Using Silica Nanoparticles as Curing Reagents for Epoxy Resins to Form Epoxy–Silica Nanocomposites

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ABSTRACT: Nanoscale colloidal silica showed high reactivity toward curing epoxy resins to form epoxy–silica nanocomposites under mild conditions. Adding a certain amount (5000 ppm) of magnesium chloride lowered the activation energy of the reaction from 71 to 46 kJ/mol. Less and more magnesium chloride both exhibited counter action on lowering the activation energy of the curing reaction. Tin chloride dihydrate and zinc acetylacetonate hydrate were also added into the curing compositions, however, showing no significant effect on promoting the curing reaction. Through this curing reaction, epoxy–silica nanocomposites containing high silica contents up to 70 wt % were obtained. Therefore, this reaction provided a novel and convenient route in preparation of epoxy–silica nanocomposites. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1237–1245, 2005

Key words: curing of polymers; epoxy; nanocomposites; silicas; nanoparticles

INTRODUCTION

The physical and chemical properties of materials in nanoscale have been found to be very different from the properties of the analogous bulk materials. This specific character provides the motivation of developing materials having novel functions and properties from the existing substances. The new functional nanomaterials are now one of the flourishingly attractive subjects in modern science and technology.

Silica particles are widely used as reinforced fillers for epoxy molding compounds and encapsulants in the modern electronic industrials.[1] Nanoscale silica particles that could be homogeneously suspended in organic solvents are now commercially available.[2] Mixing the preformed nanoscale silica particles with polymeric materials provides a convenient approach to form organic–inorganic hybrid materials.[3,5] The hybrid materials mixed in nanoscale are also known as nanocomposites and show attractive properties relative to the conventional organic–inorganic composites.[6–11]

In our previous work, by using tin chloride as a catalyst, the Si—OH groups in silanol compounds and nanoscale silica showed reactivity toward oxirane ring to result in oxirane ring-opening reaction to form Si—O—C linkages.[12,13] The above-mentioned reaction did not perform without adding tin chloride to the reaction mixture.[12] However, in this work, it was observed that the nanoscale silica particles showed surprising reactivity toward epoxy resins without need of adding other promoters or catalysts. The reactivity might be correlated to the special effect of the nanosize of the silica particles, because it was not observed with microscale. Epoxy–silica nanocomposites were obtained through directly curing epoxy resins with the nanoscale silica. The reaction kinetics of the interesting reaction behavior of the nanoscale silica and the properties of the formed nanocomposites were studied and discussed.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol-A was obtained from Chang Chun Plastics Co. (Hsinchu, Taiwan), and the commercial product of BE188 (equivalent epoxy weight, EEW = 188) was used as received. Nanoscale silica particles were purchased from Nissan Chemical Co. (Tokyo, 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. Fused silica having an average particle size of 5 μm was received from Chang Chun Plastics Co. (Hsinchu, Taiwan). Tin chloride dihydrate (Showa

