

Curing of Epoxy Resin by Hyperbranched Poly(amidoamine)-grafted Silica Nanoparticles and Their Properties

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Hyperbranched poly(amidoamine)-grafted silicas having terminal boron trifluoride groups (Silica-PAMAM:BF₃) were prepared by the treatment of terminal amino groups of the hyperbranched PAMAM-grafted silica with boron trifluoride diethyl ether complex. Silica-PAMAM:BF₃ has an ability to cure epoxy resin to give a novel epoxy resin/silica nanocomposite. It was observed that after the curing by Silica-PAMAM, the absorbance of amino groups decreased. It was confirmed by AFM that PAMAM-grafted silica nanoparticles were uniformly dispersed in the cured epoxy resin matrix. The thermal stability and glass-transition temperature of the epoxy resin/silica nanocomposite were considerably higher than those using ethylenediamine (EDA) as a curing agent in the presence of untreated silica. The storage modulus of the epoxy resin/silica nanocomposite in rubbery region increased and the peak area of tan δ curve at glass-transition region decreased in comparison with epoxy resin cured by EDA in the presence of untreated silica. In addition, the glass-transition temperature increased with increasing content of Silica-PAMAM:BF₃. The epoxy resin/silica nanocomposite was found to show higher adhesive strength between aluminum plates. Based on the above results, it is expected that silica nanoparticles are incorporated uniformly with chemical bonds in the continuous epoxy resin network.

KEY WORDS: Silica Nanoparticle / Poly(amidoamine) / Surface Grafting / Epoxy Resin / Boron Trifluoride / Amine Complex / Curing / Adhesion /

Nanoparticles, such as carbon black and silica, are widely used industrially as a filler and a pigment for polymer materials. In general, it is difficult to disperse nanoparticles uniformly into polymer matrices and solvents because of the formation of strong aggregation. In addition, mechanical properties of nanocomposites from nanoparticles and polymer are considered to depend not only on the mechanical properties of the polymer matrices but also on the properties of interfacial regions between the nanoparticle surfaces and polymer matrices. Therefore, the surface modification of nanoparticle surfaces has become of major interest lately.

The surface modification by grafting of various polymers onto nanoparticles¹⁻³ and nanofiber^{4,5} surfaces has been widely investigated. Polymer-grafted nanoparticles and nanofibers can be uniformly dispersed in solvents and polymer matrices. It is very interesting to note that by grafting of polymers onto nanoparticles, novel functional inorganic/organic hybrids may be obtained. Nanoparticles have excellent properties, such as heat resistance, high strength, resistance to chemical attack, low thermal expansion, and low electrical conductivity. By grafting of functional polymers onto the surfaces, nanoparticles may be endowed with special functions such as photosensitivity, bioactivity, crosslinking ability, and amphiphilic properties.¹⁻⁵

We have reported the surface initiated graft polymerization of various monomers onto silica nanoparticle by using previously introduced initiating groups on the surface, such as

azo⁶ and peroxyester,⁷ acylium perchlorate,⁸ and potassium carboxylate.⁹

In addition, we have reported that hyperbranched poly(amidoamine) (PAMAM) can be grown from amino groups on silica nanoparticles,¹⁰ chitosan powder,¹¹ and carbon black¹² surfaces using dendrimer synthesis methodology (Figure 1). Grafting was achieved by repeating the following two processes in methanol¹⁰⁻¹² and in solvent-free dry-system:¹³ (1) Michael addition of amino groups on the surface to methyl acrylate (MA), and (2) amidation of the resulting terminal methyl ester groups with ethylenediamine (EDA). The resulting PAMAM-grafted silica has potential as a catalyst and an enzyme support, because they have many terminal amino groups. We have pointed out that the hyperbranched PAMAM-grafted silica acts as curing agent of epoxy resin.¹⁴ In addition, the immobilizations of norbornadiene moieties onto hyperbranched PAMAM-grafted silica and the application to solar energy conversion and storage material have been reported.¹⁵

On the other hand, epoxy resin exhibits many desirable properties, such as high strength and modulus, low shrinkage during curing reaction, excellent chemical, and solvent resistance, good thermal and electrical properties, outstanding adhesion to various substrates, and easy process ability under various conditions.

