Preparation of Epoxy Resin/Silica Hybrid Composites for Epoxy Molding Compounds

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ABSTRACT: Phenolic novolac/silica and cresol novolac epoxy/silica hybrids were prepared through *in situ* sol-gel reaction of tetraethoxysilane (TEOS). The formed hybrids were utilized as a curing agent and an epoxy resin in epoxy curing compositions, respectively. Via the two-step preparation route, the resulting epoxy resin/silica hybrid nanocomposites exhibited good thermal stability, high glass transition temperatures, and low coefficients of thermal expansion. High condensation degree of the condensed silica was observed with a high content of siloxane bridges, $p > 85\%$, measured by ^{29}Si NMR. The two-step route also provides feasibility of preparation of epoxy resin/silica hybrid nanocomposites compatible with the current processes of manufacturing of epoxy molding compounds. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 4047–4053, 2003

Key words: nanocomposites; silicas

INTRODUCTION

One of the major applications of epoxy resins in electrical and electronic industrials is for use as encapsulants of electrical circuits and electronic devices. Recently, because of the rapid development of semiconductors and electronics, epoxy resins also exhibit their versatile applications in the microelectronic packages.[1] The most common composition of epoxy molding compounds is composed of *o*-cresol novolac epoxy resin, phenolic novolac resin (curing agent), brominated epoxy compounds (flame retardant), and fused silica (filler). With the multifaceted epoxy and curing agent as well as the silica filler, the molding compounds provide good electrical, thermal, and mechanical properties.

Recent developments in semiconductor and electronic packages require molding compounds possessing superior properties of low shrinking stress, good thermal stability, low dielectric constant, and low thermal expansion coefficients. On the other hand, the high-performance epoxy molding compounds also expand their usage in other applications, for example, ceramic encapsulants. According to the literature,[2–10] an organic–inorganic nanocomposite provides enhancement of organic polymeric materials' mechanical strength, anticorrosive properties,[11] thermal stability, electrical properties, and flame retardance. Therefore,

the epoxy-based nanocomposites might be potentially utilized for the above-mentioned advanced molding compounds.

Two major inorganic materials, layered clays and nano-scaled metal oxide particles, were widely utilized for the formation of organic–inorganic nanocomposites.[11] Layered clay–epoxy nanocomposites were prepared and showed attractive properties.[12–17] An organo-modified clay is needed, and the poor compatibility between clay and epoxy resin results in limitation of the clay content (10–15 wt %) in the nanocomposites. On the other hand, for the nano-scaled metal oxide particles prepared from a sol-gel process, it is reported that high inorganic contents (up to 80 wt %) have been introduced into the hybrid nanocomposites.[18,19] Moreover, the high specific surface areas of the nano-scaled particles also enhance the hybrids' mechanical properties and fluidity.[20] This implies that the nanoparticle/epoxy resin hybrid might be a promising approach to obtain a high filler-loading epoxy molding compound with good processability and other desirable properties.[21] Conventionally, the epoxy/SiO_2 hybrid derived from the sol-gel process was prepared through mixing alkoxysilane compounds and epoxy/curing agent together in a homogenous solution, followed by heating. During the heating period, the evaporation of solvent, the curing reaction of epoxy compound, and the gelation reaction of the hydrolyzed alkoxysilane occurred simultaneously.[21–24] However, the above-mentioned solution process of preparing epoxy–silica hybrid materials was not practical for use in the manufacturing process of epoxy molding compounds. Moreover, the simultaneously

released volatiles from the gelation of the alkoxysilane sol would certainly bring about undesirable effects to the resin, and difficulties in processing during the epoxy curing reaction. To provide a solution to the above-mentioned drawbacks, the sol-gel process of alkoxysilanes was carried out along with phenolic novolac resin to form a novolac–silica hybrid, which was then utilized to replace the pristine novolac as a curing agent in the epoxy molding compound's compositions. Therefore, a new approach for utilizing an epoxy–silica hybrid as the epoxy molding compound, which is compatible with the current process, is reported in this research.