TABLE I
Preparation Compositions of Silica Nanoparticle Cured Epoxy Resins

| Sample code	BE188 (g)	MIBK-ST (phr)	Catalyst (ppm)	Appearance
ESC1-20	5	20	—	Transparent and soft
ESC1-30	5	30	—	Transparent and stiff
ESC1-40	5	40	—	Transparent and stiff
ESC1-50	5	50	—	Transparent and stiff
ESC1-60	5	50	—	Transparent and stiff
ESC1-70	5	50	—	Transparent and stiff
ESC1-50/Sn	5	50	$SnCl_2$ (5000)	Transparent and stiff
ESC1-50/Mg	5	50	$MgCl_2$ (5000)	Transparent and stiff
ESC1-50/Zn	5	50	$Zn(AcO)_2$ (5000)	Transparent and stiff
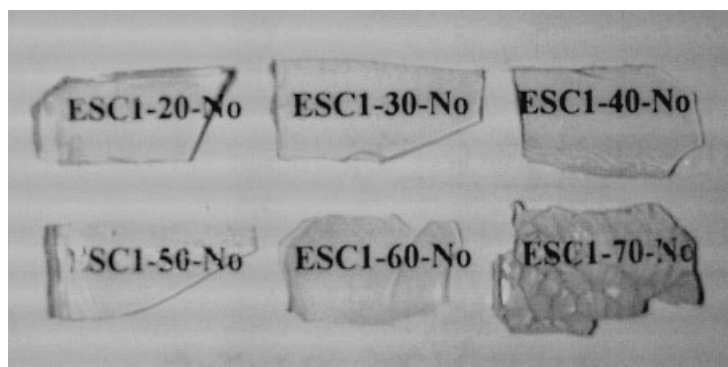
Figure 1 The transparency of the cured epoxy resins.
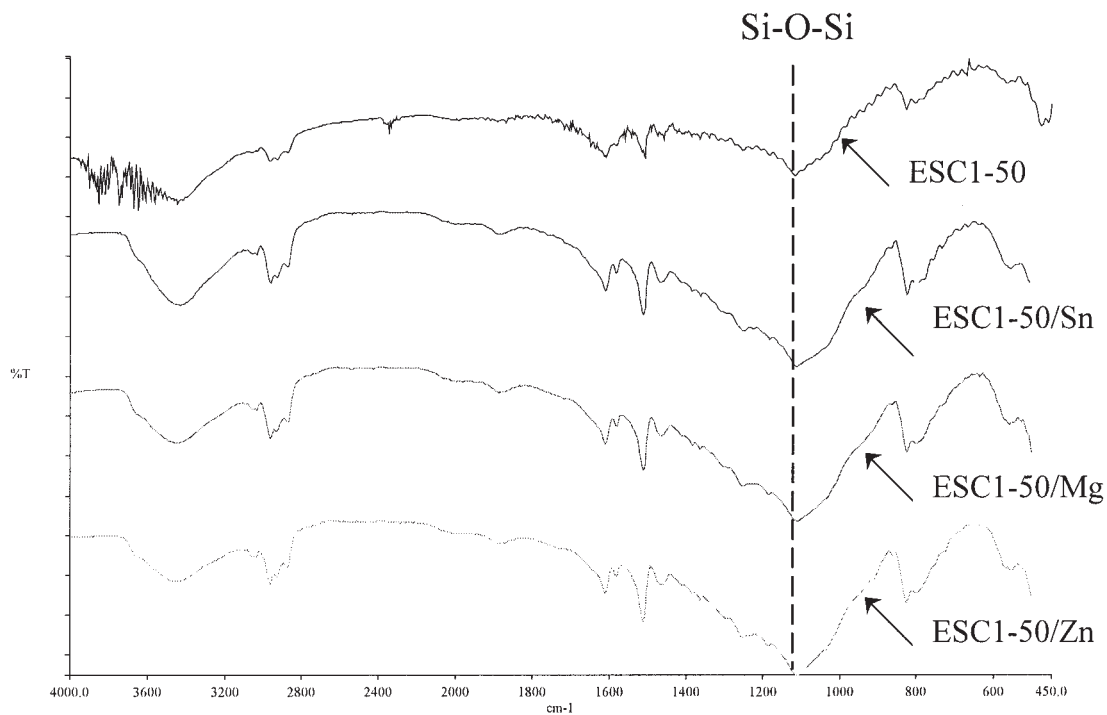

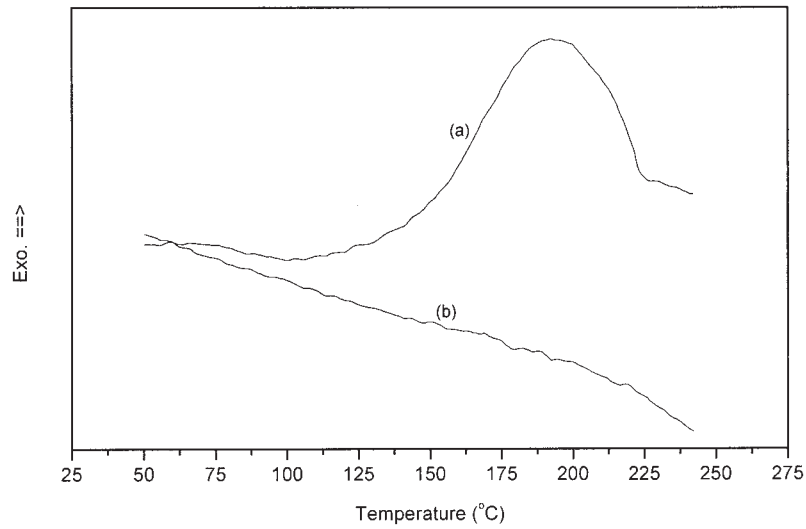**Figure 2** FTIR spectra of the silica nanoparticles cured epoxy resins.

