

Preparation and characterization of epoxy composites filled with functionalized nanosilica particles obtained via sol–gel process

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Abstract

To investigate the interfacial effect on properties of epoxy composites, uniform sized silica particles (S) were synthesized by sol–gel reaction and then modified either by substituting surface silanol groups into epoxide ring (S–epoxide), amine (S–NH₂) or isocyanate (S–NCO) groups or by calcinating them to remove surface silanol groups (CS). The modified particles are identified by infrared and raman spectroscopy, differential scanning calorimetry (DSC), and particle size analyzer. It has been found that surface modified particles can be chemically reacted with epoxy matrix, which is confirmed by exothermic peaks in DSC thermograms. In scanning electron micrographs of fractured composites, it is observed that the particle dispersion and interface are considerably affected by functional groups of fillers. Weak interfaces and aggregation of particles are observed for composites filled with CS or S–NCO. However, the aggregation of fillers is highly suppressed in composites filled with S–epoxide and S–NH₂ particles. Generally, the coefficients of thermal expansion (CTE) of composites are reduced with an increase of filler contents. Moreover, composites with strong interface exhibit an additional reduction of CTEs. Composites with weak interface show essentially no change in glass transition temperature (T_g) and damping with filler contents, while composites with strong interface show an increase of T_g and a decrease of damping with filler content. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy composites; Silica; Sol–gel reaction

1. Introduction

Organic materials cannot be used alone for high performance applications because they have limited properties. Therefore, organic/inorganic composites are frequently employed in order to overcome the limitation. One of the widely used organic/inorganic composites is an epoxy/silica system. Since epoxy resins as organic matrix have excellent heat, moisture, and chemical resistance and good adhesion to many substrates, they are mostly applied in the field of coatings, adhesives, casting, potting, composites, laminates and encapsulation of semiconductor devices [1,2]. However, epoxy resins, due to their low-mechanical properties and high coefficients of thermal expansion (CTE) value compared with inorganic materials, cannot meet the requirements especially for the applications of electrical and structural such as epoxy molding compounds (EMC). Thus, silica particles are commonly used for the reinforcement of epoxy matrix to lower shrinkage on curing, to decrease

thermal expansion coefficients, to improve thermal conductivity, and to meet mechanical requirements.

The intrinsic properties of each component, the shape of fillers, the nature of the interface, and so forth largely affect the properties of composite [3,4]. It is well known that the load applying on the composites is mainly transferred to be fillers via the interface. Therefore, for excellent properties, strong interfaces between components are needed. Another important factors of fillers for affecting composite properties are their contents and size. To enhance the properties, smaller size and larger amount of fillers are required. It has been already reported that the increase of specific surface area and contents of fillers enhance the mechanical and impact properties of composite [5]. However, when the size of fillers becomes smaller and the content of fillers becomes higher, the viscosity of composite resin will be too high to process. In that case, the interfacial strength will be more important factor due to their increasing surface area of fillers. One of the most promising solutions for enhancing processibility at high filler-loading system is suggested to be the surface modification of filler [6].

In general, sol–gel method is widely applied to prepare

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oxide particles with various properties such as large porous gel spheres and small particles with high density. The preparation procedures of silica particles from silicon alkoxides in alcoholic solution were developed by Stober et al. and their resultant particles are excellent in monodispersity [7]. The advantages of the sol–gel process over the traditional ceramic synthesis process are the abilities to form pure and homogeneous products at low temperature [8,9].

In this study, to investigate the effect of surface modification of fillers on composite properties, especially dynamic mechanical behavior and thermal properties, silica particles are synthesized by sol–gel process to get uniform size and surface properties. And then their surfaces are modified by substituting silanol groups into other functional groups by changing the degree of substitution (DS). It is also investigated how the surface modification of silica affects their dispersity and interfacial properties in composites.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, Fluka) as alkoxide, epichlorohydrin (Acros), Toluene-2,4-diisocyanate (TDI, Aldrich) and aminopropyltriethoxy silane (Aldrich) as surface modifiers were used as received without further purification. Ammonium hydroxide (Mallinckrodt AR, 26 degree) for sol–gel process of alkoxide and Potassium iodide (Aldrich) and crown ether (Aldrich) for epoxidization were used as catalyst, respectively. Toluene (Daejung) as reaction medium were dried by distillation with sodium for 3 days and then treated with $MgSO_4$ (Aldrich) for 1 day. Epoxy of diglycidyl ether of bisphenol A type (Kukdo Chem. Co., YD-128) and Curing Agent Z (Epon Chem. Co.) were used as received.

2.2. Preparation of silica particles

Methanol as medium and ammonium hydroxide as catalyst were mixed in a 2 l resin kettle, followed by dropwise addition of TEOS in methanol. It was carried out for 3 h at room temperature. The particle size analysis and the solution conductivity monitored the growth of particles. The particles obtained were separated by centrifuge and the supernatant was discarded. De-ionized water was added to remove catalyst. The washing procedure was repeated several times. The washed powders were air-dried and then vacuum-dried at 100°C for 2 days. The number of surface –OH group is estimated by the following titration method [10].

Two grams (W) of a sample of silica particles was weighed and charged in an Erlenmeyer flask (100 ml), and 80 ml of a 0.05 N aqueous solution of NaOH was added. The flask was sealed and then stirred for 24 h. The inorganic compounds were separated using a centrifuge and 10 ml of the solution was sampled and then titrated until neutralization

with a 0.05 N aqueous solution of HCl (A ml). The above procedures were repeated with blank solution. The amount of the solution of HCl for neutralization is B ml.

$$X = \frac{(B - A) * 0.05 * 8}{W}$$

X is the amount of the surface –OH groups per unit weight of the silica particles (mM/g).