EXPERIMENTAL

Materials

o-Cresol novolac epoxy (CNE, product code: CNE200) with a epoxy equivalent weight of 200 g, and novolac resin (PF, product code:PF5110) with a hydroxy equivalent weight of 105 g were purchased from Chang Chun Plastics Co., Taiwan. Tetraethoxysilane (TEOS) and triphenylphosphine (TPP) were purchased from Acros Chemical Co. and used as received.

Instrumental measurements

Infrared spectra were obtained using a Perkin-Elmer 842 Fourier Transform Infrared Spectrophotometer (FTIR). ^{29}Si NMR spectra were recorded with a Brüker MSL-300 (300 MHz) NMR spectrophotometer with poly(dimethylsilane) as an external standard. Differential scanning calorimeter (DSC) thermograms were recorded with a Thermal Analysis Instruments (TA) DSC 2010 at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a Seiko SSC-5200H TGA at a heating rate of 10°C/min under nitrogen or air atmosphere. Thermal mechanical analysis (TMA) was conducted with a Perkin-Elmer TMA 7 instrument at a heating rate of 10°C/min. Scanning electron micro-

scopic and transmission electron microscopic photomicrographs were obtained with JEOL JSM-5600 SEM and JEOL JEM1200C-XII TEM, respectively. Atomic Force Microscopy measurements were performed with a Seiko SPI3800N AFM with the dynamic force mode. Limited oxygen index (LOI) values were measured on a Stanton Redcraft Flame Meter by a modified method as reported by the literature.[25] The percentage in the O_2–N_2 mixture merely sufficient to sustain the flame was taken as the LOI.

Preparation of PF–silica hybrids

PF (3 g) was dissolved in acetone (17.5 g). The solution was stirred at room temperature for 2 h. Then 7 g of TEOS and 1.4 g of H_2O were added to the solution. After stirring at room temperature for 10 min, the solution was stirred at 85°C for 10 h and 105°C 2 h, respectively. The solution was then poured into a glass plate. The sample was kept at ambient condition for 8 h, and then heated at 40°C under vacuum for 8 h. A transparent solid product PF70 was obtained. Other PF–silica and CNE–silica hybrids were prepared through the same process with various feeding contents (Table I).

Preparation of cured epoxy resin–silica hybrids

Equal equivalents of PF–silica and CNE were mixed together along with 500 ppm of triphenylphosphine. The curing cycles were determined from DSC tracing of the curing reactions, and performed at 160°C 1 h, 175°C 1 h, 200°C 1 h, and 220°C 0.5 h for all of the mixtures. All of the curing compositions are shown in Table II.

RESULTS AND DISCUSSION

Novolac–silica (PF70-PF30) hybrid composites were prepared according to the compositions shown in Ta-

TABLE II
The Curing Compositions of PF–Silica/CNE and PF–Silica/CNE50 Samples

Series	Sample code	Compositions	
PFXC series	PF70C	PF70	CNE
	PF60C	PF60	CNE
	PF50C	PF50	CNE
	PF40C	PF40	CNE
	PF30C	PF30	CNE
PFXC50 series	PF70C50	PF70	CNE50
	PF60C50	PF60	CNE50
	PF50C50	PF50	CNE50
	PF40C50	PF40	CNE50
	PF30C50	PF30	CNE50

TABLE I
Preparation of PF–Silica Hybrids

Sample code	Compositions (wt %)		OH equivalent weight (g)
	PF	TEOS	
PF70	30	70	178
PF60	40	60	152
PF50	50	50	136
PF40	60	40	126
PF30	70	30	118
CNE50	50[a]	50	260[b]

[a] Using CNE.
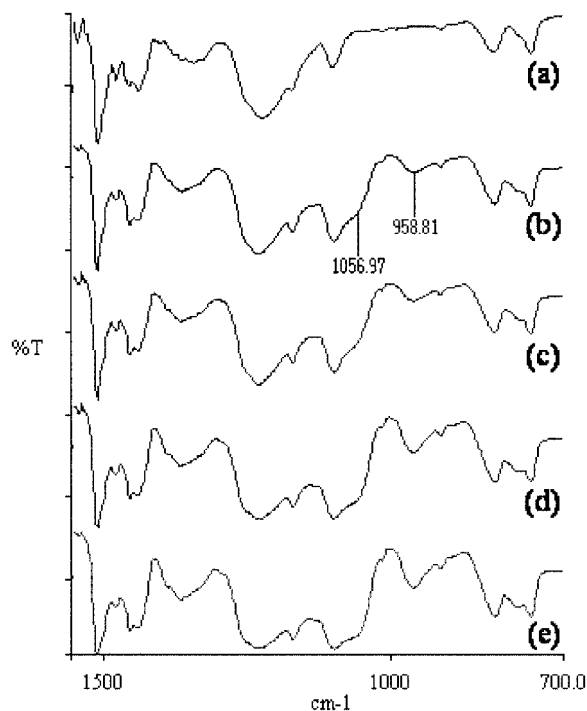[b] Epoxy equivalent weight.