Figure 3 DSC thermograms monitoring the reaction of BE188/silica (30 phr) blend: (a) nanoscale silica and (b) microscale silica.
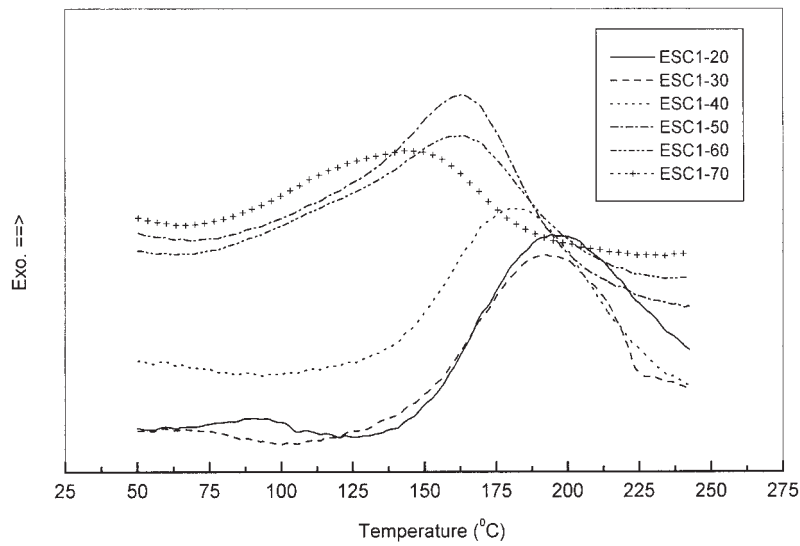

Figure 4 DSC thermograms of nanoscale silica curing BE188 reactions: the effect of the amounts of silica.
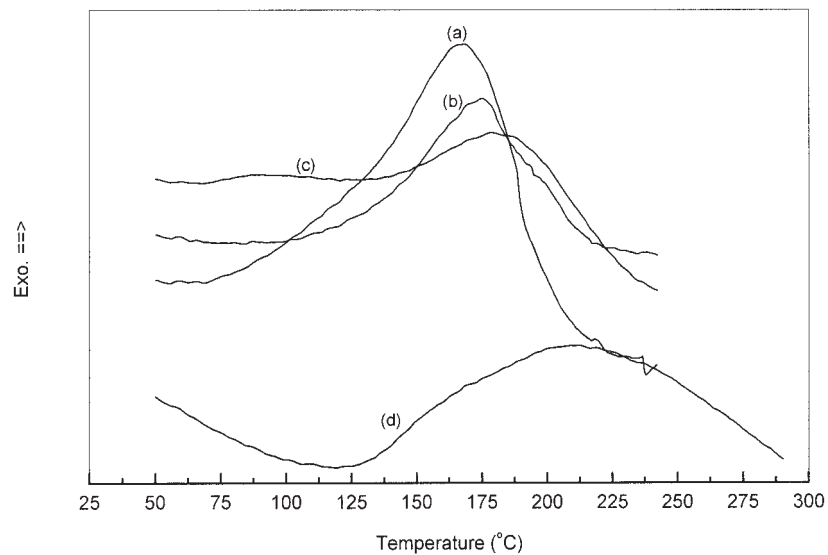

Figure 5 DSC thermograms of nanoscale silica curing Be188 reactions: the effect of adding metal salts (5000 ppm). (a) ESC1-50, (b) ESC1-50/Mg, (c) ESC1-50/Sn, and (d) ESC1-50/Zn.

TABLE II
The Activation Energies (kJ/mol) of the Silica Nanoparticles/BE188 Curing Reactions

Sample	Amount of metal salts (ppm)	Kissinger's method	Ozawa's method
ESC1-50	5000	71.3	74.8
ESC1-50/Sn	5000	72.6	76.3
ESC1-50/Zn	5000	71.5	79.0
ESC1-50/Mg	5000	46.0	50.8
ESC1-50/Mg-II	2500	72.0	74.0
ESC1-50/Mg-III	10,000	60.0	64.8

Chemical Co., Tokyo, Japan), zinc acetylacetonate hydrate (Lancaster Chemical Co., White Lund, UK), and magnesium chloride (Aldrich Chemical Co., USA) were used as received.

Experimental procedures

FTIR spectra were measured with a Perkin–Elmer Spectrum One FTIR. Differential scanning calorimetry thermograms were recorded with a thermal analysis (TA) DSC-2900 in a nitrogen gas flow of 40 mL/min. Thermogravimetric analysis (TGA) was performed by a TA TGA-2050 at a heating rate of 10°C/min under nitrogen or air atmosphere. The gas flow rate was 100 mL/min. Atomic force microscope (AFM) measurement was carried out with an AFM (Seiko SPI3800N, Series SPA-400). Scanning electron micrographs (SEM) and energy-dispersive X-ray spectroscopy (EDS) micrographs were observed with a JEOL JSM 840A SEM.