In this paper, the preparation of epoxy resin/silica nanocomposite by the curing of epoxy resin using hyperbranched

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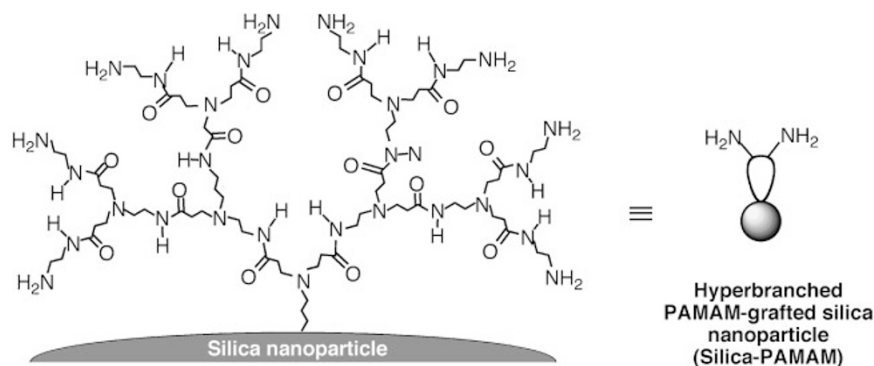


Figure 1. Schematical illustration of hyperbranched PAMAM-grafted silica nanoparticle.

PAMAM-grafted silica having BF_3 -amine complex groups as a curing agent was investigated. Moreover, the thermal, mechanical, and adhesive properties of the epoxy resin/silica nanocomposite thus obtained were investigated.

EXPERIMENTAL

Silica Nanoparticle

Silica nanoparticles used was Aerosil 200 and it was obtained from Nippon Aerosil Company, Ltd., Japan. The silica was dried *in vacuo* at 110°C for 48 h before use. The properties of the silica nanoparticle are shown in Table I. The silanol group content was determined by volumetrically measuring the amount of ethane evolved by the reaction with triethylaluminum.¹⁶

Reagents

Methyl acrylate (MA) obtained from Kanto Chemical Co., Inc. was distilled under reduced pressure. Ethylenediamine (EDA) obtained from Kanto Chemical Co., Inc. was refluxed over sodium and distilled just before use. Boron trifluoride diethyl ether complex obtained from Kanto Chemical Co., Ltd. was used without further purification. Other reagents and solvents were purified by the ordinary methods before use.

Epoxy Resin

Epoxy resin, Araldite AER 260 (Bisphenol-A type) obtained from Asahi-Ciba Ltd., Japan, was used without further purification. The epoxy equivalent and viscosity at 25.0°C are $180\text{--}200\text{ g/equivalent}$ and $1.2 \times 10^3\text{--}1.6 \times 10^3\text{ mPa}\cdot\text{s}$, respectively.

Introduction of Amino Groups onto Silica Nanoparticle Surface

The introduction of amino groups onto silica surface was

achieved by the reaction of silanol groups on the surface with γ -aminopropyltriethoxysilane (γ -APS) in solvent-free dry system. The detailed procedures were described in the previous paper.¹³ The resulting silica having amino groups was abbreviated as Silica- NH_2 .

Grafting of Hyperbranched PAMAM onto Silica Nanoparticle Surface

Grafting of hyperbranched PAMAM from the silica surface was achieved by use of methodology of polyamidoamine dendrimer synthesis, which contains repeating two processes in a solvent-free dry-system: (1) Michael addition of MA to amino groups, which were previously introduced on the surface, and (2) amidation of terminal ester groups with EDA. The detailed procedures were described in the previous paper.¹³

Determination of Percentage of Grafting

The percentage of hyperbranched PAMAM grafting onto silica nanoparticle surface was determined by the following equation:

$$\text{Grafting (\%)} = (A/B) \times 100,$$

where A is weight of hyperbranched PAMAM (g) grafted onto the surface and B is weight of silica nanoparticle charged (g). The amount of hyperbranched PAMAM grafted onto the silica surface was determined by weight loss when the PAMAM-grafted silica was heated at 800°C by use of a thermogravimetric analyzer (TGA) (Shimadzu TGA-50).

