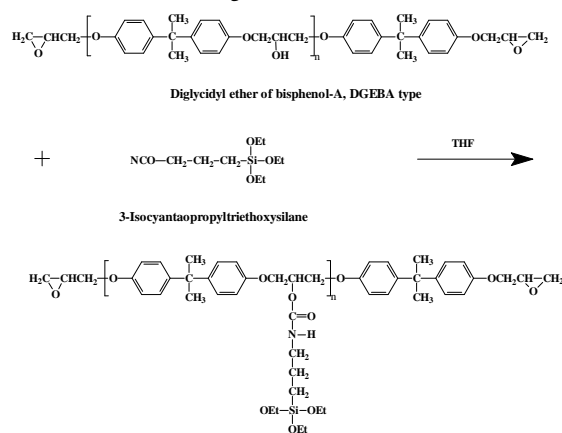
Scheme 1 Reaction process and structure of IPTS-Epoxy

Scheme 2 Reaction process and structure of SM-IATE

Scheme 3 Reaction process and structure of epoxy/SM-IATE hybrid

2.4 Fourier Transform infrared spectroscopy (FT-IR)

To identify the functional groups of monomers and nanocomposites, FTIR spectra were recorded between 4000-400 cm^{-1} with a resolution of 2 cm^{-1} on a Nicolet Avatar 320 FT-IR spectrometer, U.S.A. and then scanned more than 32 times. Thin films were prepared by the solution-casting method for monomer. The films were prepared, by mixing the finely ground solid sample with powered potassium bromide, and the mixture was pressed under high pressure at 8000-10000 kg/cm^2.

2.5 Solid state ^{29}Si nuclear magnetic resonance spectroscopy (^{29}Si NMR)

^{29}Si NMR was performed by a Bruker DSX-400WB, Germany. The samples were treated at 180℃ for 2hr and then ground into fine powder.

2.6 Thermogravimetric analysis (TGA)

Thermal degradation of hybrid was investigated by a thermogravimetric analyzer (Perkin Elmer TGA 7) from room temperature to 800℃ under nitrogen atmosphere. The measurements were conducted using 6-10mg samples. Weight-loss/temperature curves were recorded.

2.7 Differential Scanning Calorimeter (DSC)

The glass transition temperatures (Tgs) of the samples were measured by a differential scanning calorimeter (Du-Pont, model 10). The heating rate was 10℃/min. within a temperature range of 50~200℃. The measurements were made with 3~4 mg sample on a DSC plate after the specimens were quickly cooled to room temperature following the first scan. Tgs were determined at the midpoint of the transition point of the heat capacity (Cp) changed, and the reproducibility of Tg value was estimated to be within 2℃.

2.8 Morphological properties

The morphology of the fractured surface of the nanocomposites was observed with a scanning electron microscope (SEM；JEOL JSM 840A, Japan).

2.9 Si mapping technology

Energy dispersive X-ray (EDX) measurements were conducted with SEM EDX mapping (JEOL JSM 840A, Japan). The white points in the figures denote Si atoms.

2.10 Transmission electron microscope (TEM)

The TEM study was carried out using Hitachi H-7500 with an acceleration voltage of 100 kV in measurement. The samples were microtomed with Leica Ultracut cut into 60nm-thick slices. These slices were placed on mesh 200 copper nets for TEM observation.

2.11 UV-visible (UV/VIS) spectra

UV/VIS spectra were tested on a Hitachi (Japan) U-3300 spectrophotometer and the sample was prepared as a thin film on a glass substrate by spin coating.

2.12 Dynamic mechanical analysis (DMA)

The dynamic mechanical tests were carried out on a dynamic mechanical thermal analyzer(Polymer lab. DMTA MK Ⅲ) between 30℃ and 200℃ with a heating rate at a frequency of 2Hz. The rectangular bending mode was chosen and the dimensions of the specimen were 40 x 7 x 3 mm^3.

3. Results and Discussions

Characterization

FTIR of the reaction

The study for the reaction between epoxy and IPTS in scheme 1 was done in our previous paper 【9】. After the reaction, epoxy resin possesses the functional group of –OEt to proceed the sol-gel reaction. This can enhance the miscibility between organic and inorganic components.