Preparation of silica cured epoxy resins

A certain amount of MIBK-ST (30 wt % of silica in MIBK) and BE188 were mixed together with or without catalyst. MIBK was removed under reduced pressure. The resulting viscous mixture was then put in an oven to perform the thermal-curing reaction at 170°C for 2 h. The compositions of reaction mixtures were listed in Table I.

RESULTS AND DISCUSSION

The reactivity of silica nanoparticles toward curing epoxy resins was first observed with simple heating of the blended mixture of BE188 and MIBK-ST. After being heated, this mixture resulted in a transparent, hard, and brittle crosslinked resin (Fig. 1). In our previous work,[12,13] a silanol group did not show reactivity toward oxirane rings unless adding tin chloride as a catalyst. Therefore, the occurrence of this curing reaction between silica nanoparticles and BE188 is not ordinary. To compare the effects of nano- to microscale particles in curing epoxy resins, the nanoparticles were replaced with ~ 5 μm particles of fused silica in the curing composition. The reaction did not occur and left a muddylike product. It was concluded the Si—OH groups on the silica nanoparticles exhibited extrahigh reactivity toward oxirane rings. The occurrence of the silanol–epoxy addition reactions in the curing process was observed with an FTIR. Figure 2 showed the FTIR spectra of the cured samples. The absorption peak of the oxirane ring (920 cm^{-1}) was not observed for all samples, which indicates curing reac-
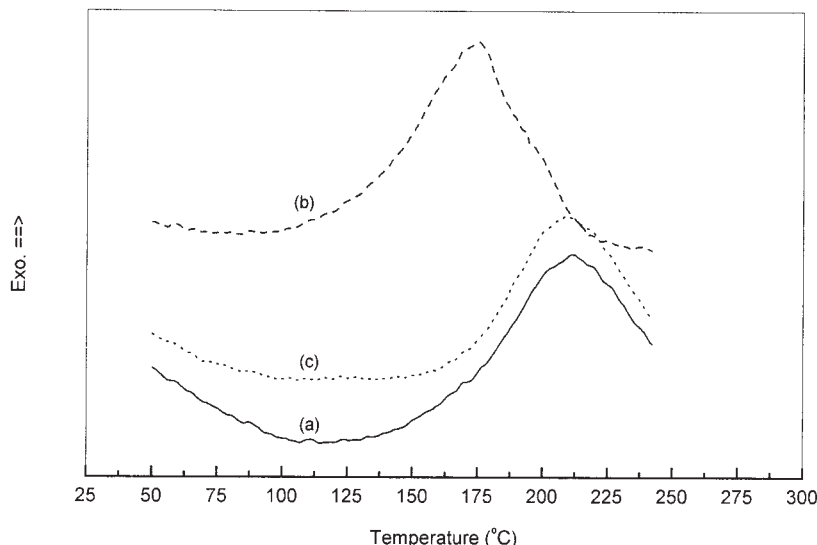