2.3. Surface modification of silica

The silicas were functionalized stoichiometrically by substituting the surface silanol groups into amine, isocyanate or epoxide ring groups. The surface modification is illustrated in Scheme 1.

2.3.1. Calcination of synthesized silica particles

On the surface of synthesized silica particles, the structure terminates in either a siloxane group ($\equiv Si-O-Si \equiv$) with oxygen on the surface, or silanol groups ($\equiv Si-OH$). It has been investigated that heating at 373 K for a prolonged period removed all physisorbed water on solid silica. Over 878 K, most of silanol groups except small amount of isolated silanol groups, could be removed by condensing water between two silanol groups [9].

From the thermodiagram of synthesized silica particle (S) as shown in Fig. 1, it could be confirmed that most of silanol groups could be excluded by heating them to 900°C. Therefore, to eliminate surface functional groups completely, the synthesized silica particles (S) were heated to 600°C for 30 min and then to 1000°C for 2 h in a furnace.

2.3.2. Inclusion of epoxide ring onto silica surface

Fifteen gram of silica particles were dispersed in 100 ml of epichlorohydrin. 0.014 g of potassium iodide (0.084 mmol) and 0.025 g of 18-crown-6-ether (0.091 mmol) were added to this solution and then refluxed for 24 h. After cooling it, the mixture was centrifuged and then washed in acetone to remove by-products.

2.3.3. Inclusion of amine groups onto silica surface

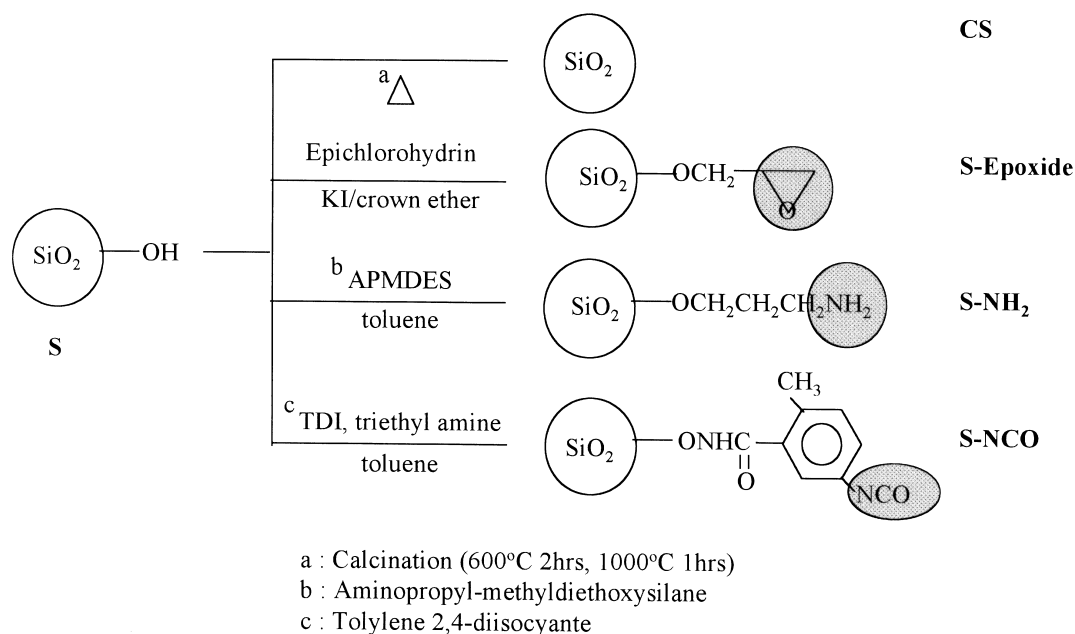
Ten gram of the synthesized silica particles were mixed with 120 ml of the solution of aminopropylmethyldiethoxy silane in dry toluene. The silica powder was centrifuged, washed three times with toluene, and cured at 150°C in a vacuum for 6 h.

2.3.4. Inclusion of isocyanate groups onto silica surface

4.73 g of TDI reacted with the prepared silica particles in dry toluene using triethylamine as catalyst. The reaction for urethane linkage formation between silanol and isocyanate group proceeded for 5 h at 40°C.

2.4. Composite preparation

All the modified particles kept at a minimum exposure to air were added in portions into liquid YD-128 epoxy and



Scheme 1.

then were dispersed into epoxy resin with ultrasonic instruments at 80°C. After mixing them uniformly, the resins were degassed at 100°C until most of entrapped bubbles were removed completely. And then, 20 phr (parts per hundred resin) of Curing Agent Z were gently mixed into minimize any air bubbles. The mixtures were cured in a preheated mold at 80°C for 2 h and then postcured at 150°C for 2 h.