The chemical structure of silane modified IATE (SM-IATE) was characterized with FTIR and NMR. In this study, we use amino group of APTS to react with oxirane group of IATE. The reaction process and structure of SM-IATE was shown in scheme2. Figure 1 shows FT-IR spectra of the reaction between IATE and APTS. Figure 2 presents FTIR spectra of oxirane group during the reaction between IATE and APTS. After the reaction, the consumption of oxirane group and the formation of the secondary—OH group were observed by disappearance of the absorption at 913 cm^{-1} and the appearance of the absorption between 3600~3000 cm^{-1}, respectively.
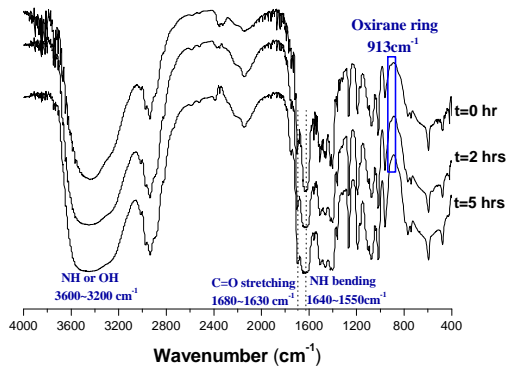
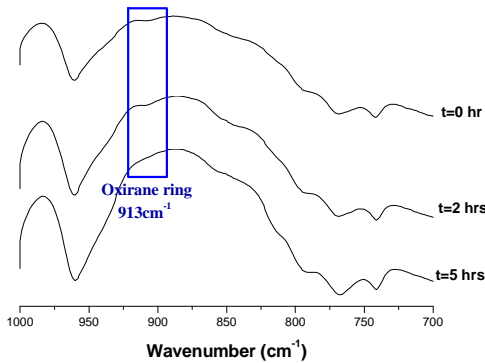Figure 1 FT-IR spectra of the reaction between IATE and APTS

Figure 2 FT-IR spectra of the reaction between IATE and APTS

^{1}H-NMR of Monomer

Figure 3 gives ^{1}H-NMR Spectrum of SM-IATE with characteristic shifts of hydrogen at δ=3.52(-OH which are from the opening ring of oxirane), δ=3.77 (-Si-O-CH$_2$CH$_3$), and δ=1.19(-Si-O-CH$_2$CH$_3$). All these characteristic NMR bands indeed match the expected SM-IATE structure. Other characteristic shifts are follows：3.61 ppm （ H, NCH$_2$CHOHCH$_2$NH ）， 3.52 ppm （ H, NCH$_2$CHOHCH$_2$NH ）， 3.52 ppm （ H, NCH$_2$CHOHCH$_2$NH ）， 3.4 ppm （ 2H, NCH$_2$CHOHCH$_2$ NH ）， 2.4 ppm （ 2H, NHCH$_2$CH$_2$CH$_2$Si），2.48 ppm（2H, NCH$_2$CHOH CH$_2$NH），1.47 ppm（2H, NHCH$_2$CH$_2$CH$_2$Si）， 1.19 ppm （3H, SiOCH$_2$ CH$_3$），0.34 ppm （2H, NHCH$_2$CH$_2$CH$_2$Si）.
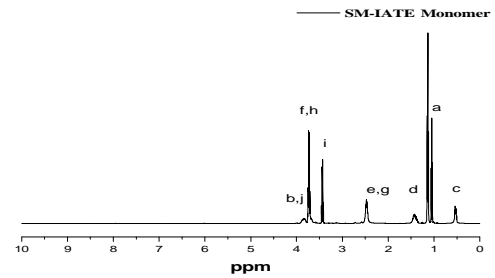