Figure 1 FTIR spectra of PF70 at various sol-gel reaction stages. (a) PF; (b) PF70, 85°C 10 h; (c) PF70 85°C 10 h, 105°C 1 h; (d) PF70 85°C 10 h, 105°C 1h; (e) PF70 85°C 10 h, 105°C 2 h.

ble I. Samples with higher TEOS loadings were also attempted. However, opaque composites were obtained. This indicates occurrence of phase separation for the higher TEOS-loading samples (i.e., larger than 70%). The gelation reaction of the hybrid composites was monitored with FTIR (Fig. 1). The absorption band at 1056 and 1100 cm^{-1} increased with increasing heat-treating period, to indicate the formation of Si—O—Si bonds.[26] Similar results were also observed for CNE50 hybrid with the absorption bands at 1079 and 1101 cm^{-1}. Figure 2 shows the AFM micrographs of PF70. No obvious phase separation and inorganic clusters were observed for both the topographic and phase images. This indicates the formation of PF–silica hybrid composites.

The obtained PF–silica hybrids were cured with cresol novolac epoxy CNE, respectively. The curing reactions were monitored with DSC measurements. From Figure 3, the incorporation of silica into novolac resin did not significantly alter its reactivity toward CNE. Therefore, the formed hybrids might be utilized in the current processing conditions for the novolac/ CNE resins. Two series of the cured epoxy resins/ silica hybrids were then prepared with various curing compositions. These two series are PFXC and PFXC50, as shown in Table II. For example, PF70C means the composition of PF70/CNE, and PF70C50 represents the composition of PF70/CNE50. With FTIR charac-

terization, the occurrence of the curing reaction was indicated by the disappearance of the oxirane absorption peak (910 cm^{-1}). Figure 4 shows the ^{29}Si NMR spectra of cured PF70C and PF70C50 resins. The three peaks were assigned to the corresponding absorptions of dihydroxy-substituted silica (Q^2, −96 ppm), mono-hydroxy-substituted silica (Q^3, −103 ppm), and non-hydroxy-substituted silica (Q^4, −109 ppm). [9,25] The total amount of siloxane bridges, p ($p = Q^2/2 + 3Q^3/4 + Q^4$) , was used to evaluate the condensation degree of the condensed silica.[9,26] High p-values over 85% were obtained for the cured epoxy resin hybrids. This indicates high conversion of the Si—OH gelation re-
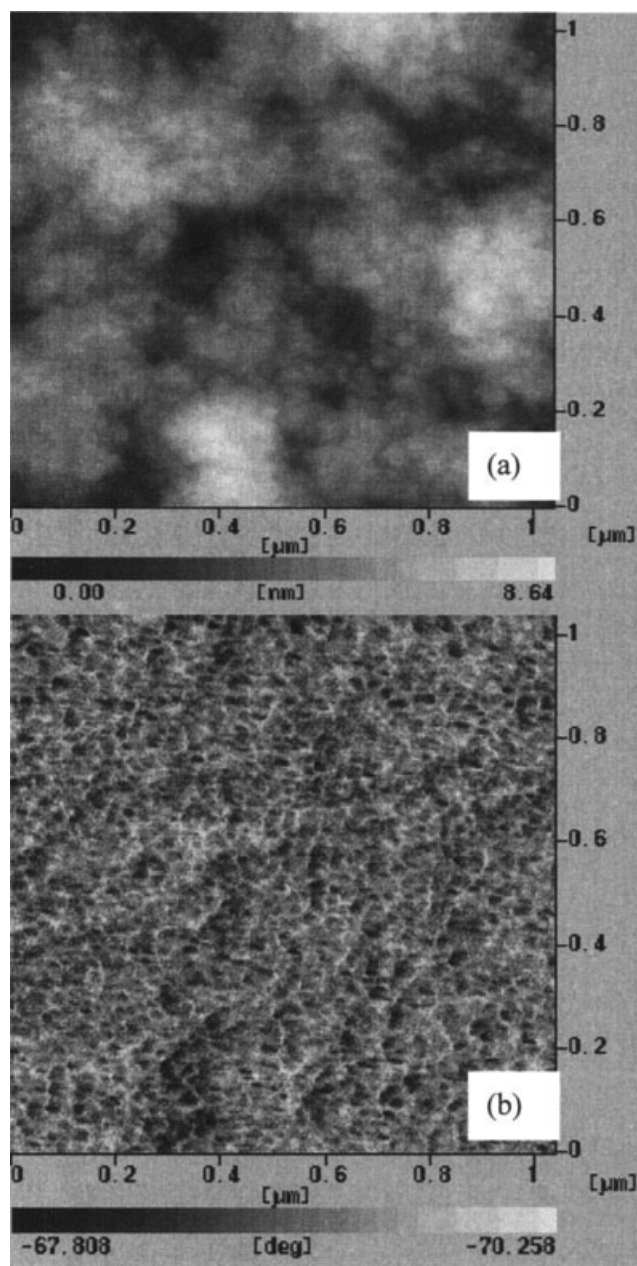