2.5. Characterizations

Thermogravimetric analyses (TA) were performed with a Rigaku Thermal Analyzer. The measurement was carried out under air with a heating rate of 10°C/min from 50 to

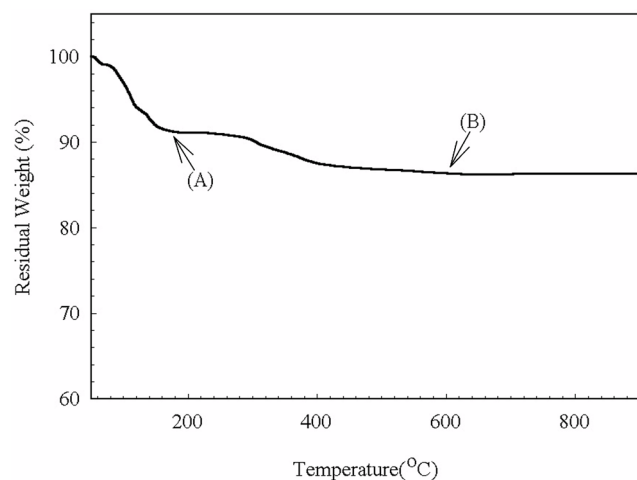


Fig. 1. TGA thermodiagram of S: (A) the dehydration temperature at which all the physisorbed water are removed; (B) the dehydroxylation temperature at which most of silanol groups are removed.

900°C. In order to estimate the DS of surface silanol groups, all of functionalized particles were titrated according to the respective titration method as suggested in Refs. [11–13]. All of the particles were treated with reagents able to react with each functional group. After the inorganic compound was separated from the solution by a centrifuge, the solution was sampled by a pipette and subjected to neutralization titration.

To examine whether modification of reaction is successfully completed and the thermal properties of the mixture of silica and epoxy, DSC (a Perkin–Elmer DSC 7) was used. Accurately weighed samples were heated in aluminum pans from 50 to 300°C at a temperature scanning rate of 10°C/min under N₂ atmosphere. Through the analysis of the exothermic peaks, the onset (T_{onset}) and exothermic temperature (T_{exo}) and the heat of reaction (ΔH) were evaluated with Perkin–Elmer DSC 7 software.

To identify surface functional groups of modified silicas, spectroscopic methods were applied. FT-IR measurements were performed on Mattson Genesis Series FT-IR with 4 cm⁻¹ resolution. Particles were mixed with dried powdery

Table 1
Typical conditions for obtaining silica particles with ca. 400 nm diameter

	Amount
TEOS (ml)	80
Methanol (ml)	800/230
NH ₄ OH (ml)	170
Rate of adding TEOS solution (ml/min)	1.1
Stirring rate (rpm)	500
Reaction time (h)	3
Reaction temperature (°C)	25

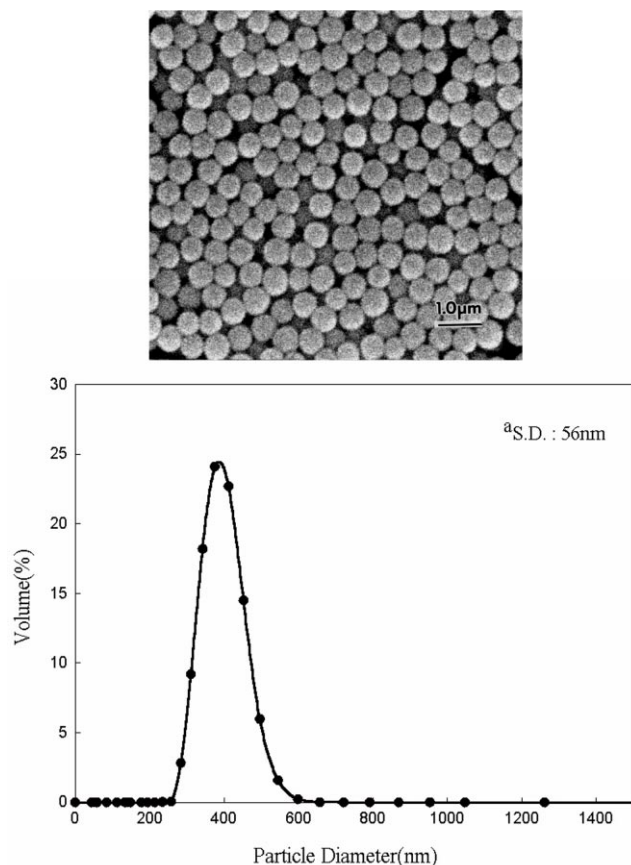


Fig. 2. SEM micrographs of prepared silica particles (S) with 400 nm diameter and their size distribution measured by particle size analyzer.

KBr, pelletized under pressure and then scanned more than 32 times. Raman measurements were carried out with Perkin–Elmer System 2000 NIR FT-Raman. Samples of FT-Raman were damped into an open-ended holder for front-surface illumination.

Particle size and its distribution were measured with laser diffraction particle analyzers (Coulter LS 230) equipped with sonication appliance.

The coefficient of thermal expansion (CTE) was measured with TMA mode of a Dupont 943 thermal mechanical analyzer. A specimen of 5 mm in thickness was tested at a heating rate of 10°C/min. The CTEs in the glassy state below T_g were taken from the slope of thermal expansion–temperature curves.

Glass transition temperature (T_g) and damping were determined by a dynamic mechanical thermal analyzer (Polymer Lab. DMTA MK III) between 100 and 250°C with a heating rate of 3°C per step at a frequency of 10 Hz. The rectangular bending mode was chosen and the dimensions of the specimen were $40 \times 7 \times 3 \text{ mm}^3$.

Scanning electron microscopy (SEM, Hitachi S-2500C) was used at an accelerating voltage of 15 kV to examine the fractured surfaces. Samples were notched by razor blade, chilled in liquid N_2 and then fractured. Due to the poor conductivity of organic materials, the fractured surfaces were coated with a thin layer (100–300 Å) of gold-palladium. This coating was carried out by placing the samples in a high-vacuum evaporator sputtering the gold metal held in the heated tungsten basket.