Figure 6 DSC thermograms of nanoscale silica curing BE188 reactions by adding different amounts of MgCl$_2$. (a) 2500 ppm, (b) 5000 ppm, and (c) 10,000 ppm.
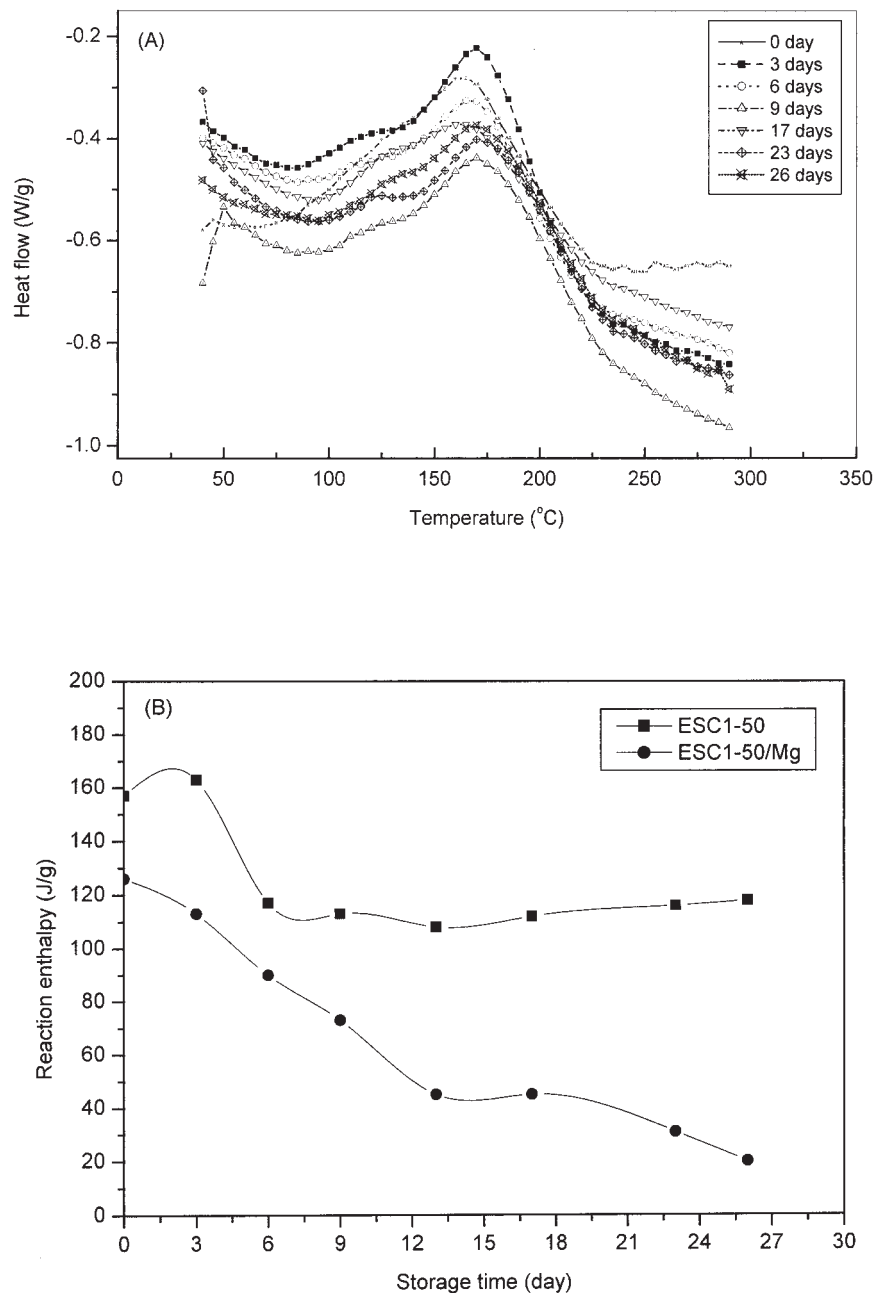
Figure 7 The storage durability of the BE188–silica mixtures monitored by DSC. (A) DSC thermograms of the ESC1-50 mixture after long-term storage; (B) the plot of reaction enthalpies obtained from DSC peak integration versus storage time.

tions on the oxirane rings. Although various contents of silica nanoparticles were introduced into the compositions (Table I), the cured resins showed a different appearance. ESC1-20 did not give a stiff and brittle product, indicating that the small amount of silica (20 phr) was not enough to completely cure BE188 resin. On the other hand, ESC1-70 showed a fractured appearance. This might be due to the high loading of the silica to result in a silica-rich composite. The transition from viscous liquid to brittle resin indicated the nanoscale colloidal silica could cure the epoxy com-

pounds, and the transparency of the resulted resins implied that this approach could be a method of preparing epoxy–silica nanocomposites.