Figure 2 AFM micrographs of PF70; (a) topographic image, (b) phase image.

actions. The formed silica particles may be directly observed by AFM and TEM.[27–29] For PF70C, silica particles with diameters of about 70 nm were observed in the AFM micrograph [Fig. 5(a)]. However, the silica particles were indistinct in the TEM micrograph [Fig. 5(b)]. Because the growth of the silica gel was heavily restricted by the novolac chains and the formed epoxy network, hyperfine particles of silica might possibly form in the hybrids.[30] However, the hyperfine particles were indistinct in TEM micrographs due to similarity of the specimen thickness and the scale of the domains.[31] Nevertheless, both of the TEM and SEM micrographs of the formed hybrids did not show any macroscopic phase separation. The formation of the cured epoxy resin–silica hybrid composites in molecular scale (nanoscale) was demonstrated.

Thermal properties of the cured epoxy resin–silica hybrids were measured with DSC and TGA, and the results are listed in Table III. The cured PF–CNE resin exhibited a glass transition temperature (T_g) of about 195°C. Incorporating silica into the cured resin network would further restrict polymer chain motion, and subsequently increases the resin T_gs. The cured PFXC series resins showed barely distinct T_gs at temperatures around 200°C (Table III). For hybrids with higher silica contents, the motion of polymer chain was heavily inhibited by the formed silica network. Therefore, T_g was not detectable in the DSC measurements for the cured PFXC50 series resins due to their high silica contents. From TGA measurements (Figs. 6 and 7), the cured epoxy resin–silica hybrids showed similar weight loss pattern as the cured PF–CNE resin did. The decomposition temperatures (T_d, temperature taken at 5% weight loss; about 370°C) of the hybrids were as high as that of the cured silica-free resin, and higher than those of other epoxy resin–silica hybrids prepared from simultaneous gel-curing process.[9] The high T_ds of the cured hybrids resins also
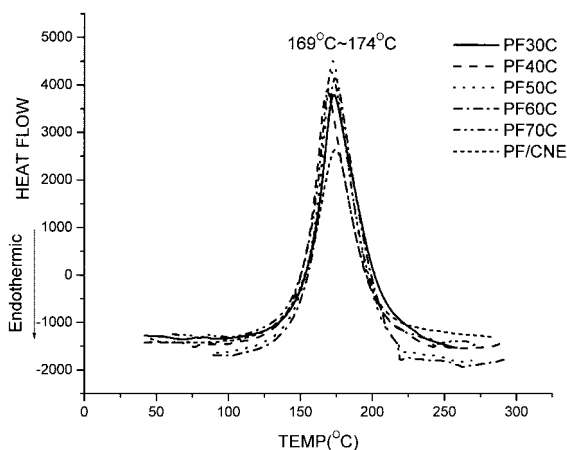