Preparation of Hyperbranched PAMAM-grafted Silica Nanoparticle Having BF_3 -amine Complex Groups

Preparation of hyperbranched PAMAM-grafted silica nanoparticle having BF_3 -amine complex groups was carried out by the reaction of terminal amino groups of hyperbranched PAMAM on the silica surface with boron trifluoride diethyl ether complex.¹⁷ A typical example is as follows. Into a 100 mL flask, 0.10 g of hyperbranched PAMAM-grafted silica, 0.15 g of boron trifluoride diethyl ether complex, and 10 mL of diethyl ether as solvent were charged. The mixture was stirred with a magnetic stirrer for 24 h at 0°C . After the reaction, the solvent and unreacted boron trifluoride diethyl ether complex

Table I. Properties of silica nanoparticle

Silica nanoparticle	Specific surface area (m^2/g)	Particle size (nm)	Silanol groups (mmol/g)
Aerosil 200*	200	12	1.37

*Nippon Aerosil Co., Ltd., Japan.

was removed by evaporation and the resulting silica was repeatedly washed with diethyl ether.

Curing of Epoxy Resin

Curing of epoxy resin was carried out by the reaction of terminal BF_3 -amine complex groups of hyperbranched PAMAM-grafted silica surface with epoxy groups of epoxy resin. A typical example is as follows. Into a sample tube, 0.35 g of PAMAM-grafted silica having BF_3 -amine complex groups and 2.5 g of epoxy resin were added. The mixture was uniformly mixed with a rotation and revolution super-mixer (Thinky Model AR-100). The mixture was poured into a poly(tetrafluoroethylene) sheet, which was coated with a fluorine releasing agent, and cured at 160°C for 24 h in an electric oven. Size of sample was $30 \times 5.0 \times 1.0$ mm.

Characterization of Epoxy Resin Cured by PAMAM-grafted Silica Having BF_3 -amine Complex Groups

The surface morphology of epoxy resin/silica nanocomposite was observed by use of an atomic force microscope (AFM) (Shimadzu Model SPM-9500). All images were obtained in the phase-contrast mode at room temperature.

The thermal property of the epoxy resin/silica nanocomposite was determined using a thermogravimetric analyzer (TGA) (Shimadzu Model TGA-50) in nitrogen. The temperature range was from room temperature to 600°C , and the heating rate was $10^\circ\text{C}/\text{min}$. The dynamic mechanical property of the epoxy resin/silica nanocomposite was determined using a dynamic mechanical analyzer (DMA) (Shimadzu Model Tritec2000) in air. The frequency and amplitude of the vibration were adjusted to 1.0 Hz and ± 0.05 mm, respectively. The temperature range was from 30 to 200°C and the heating rate was $2^\circ\text{C}/\text{min}$.

The adhesive strength of the epoxy resin/silica nanocomposite between alumina plates was measured using an Instron-type tensile machine (Shimadzu Model AGS-10KNG) at a crosshead speed of $0.2\text{ mm}/\text{min}$ at 25°C under 50% relative humidity. A test sample was prepared as shown in Figure 2.