The curing reaction between the silica nanoparticles and BE188 was monitored with DSC. The reactivity difference between the nanoscale silica and microscale silica was clearly observed with DSC thermograms, as shown in Figure 3. For the nanoscale silica/BE188 blend, the exothermic behavior was observed starting at $\sim 130°C$ and showed an exothermic peak at 182°C. On the other hand, the exothermic behavior of the
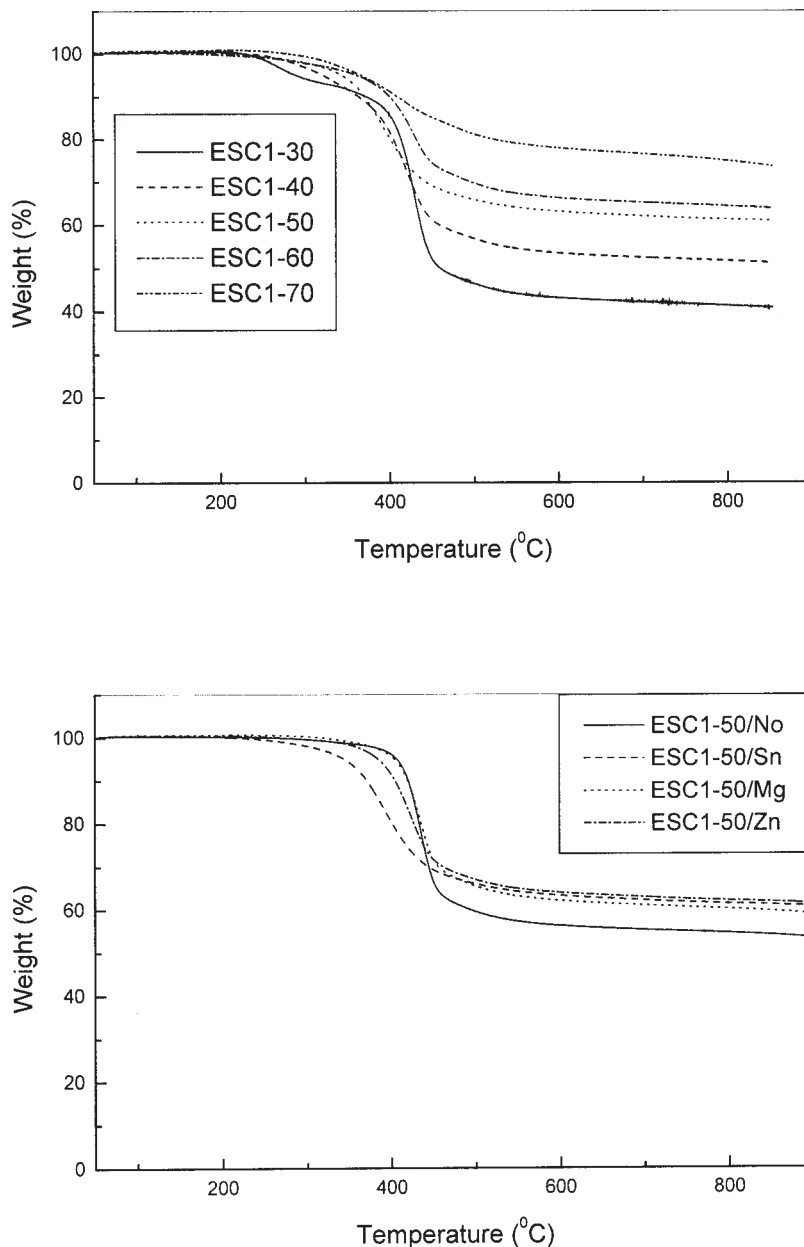
Figure 8 TGA thermograms of the prepared silica cured epoxy resins.

microscale silica/BE188 blend was not observed even at temperatures as high as 250°C. The effect of the nanoscale silica amounts on the silica/BE188 curing reactions was read from Figure 4. The reaction temperatures, as well as the exothermic peaks, shifted to a low temperature region with increasing amounts of the nanoscale silica. This could be understood with the increased surface area of the nanoscale silica. Figure 5 exhibited the effect of the addition some metal salts as reaction catalysts on the curing reactions of silica and BE188. It was surprising to find that adding these metal salts shifted the exothermic peaks toward high temperature regions, especially for zinc acetylaceto-