3. Results and discussion

3.1. Silica preparation

In sol–gel process, many researchers have already reported that the size and uniformity of resultant silica particles are greatly affected by the concentrations of TEOS, water and catalysts, the types of catalysts, reaction temperature, etc. [14–16]. Especially, the types of catalysts, acidic or basic, have been considered as the most important factors

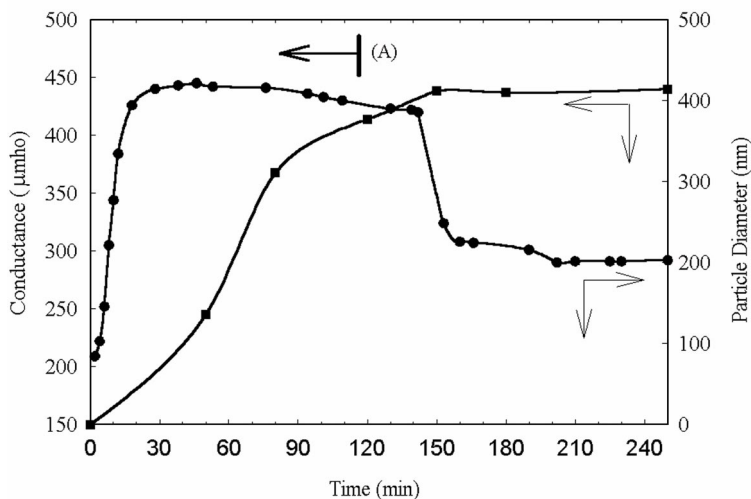


Fig. 3. Conductivity of reaction medium and particle size as a function of time by adding the mixture of 0.275 M TEOS and methanol completion of adding TEOS solution.

Table 2
Degree of substitution of surface functional groups of prepared silica particles

Code	Substituted functional group	DS ^a (mol%/g)
S	Silanol	0.18093
CS	No functional group	–
S–NH ₂ ^b	Amine	0.05875
S–NCO	Isocyanate	0.05646
S–epoxide	Epoxide ring	0.05446

^a Degree of substitution (mol% of functional groups per unit gram of silica).

^b Feed ratio of APMEDES (%).

in determining which mechanisms in silica growth are dominant. These mechanisms are generally classified into two types such as cluster–cluster growth under acidic catalysts and cluster–monomer growth under basic catalysts [17].

In this study, in order to exclude the size and shape effects of fillers on composites, silica particles with uniform diameter (ca. 400 nm) and spherical shape are synthesized by following the cluster–monomer growth mechanism. The typical conditions for obtaining silica particles with 400 nm diameter are shown in Table 1. And their size and shape are shown in Fig. 2. Measuring the conductivity of medium and particle size monitored their growing processes. It has been reported that the conductivity of medium increases with the formation of hydrolyzed TEOS and decreases with the

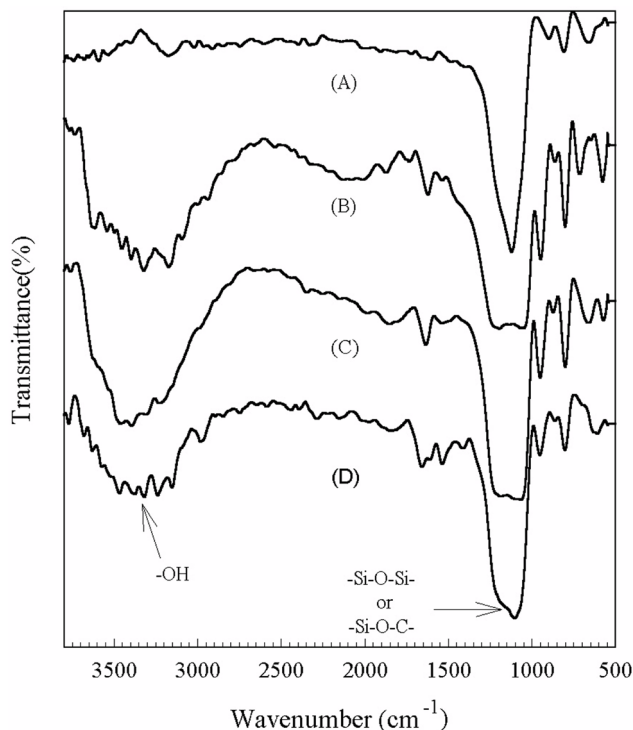


Fig. 4. IR spectra of: (A) CS; (B) S–epoxide; (C) S–NH₂ and (D) S–NCO.

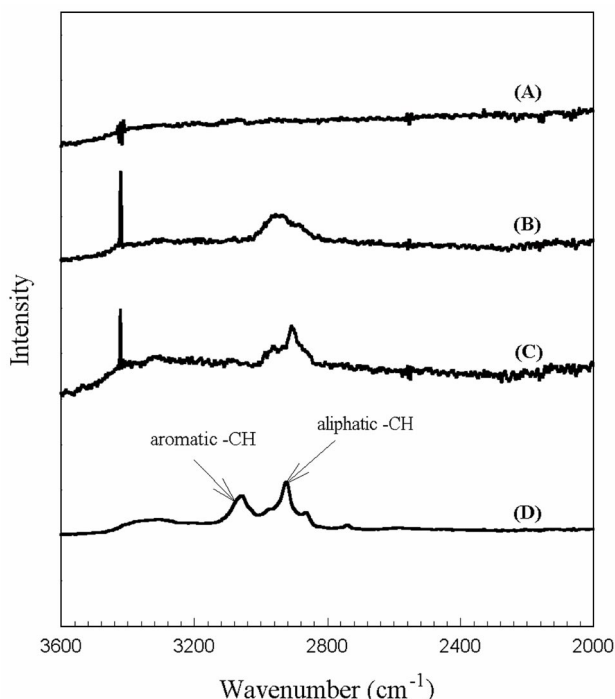


Fig. 5. Raman spectra of: (A) CS; (B) S–epoxide; (C) S–NH₂ and (D) S–NCO.

formation of siloxane linkage as shown below.