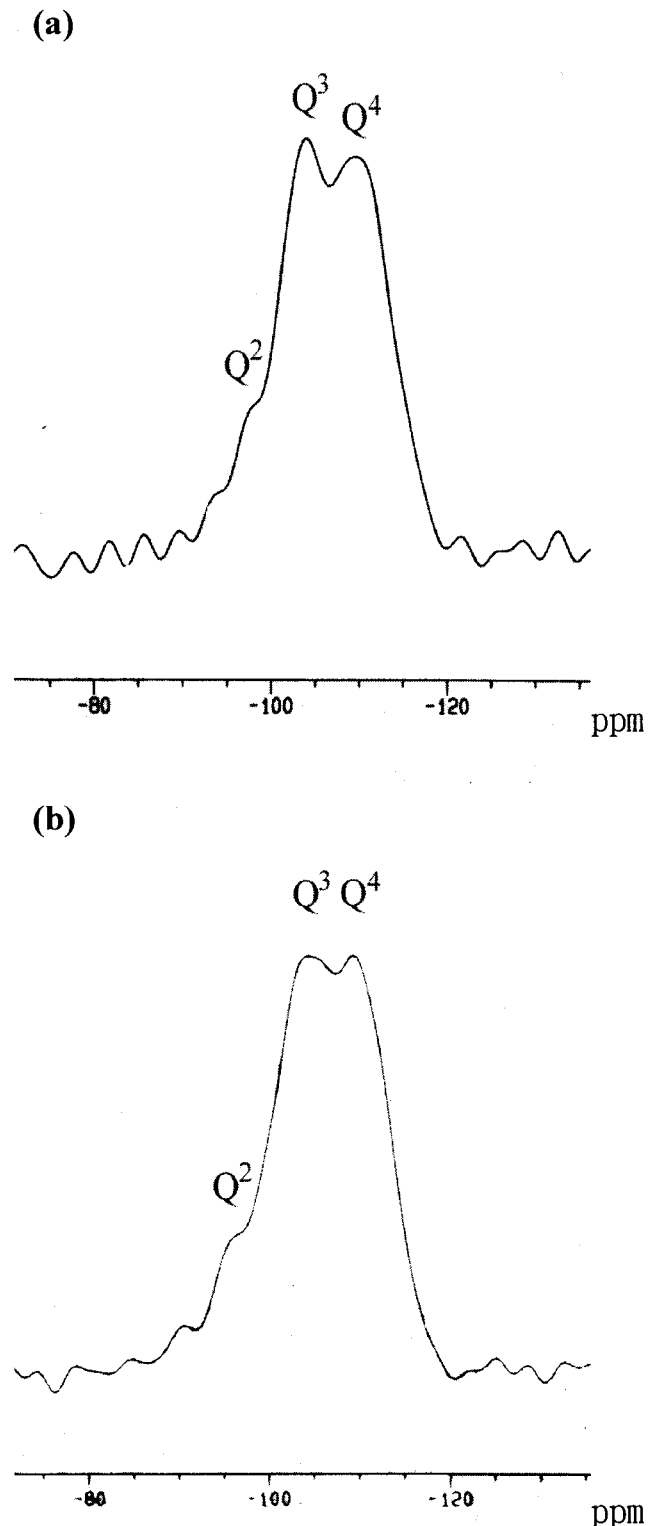**Figure 3** DSC thermograms of CNE cured with various PF–silica hybrids.

Figure 4 ^{29}Si NMR of the cured epoxy resin–silica hybrids of (a) PF70C and (b) PF70C50.