RESULTS AND DISCUSSION

Grafting of Hyperbranched PAMAM onto Silica Nanoparticle

Table II shows the percentage of hyperbranched PAMAM grafting onto the silica surface and the amino group content of the silica after the grafting reaction in a solvent-free dry system.¹³ The hyperbranched PAMAM grafting and amino

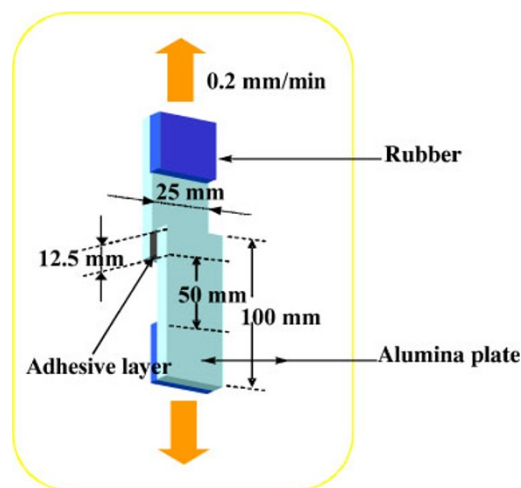


Figure 2. Shape and dimension of adhesive strength test.

group content of silica nanoparticle increased with the number of repeated reaction cycles. However, when silica having no amino groups was used, no grafting of PAMAM onto the surface and no increase in surface amino group content were observed, even after repeated reaction cycles of 6-times.

These results clearly shows that PAMAM grows from amino groups on the silica nanoparticle surface in the solvent-free dry system.

However, the grafting and amino group content at every reaction cycles were considerably smaller than those of theoretical value. This may be due to the fact that the grafted chains on the silica surface interfere with the propagation of PAMAM from the surface because of steric hindrance.¹⁰⁻¹³

Figure 3 shows FT-IR spectra of (A) γ -APS-treated silica (Silica- NH_2), (B) PAMAM-grafted silica (RC3: reaction cycles of 3-times), and (C) PAMAM-grafted silica (RC6). FT-IR spectra of PAMAM-grafted silicas show new absorptions at 1650 cm^{-1} and 1550 cm^{-1} , which are characteristic of PAMAM, and the intensity increased with increasing reaction cycles. These results also indicate that hyperbranched PAMAM grows from amino groups on the silica nanoparticle surface in the solvent-free dry system.

Preparation of Hyperbranched PAMAM-grafted Silica Nanoparticle Having BF_3 -amine Complex Groups

It is well known that the amino groups easily react with boron trifluoride to give BF_3 -amine complex.¹⁷ In general, boron trifluoride amine complex is known as a effective latent

Table II. Percentage of grafting and amino group content of Silica-PAMAM obtained from a solvent-free dry-system

Silica	Reaction cycles	Experimental value		Theoretical value	
		Grafting (%)	Amino groups (mmol/g)	Grafting (%)	Amino groups (mmol/g)
Silica*	RC-6	0	0	—	—
Silica- NH_2	RC-0	—	0.4	—	—
Silica- NH_2	RC-3	50.7	2.6	67.0	3.4
Silica- NH_2	RC-6	99.0	5.9	603.2	26.9

*Silica having no amino groups.

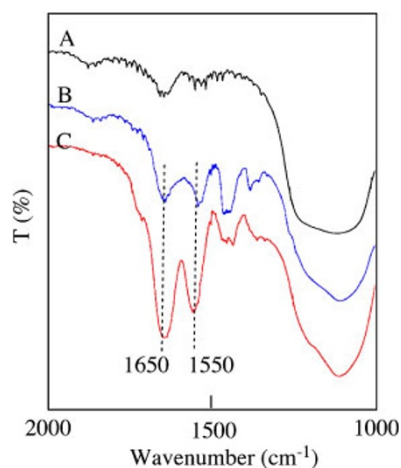


Figure 3. FT-IR spectra of (A) γ -APS-treated silica nanoparticle (Silica-NH₂), (B) Silica-PAMAM (RC3) (grafting = 38.3%), and (C) Silica-PAMAM (RC6) (grafting = 129.4%).