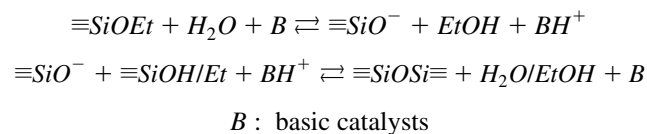


Fig. 3 shows that, after the complete adding of TEOS, the conductivity of medium and the growth of particles become constant almost at the same time. These results indicate that silica cluster may grow through the consumption of monomeric silicic acid ionic species ($\equiv \text{Si-O}^-$) [18].

3.2. Modification of silica

The name and degree of substitutions of modified silicas are listed in Table 2. The modified silicas were characterized with IR, Raman, DSC and titration method. Fig. 4 gives FT-IR spectra for prepared silica particles. The broad band between 3100 and 3700 cm^{-1} related to the presence of

Table 3
 ΔH , T_{onset} and T_{exo} characteristics of (A) YD-128/S, CS, S–NH₂ or S–NCO and (B) Curing Agent Z/S–epoxide

Sample	ΔH (J/g _{epoxy})	T_{onset} (°C)	T_{exo} (°C)
A Epoxy/S	5.24	133.5	141.2
Epoxy/CS	0.0	–	No peaks
Epoxy/S–NH ₂	280.65	76.5	130.63
Epoxy/S–NCO	52.98	185.0	216.03
B S–epoxide/curing agent	26.74	65.8	119.91

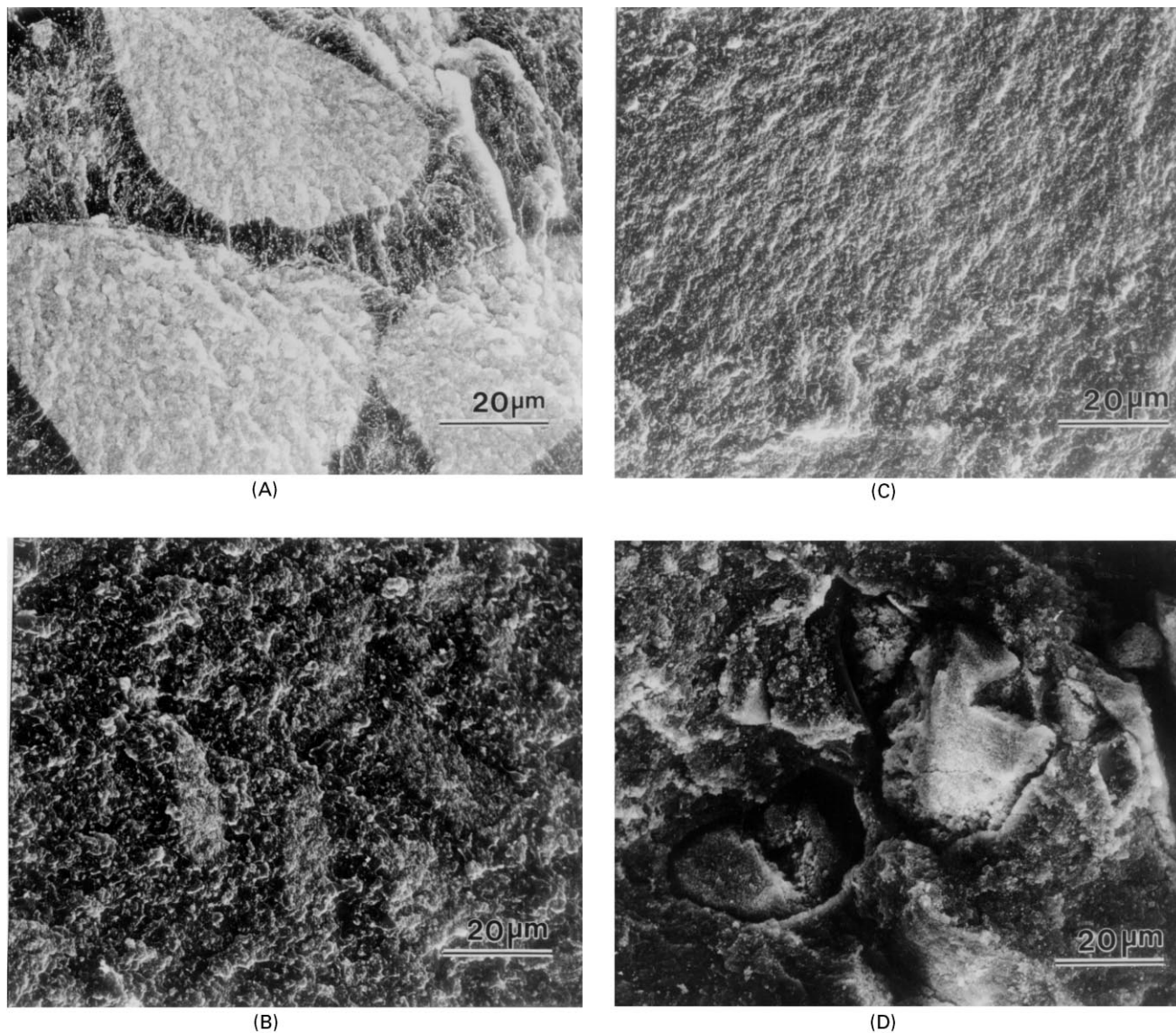


Fig. 6. SEM micrographs of fractured epoxy composites cured with 20 phr Curing Agent Z and filled with: (A) CS; (B) S-epoxide; (C) S-NH₂ and (D) S-NCO by 70 wt.%.