indicates the high conversion of the gel reaction of silane compounds. This further implies that these materials could be sustained in a high temperature processing environment, and therefore, is potentially use-
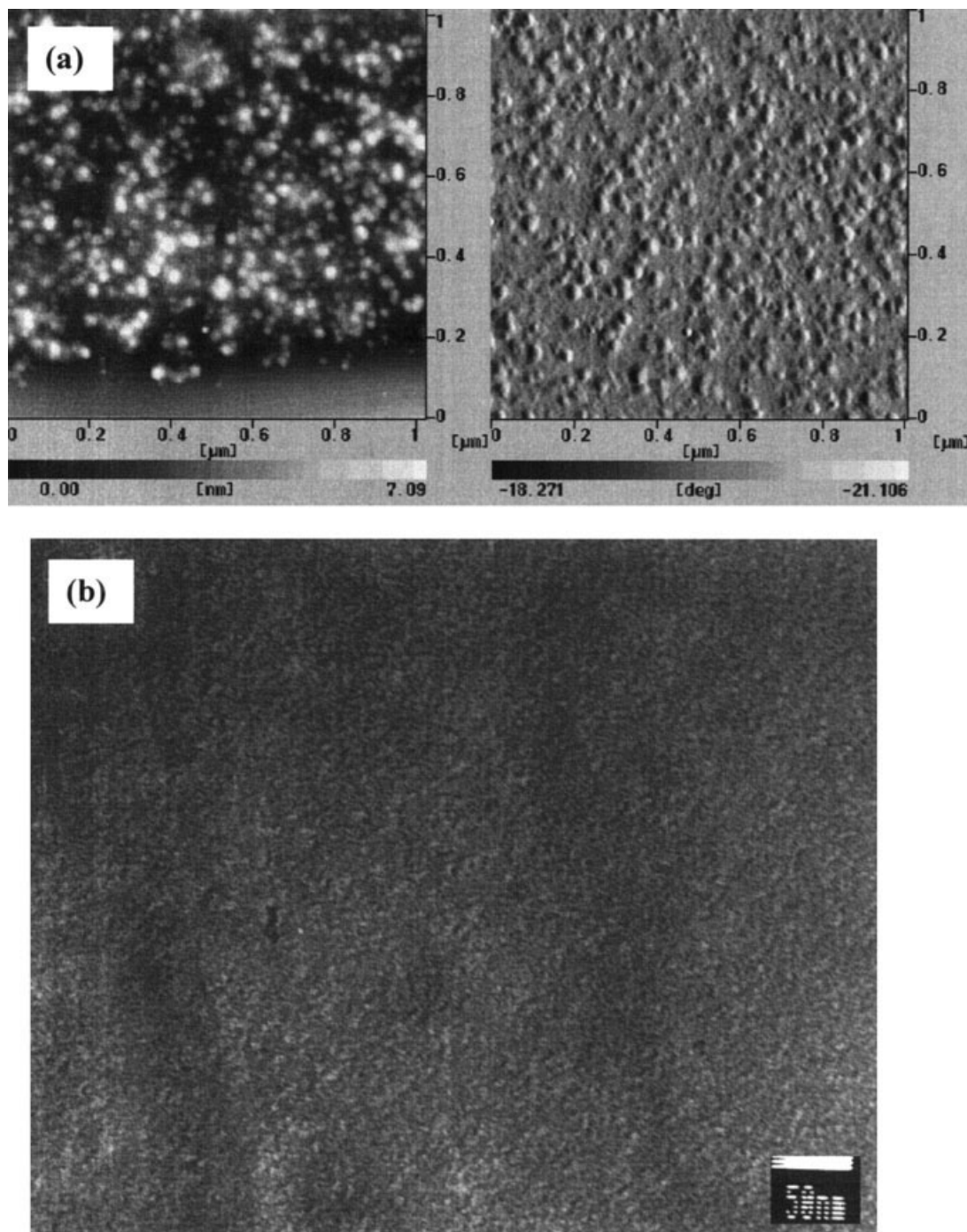
Figure 5 (a) Topographic (left) and phase (right) images of AFM micrograph of PF70C; (b) TEM micrograph of PF70C.

ful for advanced molding compounds. Moreover, silica is also known for its excellent thermo-oxidative stability to provide a retarding effect on the thermal degradation of the organic component of the hybrids. Silica can also enhance heat resistance to the hybrid resins, especially at high temperature region, and subsequently increases char formation. As shown in Table III, the char formation of the hybrids was enhanced with incorporation of silica, and increased with increasing silica content. The thermal stability of the

hybrids was further investigated using the method of integral procedure decomposition temperature (IPDT), which represent polymers' inherent thermal stability.[32–35] Introduction of silica into the epoxy resins indeed increased the hybrids' IPDT. The IPDT values of the hybrids increased with increasing silica content. The high IPDT values of the hybrids might result from their limited production of volatile fraction. This is due to the incorporation of silica. Meanwhile, the superior thermal stability of silica at high