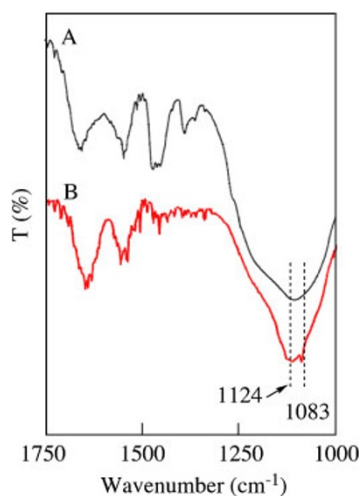


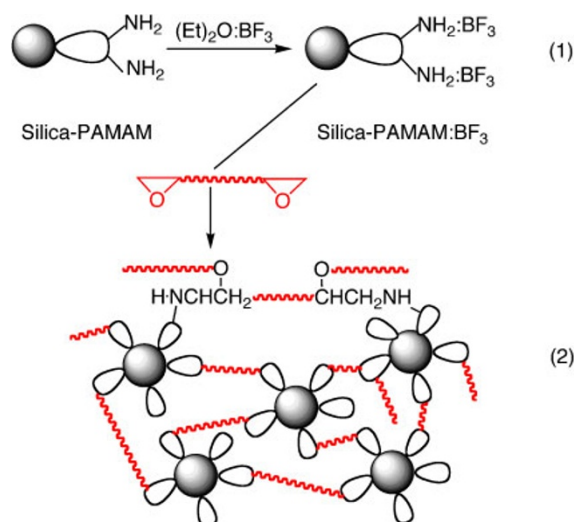
Figure 4. FT-IR spectra of (A) Silica-PAMAM and (B) Silica-PAMAM:BF₃ (RC 3).

curing agent of epoxy resin.¹⁸ Therefore, BF₃ complexation of terminal amino groups of PAMAM-grafted silica was achieved by the treatment of PAMAM-grafted silica with boron trifluoride diethyl ether complex.

Figure 4 shows FT-IR spectra of (A) hyperbranched PAMAM-grafted silica and (B) PAMAM-grafted silica having BF₃-amine complex groups (Silica-PAMAM:BF₃). As shown in Figure 4, FT-IR spectra of Silica-PAMAM:BF₃ shows new absorptions at 1124 and 1083 cm⁻¹, which are characteristic of BF₃-monoethylamine group. This result suggests that the terminal amino groups of PAMAM-grafted silica react with boron trifluoride to give BF₃-amine complex groups onto PAMAM-grafted silica (Scheme 1 (1)).

Curing of Epoxy Resin by Silica-PAMAM

Figure 5 shows FT-IR spectra of mixture of epoxy resin and Silica-PAMAM:BF₃ (A) before heating and (B) after heating at 160 °C for 24 h. It was found that absorbance of the mixture at



Scheme 1. (1) Introduction of BF₃-amine complex groups to terminal amino groups of hyperbranched PAMAM-grafted silica nanoparticle and (2) curing reaction of epoxy resin.

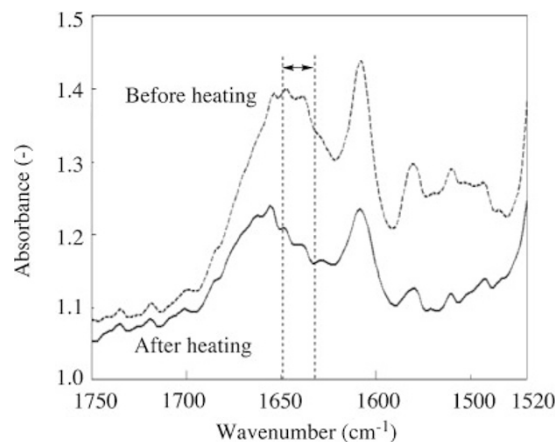


Figure 5. FT-IR spectra of mixture of epoxy resin and Silica-PAMAM:BF₃ before heating and after heating at 160 °C for 24 h.

1650–1638 cm⁻¹, which is characteristic of primary amino groups, decreased after the heating. The results suggest that primary amino groups of Silica-PAMAM reacted with epoxy groups of epoxy resin to give secondary amino groups whose absorption is known to be very weak.

Therefore, it was concluded that Silica-PAMAM was incorporated into epoxy resin with chemical bonds as shown in Scheme 1 (2).