Figure 3 ^{1}H-NMR spectrum of SM-IATE monomer

FTIR of Hybrid

Infrared spectroscopy was used to characterize the formation of inorganic backbone through the sol-gel reactions. Scheme 3 shows the reaction process and structure of epoxy/SM-IATE hybrid Figure 4 shows FT-IR spectra of Epoxy/SM-IATE hybrid. The Si-O-Si group can be detected in the hybrid at 1100~1080 cm^{-1}. It indicated the condensation reaction of Si-OH happened. It will form the connections between the organic and inorganic phases. There are covalent bonds between organic and inorganic moieties. The peak at 913 cm^{-1} disappeared in the cured hybrid. This implied the oxirane rings have reacted with curing agent completely. The hybrids possess the networks and will enhance the thermal properties.
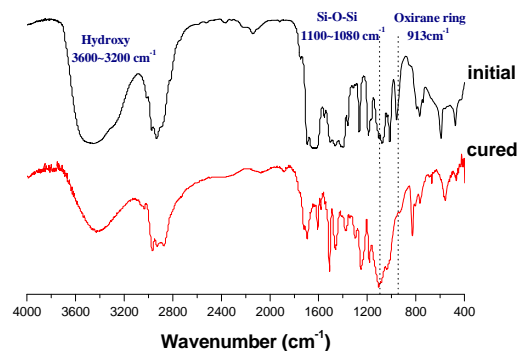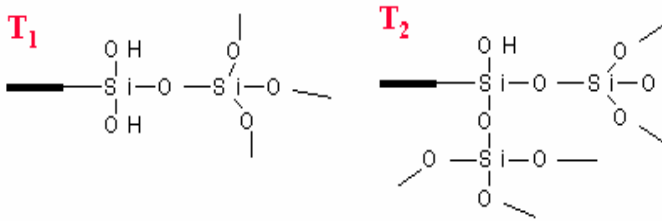

Figure 4 FT-IR spectra of Epoxy/SM-IATE hybrid

^{29}Si NMR of Hybrid

Figure 5 show ^{29}Si Solid-state NMR spectra of Epoxy/SM-IATE. For 3-isocyanatopropyltriethoxysilane, mono-, di, tri, tetra-substituted siloxane bonds are designated as T^1, T^2, T^3. For 3-isocyanatopropyltriethoxysilanes with mono-, di-, tri-, tetra-substituted siloxane bonds are designated as T^1, T^2, T^3. The definition of T^s was shown as following:

The chemical shifts of T^2 and T^3 are –56 and –65 ppm , respectively, and conform to the literature values 【10】. Results revealed that T^3 are the major microstructures, forming the network structure. The network structure will promote the thermal stability of epoxy resin.
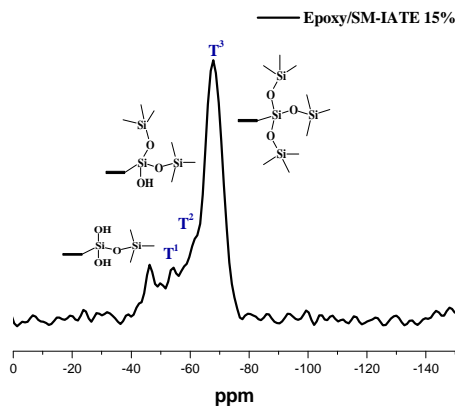

Figure 5 ^{29}Si Solid-state NMR spectra of Epoxy/SM-IATE 15%

Morphological Properties

Figure 6 presents a SEM photograph of the morphology of the composites. Figure 7 shows Si mapping of epoxy nanocomposites. The fracture surface was very dense. According to these figures, the particles were uniformly dispersed in the polymer matrix without macro phase separation. Separated epoxy and inorganic components domains were not observed to demonstrate the homogeneity. This result revealed that the nanocomposites exhibit good compatibility between organic and inorganic phases. Figure 8 presents the TEM microphotographs of fractured surface of Epoxy/SM-IATE 15. From this figure, the sizes of particles are smaller than 100nm. The hybrids are nanocomposites. Figure 9 shows the photographs of epoxy/SM-IATE 15 hybrid that possess good