Si-OH and -NH₂ (S-NH₂) are detected. However, Fig. 4(A) shows that, by heating particles (S) up to 1000°C, most of silanol groups are eliminated and therefore, the peak of -Si-O-Si- (1100 cm⁻¹) has only one strong band because all of unsymmetrical -Si-O-Si- groups and -Si-O-C- groups are removed by calcination. Unfortunately, due to the strong and broad peaks of -Si-O (1250–1020 cm⁻¹), and -OH (3300–3700 cm⁻¹) groups having polar bonding, it is quite difficult to identify other functional groups only by IR spectrometer. Therefore, Raman spectroscopic analyses are carried out to observe aliphatic or aromatic CH groups formed by the substitution of surface silanol groups. Fig. 5 shows that the aliphatic CH groups (S-NH₂, S-NCO and S-epoxide) at 2900 cm⁻¹ and the aromatic CH (S-NCO) at 3100 cm⁻¹ are detected, respectively. From these spectroscopic analyses, it can be

ascertained that functional groups are successfully introduced onto the silica surface.

The exothermic peaks in DSC analysis of modified silica particles/epoxy or curing agent reveal the possibilities that chemical bonding at interface with epoxy matrix may be formed when curing the composites. For the precise investigation into the exothermic peaks, S, CS, S-NH₂ and S-NCO were mixed stoichiometrically with YD-128 to obtain the data such as the onset temperature (T_{onset}), the exothermic peak temperature (T_{exo}) and the heat of reaction (ΔH) evolved in the curing, as shown in Table 3. In case of S-epoxide, they were mixed with curing agent for ascertaining their reactivity. Table 3 shows the possibilities that S-NH₂, -NCO and -epoxide particles may have strong interface in epoxy composites because they react chemically with epoxy or curing agent. Especially, the strongest