Surface Morphology of Epoxy Resin/Silica Nanocomposite

The surface morphology of the epoxy resin/silica nanocomposite, which was prepared by the curing of epoxy resin with Silica-PAMAM:BF₃, was compared with that of epoxy resin cured by EDA as a curing agent in the presence of untreated silica by AFM. The results are shown in Figure 6.

The surface morphology of epoxy resin cured by EDA in the presence of untreated silica was found to be rough because of the aggregation of untreated silica nanoparticles. On the other

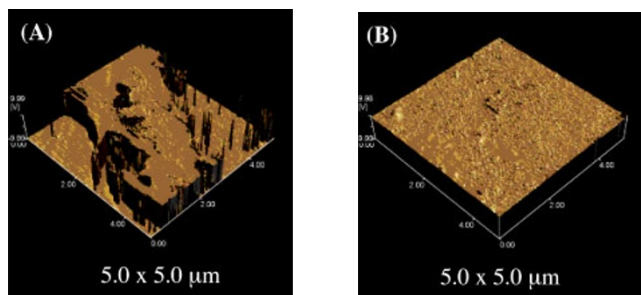


Figure 6. AFM images of epoxy resin cured by (A) EDA in the presence of untreated silica nanoparticle and (B) Silica-PAMAM:BF₃ (RC 3).

hand, the surface morphology of epoxy resin/silica nanocomposite using Silica-PAMAM:BF₃ was very smooth.

The result suggests that the PAMAM-grafted silica nanoparticles were dispersed and incorporate uniformly with chemical bonds in the continuous network of epoxy resin as shown in Scheme 1 (2).

Thermal Stability of Epoxy Resin/Silica Nanocomposite

The thermal stability of the epoxy resin/silica nanocomposite using Silica-PAMAM:BF₃ was investigated by using TGA. The results are shown in Figure 7. The 10% weight loss temperature of the epoxy resin/silica nanocomposite using Silica-PAMAM:BF₃ and using EDA in the presence of untreated silica was determined to be 392 °C and 348 °C, respectively.

The result indicates that the thermal stability of the epoxy resin cured by Silica-PAMAM:BF₃ was superior to that by EDA in the presence of untreated silica; namely, the heat resistance of the epoxy resin was significantly improved. This may be due to the fact that silica nanoparticles were incorporated into network of epoxy resin with chemical bonds as mentioned above.

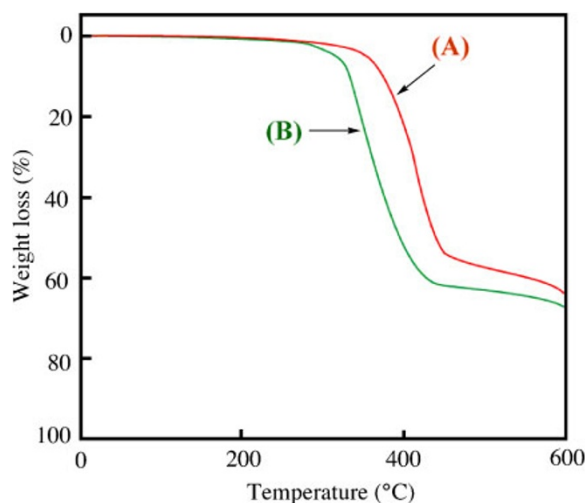


Figure 7. TGA curves of epoxy resin cured by (A) Silica-PAMAM:BF₃ (RC3) and (B) EDA in the presence of untreated silica nanoparticle.