transparency. From figure 9, it can be seen that epoxy/SM-IATE 15 hybrid shows a clear appearance and a little yellow color. The results give sufficient support to the formation of epoxy hybrid, i.e., the mixing of epoxy and inorganic components is in nano-scale.
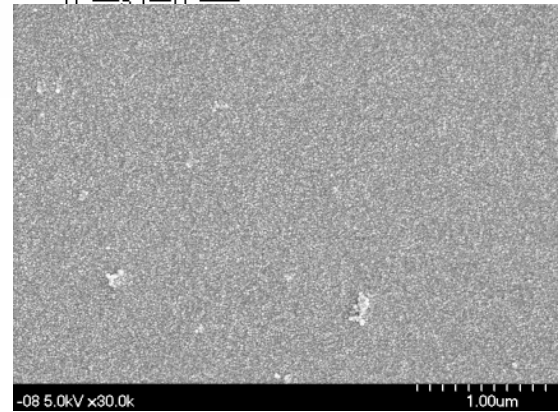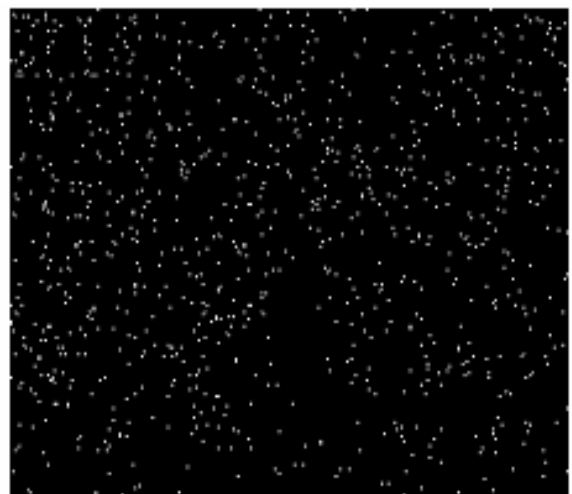

Figure 6 SEM microphotographs of fractured surface of Epoxy/SM-IATE 15

Silicon Ka1

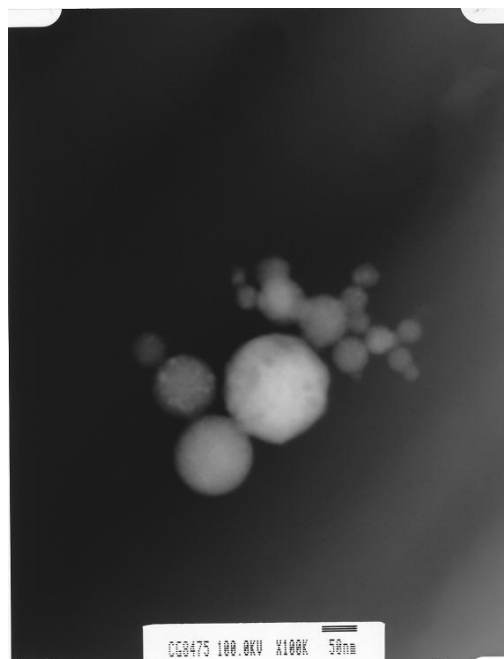Figure 7 Si-mapping of Epoxy/SM-IATE 15 fractured surface

Figure 8 TEM microphotographs of fractured surface of Epoxy/SM-IATE 15/D400

Figure 9 Photographs of Epoxy/SM-IATE 15 hybrid

UV/VIS

Figure 10 shows the UV/VIS spectrum of epoxy with different SM-IATE contents. There is no obvious absorbance over a range of 400 ~ 800 nm. This phenomenon revealed the hybrids possess excellent optical transparency. The transmittance of the composites films increases slightly with increasing content of inorganic moiety. This transmittance may be used as a criterion for the formation of a homogenous phase. These results demonstrate the excellent optical transparency of hybrids, which is the most important characteristic for their application in protective coating.
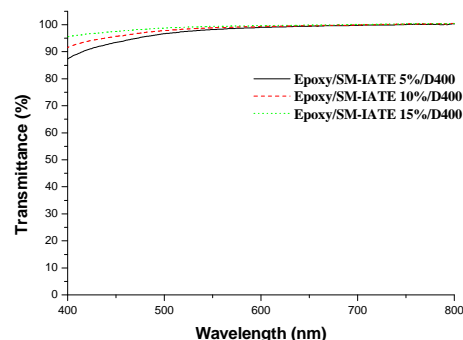