TABLE III
Thermal Analysis of the Epoxy Resin–Silica Hybrids

Sample	T_g (°C)	$T_d{}^b$ (°C) N$_2$	$T_d{}^b$ (°C) Air	Char yield (%) N$_2$	Char yield (%) Air	IPDT (°C)
PF-CNE	195	374	374	28.1	0	807
PF30C	200[a]	368	370	36.5	3.6	927
PF40C	198[a]	370	371	38.1	3.9	951
PF50C	200[a]	368	369	41.0	5.3	973
PF60C	203[a]	371	371	41.0	5.7	986
PF70C	201[a]	370	368	44.7	6.9	1051
PF30C50	—	369	371	37.5	6.5	950
PF40C50	—	370	370	40.7	7.4	990
PF50C50	—	373	370	43.0	8.2	1032
PF60C50	—	372	371	47.3	8.9	1096
PF70C50	—	369	370	50.0	10.7	1124

[a] Barely distinct.
[b] Temperature taken at 5% weight loss.

Figure 7 TGA thermograms of the cured epoxy resin-silica hybrids under air atmosphere.

temperatures also contributed to level up the resins' IPDT.[32–35]

According to Van Krevelen's proposition,[36] polymeric material flame retardance can be evaluated with their char yields. High char yields imply less production of combustible compounds and low heat release. Both would depress the chain reactions of combustion. The flame retardance of the cured epoxy resin–silica hybrids was evaluated with measuring their LOI values. The silica-free PF–CNE resin showed a LOI value of about 22.5. The hybrids' LOI values were measured to be in the neighborhood of 23–24. It is important to note that the enhancement on LOI values was not as significant as on char formation for the hybrids. Similar result was also observed in the previous work.[9] It is suggested that the flame retardance of the polymers can be effectively enhanced by the presence of silica only when the silica is associated with some char generator, like phosphorus.
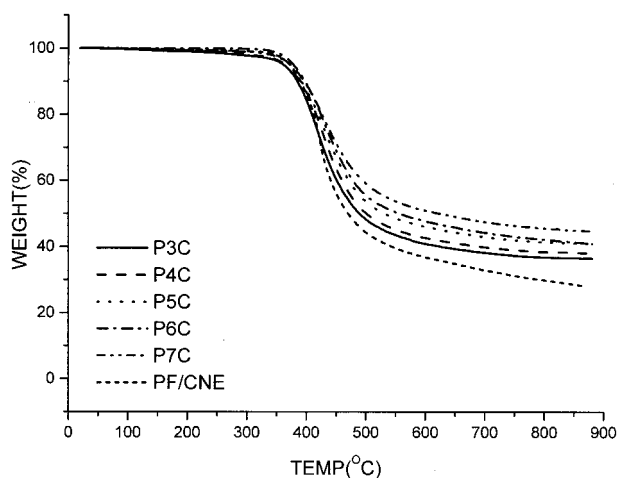
Introduction of nano-scaled silica into epoxy resins was also found to lower the resin coefficient of thermal expansion (CTE). For the cured PFXC series hybrids, the CTEs were about 69–78 ppm, which were lower than that of the cured silica-free PF–CNE (80 ppm). With higher silica contents, even lower CTEs of 65–78 ppm were found for the cured PFXC50 series hybrids. It was demonstrated that formation of epoxy resins-silica hybrid composites could increase the resin dimension stability.

CONCLUSIONS

Epoxy resin-silica hybrid composites based on cresol–novolac epoxy, and phenolic novolac curing agent were prepared through a newly modified procedure. The nano-scaled silica was introduced into PF or CNE resin through a conventional sol-gel process. The formed hybrids were then processed according to the molding compounds' compositions. High glass transition temperatures, excellent thermal stability, improved flame retardance, and low coefficient of thermal expansion were obtained for the cured epoxy–silica samples. This preparation procedure provides the resulting hybrids with improved processability and desirable properties for use as epoxy molding compounds.

Figure 6 TGA thermograms of the cured epoxy resin–silica hybrids under nitrogen atmosphere.

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