nate hydrate. Because these metal salts were commonly utilized as promoters for the addition reaction between hydroxyl and oxirane groups, the retardation effect of these melt salts was unusual. The activation energies of the nanoscale silica/BE188 curing reactions without and with addition of metal salts were obtained from the DSC thermograms at various heating rates by using the calculation approaches proposed by Kissinger[14] and Ozawa.[15] The results are tabulated in Table II. All of the reactions, excepting ESC1-50/Mg, exhibited a similar activation energy of ~ 70 kJ/mol. However, the relative low Ea of ESC1-50/Mg (46.0 kJ/mol) was noteworthy that magnesium
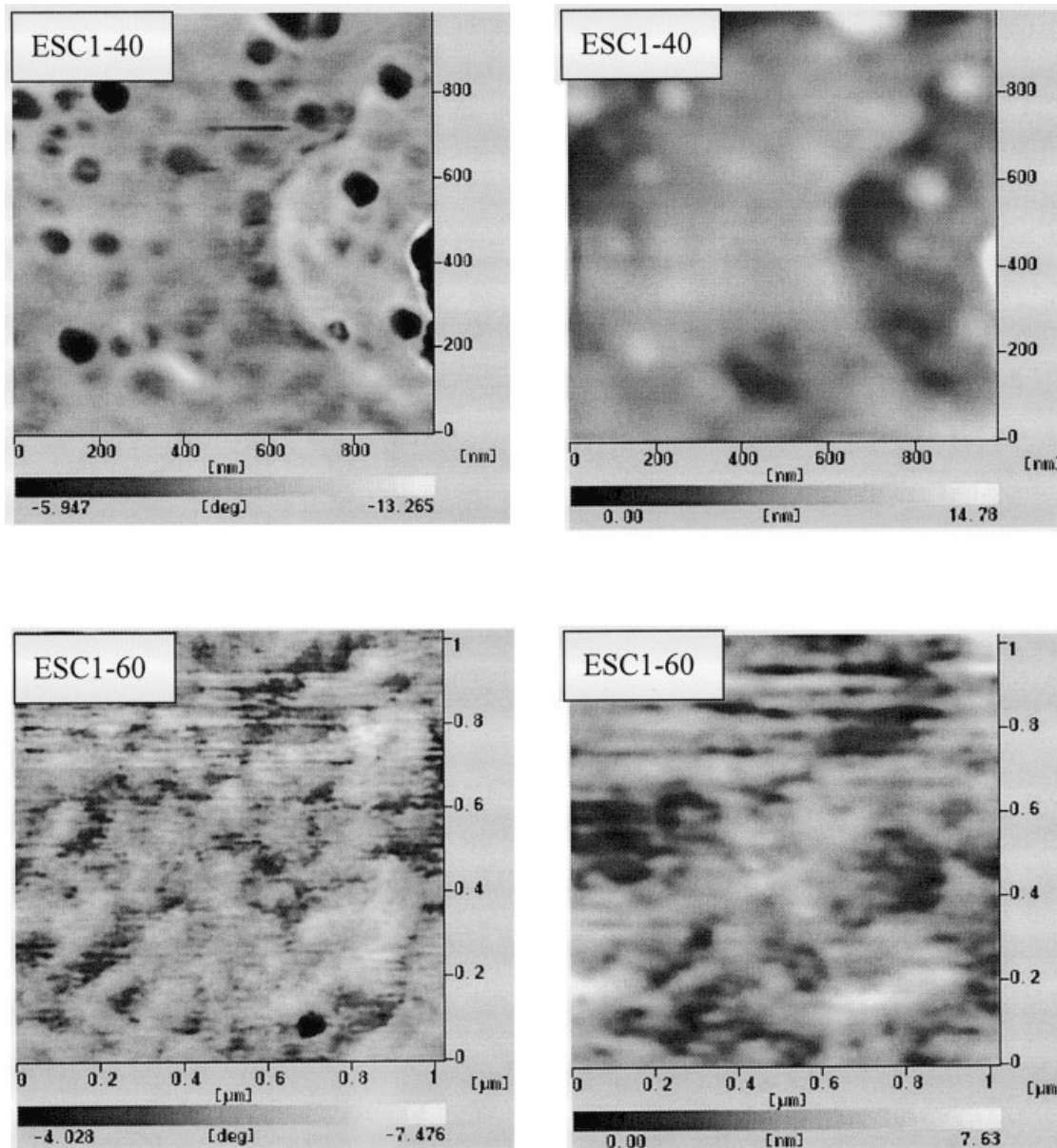
Figure 9 AFM microscopic photographs: Left: phase image; Right: topographic image.

chloride hydrate might lower the energy gap of the curing reaction and promote the curing reaction. Therefore, curing reactions with adding various amounts of MgCl$_2$ were further examined. Changing the amount of added MgCl$_2$ indeed altered the curing reaction, including reaction temperature (Fig. 6) and activation energy (Table II). MgCl$_2$ (2500 ppm) did not alter the activation energy, which implied that this small amount of MgCl$_2$ catalyst was not enough to promote the curing reactions. However, excess MgCl$_2$ played a contrary effect on promoting the curing re-action, as demonstrated with the addition of 10,000 ppm MgCl$_2$. It is speculated that the excess MgCl$_2$ might block the reaction site of the silanol groups on the surface of the silica nanoparticles.