Figure 10 UV/VIS Spectrum of Epoxy with different SM-IATE contents

Thermal Properties

Figure 11 presents DSC curves of epoxy resin with various SM-IATE contents. No obvious exothermic/endothermic peaks were observed, and this confirmed the high conversion of the condensation reaction of silanol groups in the curing reaction. The temperature at the baseline shift was read as T_g of the resin. The T_g of pure epoxy is 50℃. Introducing SM-IATE into the epoxy enhanced T_g of the resulting resins. The T_gs of hybrids increase with increasing of SM-IATE contents. Figure 12 shows the temperature dependence of tanδ (damping) for epoxy resin with various SM-IATE contents. The tanδ peaks which reflected the micro-Brownian segmental motions of epoxy resin were defined as the glass transition temperature. The addition of inorganic filler in matrix made it difficult to move the polymer chain and therefore damping decreased and glass transition temperature were shifted to higher temperature【10】. The relaxation strength (the height of the tanδ peak) decreased with increasing inorganic contents. Such a reduction of tanδ peak for orgaic-inorganic hybrid materials was attributed to the increase in crosslink of polymer with inorganic network or the entrapment of the polymer chains within inorganic networks, resulting in the reduction of the polymer chain mobility【11】.The hybrids exhibit single T_g, ie., they indicate homogenous morphology. The tanδ peaks were broadened as higher inorganic contents, indicating an increase in phase separation【12-13】

Thermogravimetric analysis (TGA) is one of the commonly used techniques for rapid evaluation of the thermal stability of different materials, and also indicates the decomposition of polymers at various temperatures. Figure 13 shows the TGA thermograms of epoxy resin with various contents, from room temperature to 800℃, in nitrogen

atmosphere. Table 2 shows weight loss characteristics of the epoxy resin with various contents of SM-IATE. Figure 14 shows the weight loss temperature versus weight loss for epoxy resin with various SM-IATE contents. The thermal stability of hybrids was lower than pure epoxy when the thermal degradation just occurred. The Si-O group of SM-IATE is able to absorb more thermal energy and its vibration can dissipate the thermal decomposition energy【8】. The char yields of hybrids are higher than pure epoxy during high temperature. High temperature thermal stability can be increased with the addition of silicon-containing compounds because their products are silicon dioxide, which cannot be degradated further. The phenomena revealed the thermal stability of hybrids increased with the contents of inorganic components. Apparently, enhancement of thermal stability of hybrids has been achieved by incorporation of silicon and nitrogen into epoxy resins with bringing a Si-N synergistic effect.【14-16】

The integral procedure decomposition temperature(IPDT) proposed by Doyle【17】 has been correlated the volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials【18-19】. From Table 2, the IPDT of pure epoxy was 464℃ and the IPDTs of hybrids were higher than that of pure epoxy. The thermal stability of hybrids increased with the contents of inorganic components. The inorganic components can improve the thermal stability of pure epoxy.
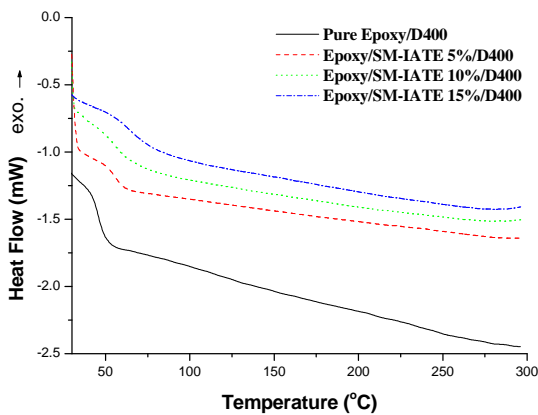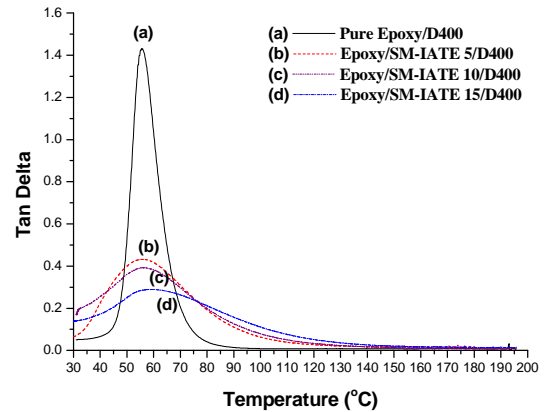