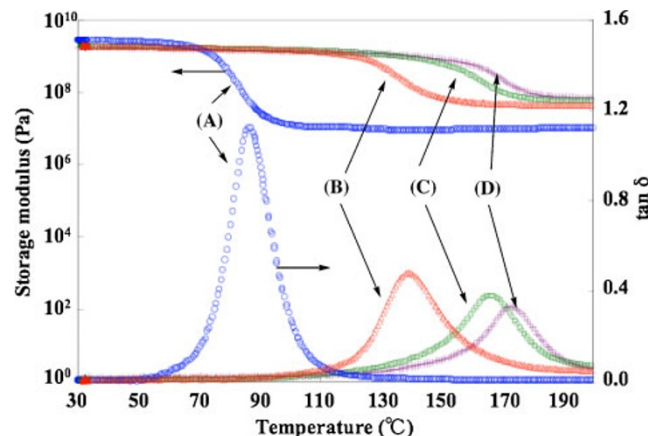


Figure 8. DMA curves of epoxy resin cured by (A) EDA in the presence of untreated silica nanoparticle, (B) Silica-PAMAM:BF₃ (RC3: 10 wt%), (C) Silica-PAMAM:BF₃ (RC3: 20 wt%), and (D) Silica-PAMAM:BF₃ (RC3: 30 wt %).

Dynamic Mechanical Properties of Epoxy Resin/Silica Nanocomposite

The dynamic mechanical properties of the epoxy resin/silica nanocomposite cured by several curing agents were shown in Figure 8. The storage modulus of epoxy resin cured by EDA in the presence of untreated silica decreased at glass-transition region and was very low in the rubbery region.

It is well known that the decrease in the modulus in glass-transition region is attributed to the micro-Brownian motion of the network chains.¹⁹ It is interesting to note that the modulus in the rubbery region and glass-transition region of epoxy resin/silica nanocomposite using Silica-PAMAM:BF₃ increased with increasing content of Silica-PAMAM:BF₃.

In addition, the storage modulus of resin/silica nanocomposite using Silica-PAMAM:BF₃ maintained a high value even in the high temperature region. The glass-transition temperature of resin/silica nanocomposites containing 30 wt % of Silica-PAMAM:BF₃ exceeded 170 °C.

Based on the above results, it is concluded that the micro-Brownian motion of the epoxy network is strongly restricted because of incorporation of silica nanoparticle into the network of epoxy resin by chemical bonds.

Effect of Curing Conditions on the Mechanical Properties of Epoxy Resin/Silica Nanocomposite

Figure 9 shows the effect of temperature on the curing of epoxy resin by Silica-PAMAM:BF₃. It was found that glass-transition temperature of epoxy resin cured at 160 °C was higher than that at 120 °C. These results indicate that the epoxy resin cured by Silica-PAMAM:BF₃ was accelerated with increasing curing temperature.

Figure 10 shows the effect of hyperbranched PAMAM grafting on the properties of epoxy resin cured by Silica-PAMAM:BF₃. The remarkable effect of PAMAM grafting on the glass-transition temperature of epoxy resin cured by PAMAM-grafted silica was observed: the glass-transition temperature decreased with increasing PAMAM grafting. This

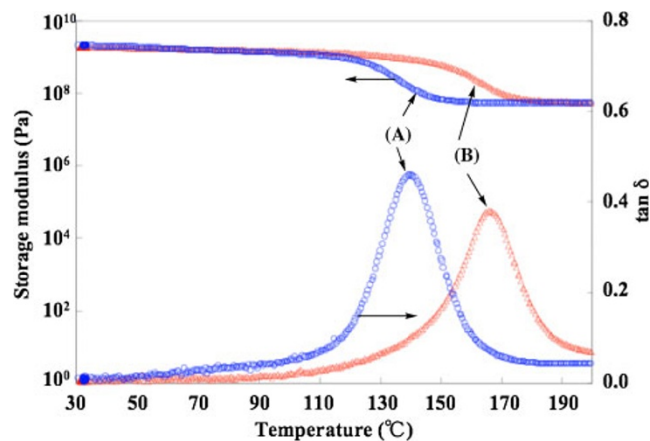


Figure 9. DMA curves of epoxy resin cured by Silica-PAMAM:BF₃ (RC3) (A) at 120°C and (B) at 160°C.