For processing convenience and application in the premixed electronic encapsulants, thermally latent agents for curing epoxy resins are highly expected to provide long-term storage stability under ambi-ent conditions.[16–18] This characteristic was moni-tored with DSC. Below 25°C, the mixture of ESC1-50 showed a storage stability over 26 days (Fig. 7). By adding MgCl$_2$ catalyst, the storage stability was sig-nificantly decreased. This result could be under-stood with the low activation energy of the ESC1-50/Mg curing composition. On the other hand, for ESC1-50 during the first 6 days the reaction en-thalpy dropped from about 160 to 120 J/g, which was just similar to the initial reaction enthalpy of ESC1-50/Mg. However, here we do not have an
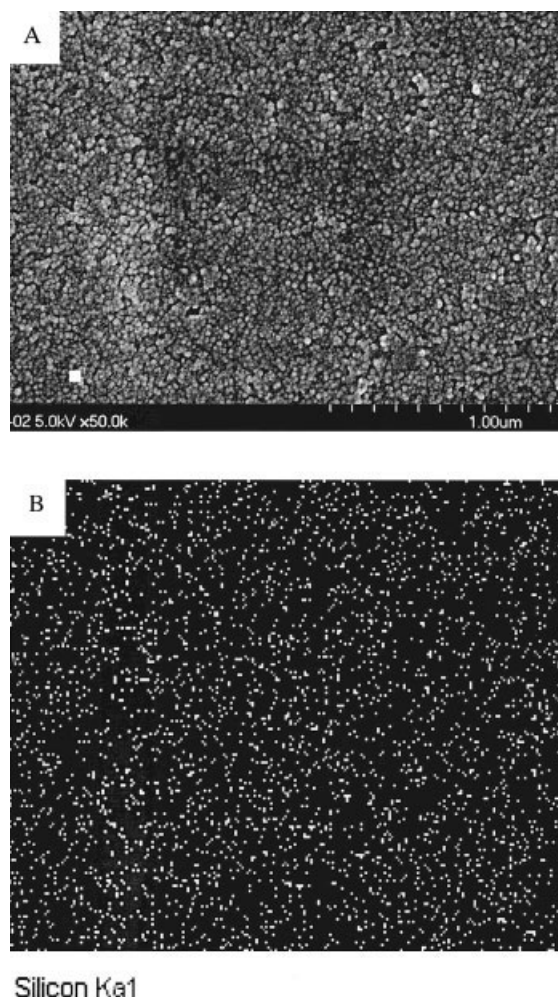
Figure 10 (A) SEM and (B) EDS Si-mapping micrographs of ESC1-50.

exact idea to illustrate this behavior, and it needs further study.

The thermal properties of the cured epoxy resins were evaluated with DSC and TGA. From DSC measurements, the cured samples did not exhibit obvious glass transition behavior until 250°C. The high thermal transition temperatures (T_g's) of the cured epoxy resins should mainly come from the high crosslinking density of the samples. On the other hand, the silica particles incorporated in the epoxy networks would seriously inhibit the chain mobility of the epoxy resins and also result in high T_g's. Figure 8 showed the TGA thermograms of the cured resins containing various silica contents. The weight loss rates of the resins were significantly reduced with the nanosilica to improve the thermal stability of the epoxy resins. In Figure 8, the TGA thermograms of cured epoxy resins with different metal salts were also shown. The variation on the weight loss patterns of the cured samples was noteworthy. Adding tin chloride dihydrate or zinc acetylacetonate hydrate

into the curing compositions resulted in cured samples showing relatively poor thermal stability. However, adding magnesium chloride hydrate did not harm the cured resins' thermal stability. The relatively poor thermal stability of the cured resins with tin chloride dihydrate and zinc acetylacetonate hydrate might be due to their uncompleted curing reaction, because these two salts might block some of the reactive sites of the silica nanoparticles. On the other hand, the relatively high char yields of the cured resins with adding metal salts might be owing to the action of the metal salts, which enhanced the dehydration reaction to form the carbonous char.

Figure 9 showed the AFM topography images and phase images of the silica cured epoxy resins, to investigate the homogeneity of the cured resins. From the micrographs, it can be seen that the silica particles were homogeneously dispersed in the resin matrix. For ESC1-40, the silica particles with diameters of about 20–30 nm were observed. However, for ESC1-60, the high silica content led to this cured material being silica-rich. The silica particles, therefore, might approach together to exhibit silica grains greater than the size of the original colloidal silica. The homogeneity of the cured resins was furthered characterized with SEM and EDS Si-mapping (Fig. 10). Homogeneous distributions of silicon on the surface of the fracture sections of the silica cured resins were observed for all samples. There was no aggregation of the silica being observed from the SEM-EDS Si mapping photograph.

CONCLUSIONS

Commercially available nanoscale colloidal silica was observed to show reactivity toward curing epoxy resins under mild temperatures of $\sim 170°C$ without adding any catalyst. The curing reaction showed dependence on the amounts of the loaded silica. An optimum amount of $MgCl_2$ added into the curing composition showed a significant effect on lowering the reaction temperature and activation energy of the curing reaction between epoxy resin and colloidal silica. The reaction indicated another convenient approach to prepare epoxy–silica nanocomposites.

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