Figure 12 Temperature dependence of tan δ for epoxy resin with various SM-IATE contents

Figure 13 TGA thermograms of epoxy resin with various SM-IATE contents
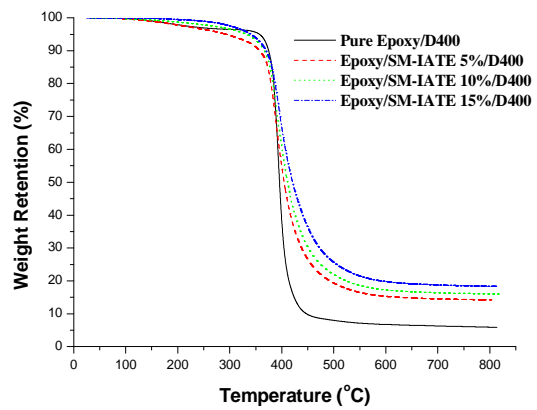

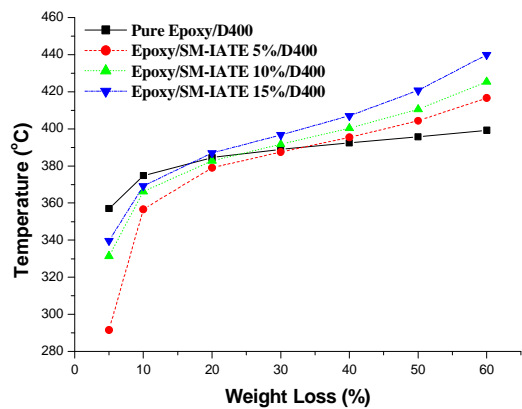Figure 11 DSC of Epoxy resin with various SM-IATE contents

Figure 14 Weight loss temperatures versus weight loss for epoxy resin with various SM-IATE contents

Table 1 Compositions of Epoxy/SM-IATE hybrid materials

SAMPLE	Epoxy (wt%)	SM-IATE (wt%)	N Contents (wt %)	Si Contents (wt %)	N+Si Contents (wt %)
Epoxy	100	0	0.00	0.00	0.00
SM-IATE 5	95	5	3.26	2.05	5.31
SM-IATE 10	90	10	3.55	2.40	5.95
SM-IATE 15	85	15	3.84	2.75	6.59

Table 2 Weight loss characteristics of the epoxy resin with various contents of SM-IATE

	IPDT (℃)	Temperature at Characteristic Weight Loss（℃）						Residue（%）800℃
		10%	20%	30%	40%	50%	60%	
Pure Epoxy	464	375	385	389	392	396	399	5.9
SM-IATE 5	594	357	379	388	395	404	417	14.2
SM-IATE 10	631	366	383	392	400	411	425	16.0
SM-IATE 15	689	369	387	397	407	421	440	18.4

4. Conclusions

Novel epoxy nanocomposites containing silicon and nitrogen were prepared successfully via the sol-gel method. The structures of monomers and composite were confirmed by FTIR, ^{1}H-NMR and ^{29}Si-NMR. This result revealed that the nanocomposites exhibit good compatibility between organic and inorganic phases from SEM, EDX and TEM. These results demonstrate the excellent optical transparency of hybrids by UV/VIS and photographs. The inorganic components enhance the thermal stability of epoxy. Owing to their optical transparency and high thermal stability, epoxy nanocomposites may have potential applications in protective coating at elevated temperature.

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