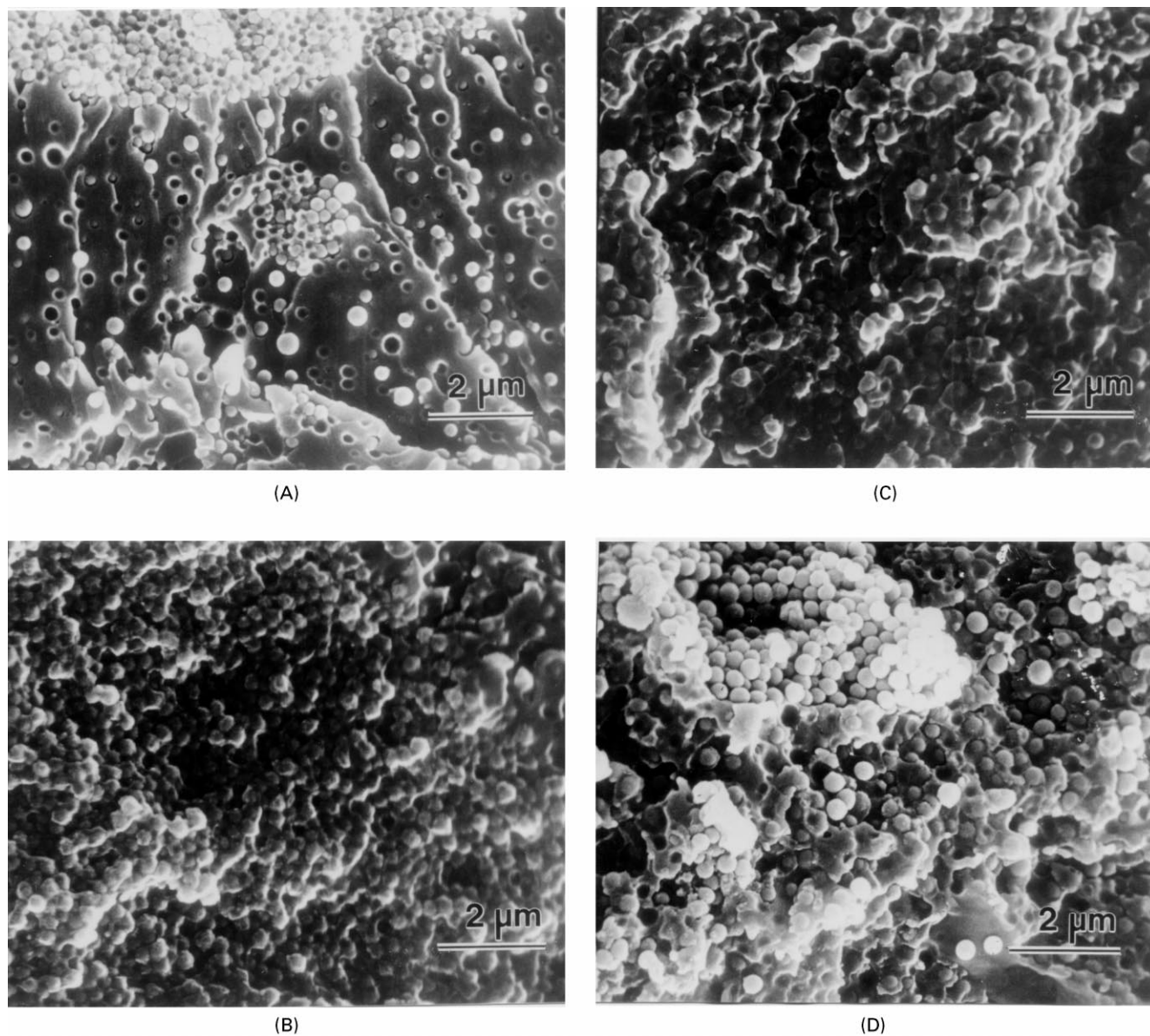


Fig. 7. SEM micrographs of fractured epoxy composites cured with 20 phr Curing Agent Z and filled with: (A) CS; (B) S-epoxide; (C) S-NH₂ and (D) S-NCO by 70 wt.%.

interface is expected to be formed in the S-NH₂ system but the poorest interface is, in the CS system.

The maximum exothermic heat is given off in the combination of epoxy and S-NH₂ particles. This may result from

Table 4
The CTEs of epoxy cured with 20 phr Curing Agent Z and filled with CS, S-epoxide, S-NH₂ and S-NCO

Filler contents (wt.%)	Linear thermal expansion coefficients (μm/m°C)				
	CS	S	S-epoxide	S-NH ₂	S-NCO
50	46.8	34.8	37.2	29.7	45.0
60	43.6	33.2	35.3	27.4	45.2
70	37.1	30.5	31.8	24.3	44.2

the reason that the reactive primary amines are shortly attached to silica surfaces compared with other modified particles. Therefore, most of surface functional groups on S-NH₂ particles can have chances to react with epoxy. However, in case of S-NCO particles, epoxy resin cannot wet their surfaces sufficiently, because they have bulky side chains such as aromatic ring. Thus, lots of isocyanate groups may be left without being reacted. This deficient reactivity will be the possible cause for poor interface.

3.3. Morphological investigation of fractured surface

Fracture surfaces of the composite samples show how the modification of silica surface affects the dispersion and interfacial properties in epoxy matrix. When epoxy

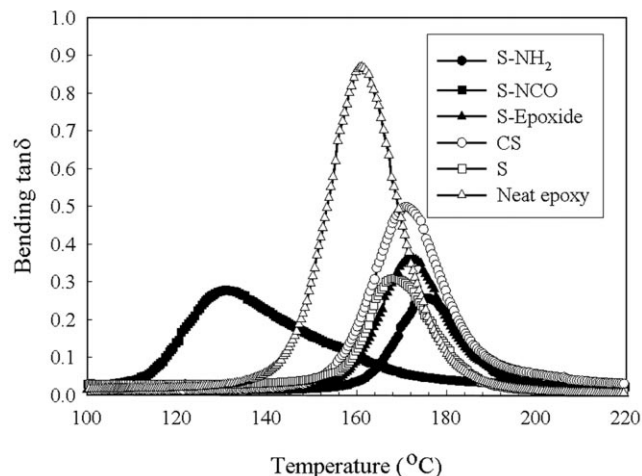


Fig. 8. Temperature dependence of the $\tan \delta$ for epoxy composites cured with 20 phr Curing Agent Z filled with 70 wt.% particles and neat epoxy.

composites are filled with CS having no functional group, most of fillers are aggregated as shown in Fig. 6(A). But in case of S-epoxide and S-NH₂ having reactive groups, suppressed aggregation is detected due to their enhanced resin-wettability. However, although S-NCO also has reactive groups, most of particles are aggregated even more severely than CS particles. This severe aggregation may be due to the reason that the onset temperature for reacting S-NCO with epoxy resin is higher than those for mixing and curing of composite, as shown in Table 3, and their bulky side groups make it more difficult for the epoxy resin to wet the silica surface. At the higher magnification investigation (Fig. 7), the interfacial strength can be examined more clearly. The poor interface is observed in CS and S-NCO systems. However, chemically reactable silica particles such as S-epoxide or S-NH₂ show strong interfaces in epoxy composites. Even at the micron scale

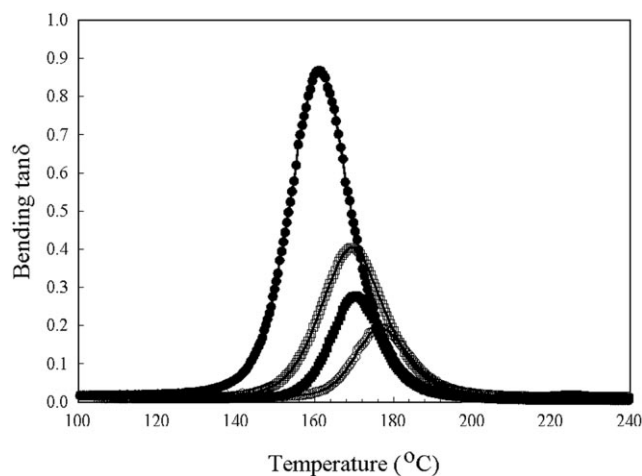


Fig. 9. Temperature dependence of the $\tan \delta$ for epoxy composites cured with 20 phr Curing Agent Z and filled with S-NH₂ (□) 50 wt.%; (■) 60 wt.%; (○) 70 wt.% and (●) neat epoxy.

investigation of fractured surfaces, it is shown that S-NH₂ particles are not aggregated.