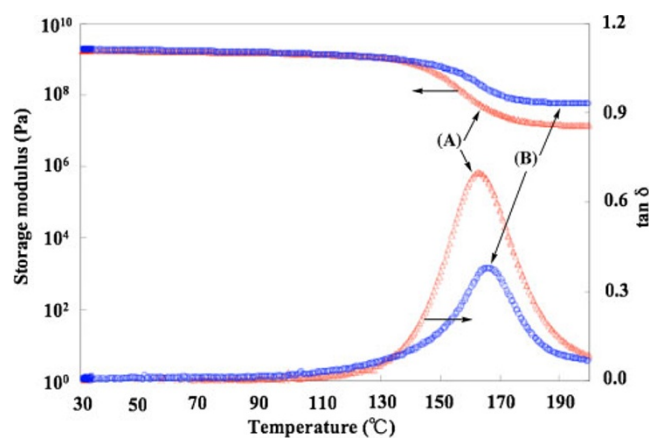


Figure 10. DMA curves of epoxy resin cured by (A) Silica-PAMAM:BF₃ (RC6), (B) Silica-PAMAM:BF₃ (RC3).

may be due to the fact that degree of crosslinking decreased with increasing amino group content of silica because of steric hindrance.

Adhesive Strength of Epoxy Resin/Silica Nanocomposite

The adhesive strength of the epoxy resin/silica nanocomposite between aluminum plates was investigated. Figure 11 shows the adhesive strength between aluminum plates bonded with untreated silica system (bonded with epoxy resin cured by EDA in the presence of untreated silica) and the epoxy resin/silica nanocomposite systems containing different amount of Silica-PAMAM:BF₃. The aluminum plate bonded by untreated silica system showed a very low adhesive strength. On the contrary, the aluminum plate bonded by the epoxy resin/silica nanocomposite showed considerably high adhesive strength. The result indicates that incorporation of Silica-PAMAM:BF₃ into epoxy matrix was effective for improving the adhesive strength between the aluminum plates.

In addition, the adhesive strength increased with increasing amount of Silica-PAMAM:BF₃ as curing agent. The result suggests that the adhesive strength of the epoxy resin between

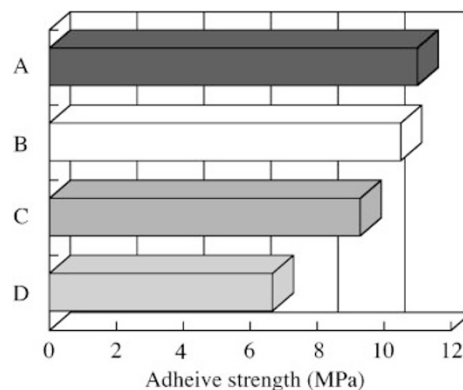


Figure 11. Adhesive strength of epoxy resin cured by (A) Silica-PAMAM:BF₃ (RC3: 30 wt%), (B) Silica-PAMAM:BF₃ (RC3: 20 wt%), (C) Silica-PAMAM:BF₃ (RC3: 15 wt%), and (D) EDA in the presence of untreated silica nanoparticle.

aluminum plates was significantly improved by use of Silica-PAMAM:BF₃ as curing agent. This may be due to the incorporation of silica nanoparticles into network of epoxy resin by chemical bonds.

CONCLUSIONS

1. The terminal BF₃-amine complex groups of hyperbranched PAMAM-grafted silica nanoparticle act as effective curing agent of epoxy resin.
2. The hyperbranched PAMAM-grafted silica nanoparticle was homogeneously dispersed in the continuous epoxy network to give epoxy resin/silica nanocomposite.
3. The storage modulus in the rubbery region and glass-transition temperature of the epoxy resin/silica nanocomposite increased with increasing the amount of Silica-PAMAM:BF₃ as curing agent.
4. The hyperbranched PAMAM-grafted silica nanoparticle showed a very high adhesive strength between aluminum plates.
5. It was considered that silica nanoparticles would be incorporated uniformly with chemical bonds into the network of epoxy resin by use of Silica-PAMAM:BF₃ as curing agent.

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