3.4. The CTEs of composites

The main causes of internal thermal stress failure of epoxy composites are considered to be the residual stresses due to shrinkage in the curing process and CTEs mismatch among the components. From the following equation expressing the thermal stress (S) of composites, it can be known that thermal stress is highly affected by the CTEs and flexural modulus of matrix [19–21].

$$S = k \int (\alpha_m - \alpha_x) E_m dT \quad (1)$$

where k is a constant, α_m and α_x are thermal expansion coefficients of matrix and other non-organic components, respectively, and E_m is a flexural modulus of matrix. From Eq. (1), it can be known that decreasing CTEs or flexural modulus of matrix reduces either thermal stress. In general composite systems, the expansion of the matrix is constrained, due to the presence of inorganic filler [20]. Therefore, as shown in Table 4, CTEs of composites reduce as the increase in the content of silica. However, with an increase in filler contents, the increase of elastic modulus and viscosity of resin result in poor moldability. Table 4 also shows that the CTEs are significantly affected by interfacial properties of fillers. In strong interfacial system, thermal expansion of composites is more reduced compared with that in poor interface system. From these results, it can be inferred that functionalized fillers such as S-epoxide and S-NH₂ reacting with epoxy matrix may have acted as the rigid crosslinking points in composites.

3.5. Dynamic mechanical properties of composites

Figs. 8 and 9 show the temperature dependence of $\tan \delta$ (damping) for the composites investigated. The DMTA results reconfirmed that the entire properties of composites are greatly affected by the content and interfacial characters of fillers. It has been reported that in sulfonated PS/alumina composite system, the addition of rigid fillers in matrix made it difficult to move the polymer chain and therefore damping decreased and glass transition temperature (T_g) were shifted to higher temperature [22]. Consistently, in this study, the damping is strikingly changed with the interfacial properties at the investigation with fixed loading of fillers as shown in Fig. 8. The damping lowers when fillers are better dispersed and bonded strongly with matrix. This may be due to the decrease in the friction by filler/filler and filler/matrix, which were suggested as the main reason for damping in composite system [3,23]. In addition, the T_g s of filled composites except for the S-NCO systems are detected in higher temperature than that of neat epoxy and show the tendency of slight increase as the interfacial strength. The broad peak of $\tan \delta$ in S-NCO system reveals

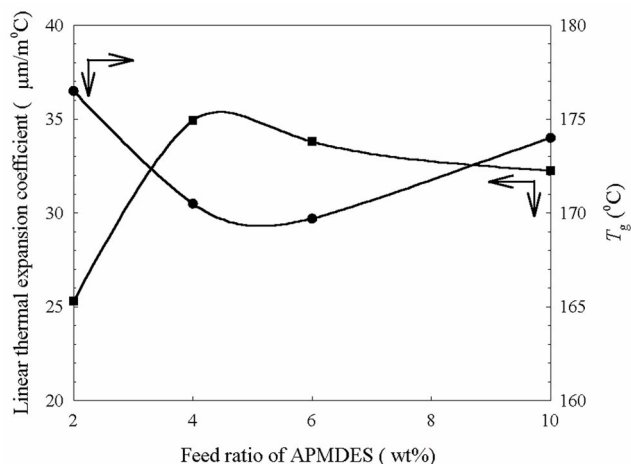


Fig. 10. Effect of number of surface amino groups on S–NH₂ particles on epoxy composites cured with 20 phr Curing Agent Z.

that lot of isocyanate groups on S–NCO particles still remained even after post-curing of composites.

Fig. 9 shows that the reduction of damping and the increase of T_g of composites occur with the contents of S–NH₂. Such increases in T_g are thought to result from the constrained chain mobility by well-dispersed fillers. However, in weak interface system (CS), no significant changes in damping and T_g are observed due to the severe aggregation of fillers.

3.6. Effects of the amount of surface functional groups

In order to find the optimum amount of surface functionalities, the variations of T_g and CTEs were investigated by changing the feed amount of APMDDES when preparing S–NH₂ particles. Increases in feeding amount have substituted surface silanol groups into amino group almost proportionally. Fig. 10 shows that the properties of epoxy composites are highly affected by the amount of surface amino groups. The increase in T_g and decrease in thermal expansion of composites are shown due to better interface by around 5 wt.% of APMDDES, but unexpectedly, over that amount, their values turn to the contrary. It was expected that increase in surface functional group would make the properties of composites improve and then over the optimum DS, properties would be saturated. Instead of saturation in properties, increase in T_g and decrease in CTE have happened. This may be due to the reason that extra amine groups, in epoxy-amine curing system, make the cross-link density of epoxy composites reduced, and therefore, their properties show the tendency to weaken.

4. Conclusions

The properties of epoxy/silica composites are highly

influenced by the interfacial strength between matrix and fillers. Compared with S–NCO with bulky substituents, S–epoxide and S–NH₂ with smaller and more reactive substituents show the better distribution of silica particles in epoxy matrix, because of better resin-wetability. Furthermore, strong interfaces are observed in fracture surfaces of composites filled with silica particles reactable with matrix below the temperatures of mixing and curing.

Among the various modified epoxy/silica systems investigated, S–NH₂ system having the highest reaction heat shows the best dispersion of fillers and the strongest interfaces. Even at the same level of filler loading, the amount of the reductions of CTEs and damping and the increase of T_g of matrix are much higher for S–epoxide and S–NH₂ systems than those of CS and S–NCO systems, confirming that functional groups such as epoxide and NH₂ on the surface of silica particles produce very strong interface between matrix and filler.

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