

# Curing of Epoxy Resin by Ultrafine Silica Modified by Grafting of Hyperbranched Polyamidoamine Using Dendrimer Synthesis Methodology

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Received 8 March 2000; accepted 11 May 2000

**ABSTRACT:** Hyperbranched polyamidoamine-grafted silica was prepared according to dendrimer synthesis methodology. The modified silica was dispersed uniformly in epoxy resin, and the curing of epoxy resin proceeded successfully by heating in the presence of the modified silica; the gel fraction of the epoxy resin cured by the hyperbranched polyamidoamine-grafted silica (grafting = 80.2%) reached 77% at 170°C after 48 h. The gel fraction increased with increasing terminal amino group content of the hyperbranched polyamidoamine-grafted silica. In addition, the curing ability of the silica increased by complexation of the terminal amino groups of the grafted polyamidoamine with boron trifluoride. The modulus of elasticity of the curing materials obtained using the modified silica as a curing agent was lower than that using conventional a curing agent such as ethylenediamine in the presence of untreated silica. On the other hand, the heat resistance of the curing product using the modified silica was superior to that using ethylenediamine, but no difference in glass-transition temperature was observed. It is expected that hyperbranched polyamidoamine grafted-silica is incorporated uniformly with chemical bonds in the matrix of the epoxy resin. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 573–579, 2001

**Key words:** ultrafine silica; surface grafting of polymer; hyperbranched polyamidoamine; dendritic polymer; epoxy resin; curing agent

## INTRODUCTION

Inorganic powders such as silica, carbon black, and ferrite are widely used industrially as pigments and fillers for plastic and rubber. In general, it is difficult to disperse inorganic powder uniformly into a polymer matrix or an organic solvent. In addition, the mechanical properties of

inorganic powder-polymer composite materials are considered to depend not only on the mechanical properties of the polymer matrix but also on the properties of interfacial regions between the powder surface and polymer matrix. Therefore, surface modification and application of inorganic particles have become of major interest lately.<sup>1–3</sup>

It has been reported from our laboratory that surface grafting of various polymers onto ultrafine silica can be achieved by the polymerization of monomers initiated by initiating groups previously introduced onto the surface.<sup>4–7</sup> In addition, we have reported the grafting of hyperbranched polymers onto a silica surface by postpolymerization initiated by the pendant initiating groups of

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Contract grant sponsor: Ministry of Education, Science, Sports and Culture of Japan for a grant-in-aid; contract grant number: 11650708.

*Journal of Applied Polymer Science*, Vol. 80, 573–579 (2001)  
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grafted chains on the surface.<sup>8,9</sup> On the other hand, surface modification of gold, silicone, and alumina by grafting of hyperbranched polymers has been reported by Bergbreiter and his coworkers.<sup>10–12</sup> As an example is the report on the grafting of hyperbranched, hydrophilic fluorinated polymers onto gold and silica surface has been reported.<sup>10</sup>

Recently, hyperbranched polymers, designated as “dendrimer,” have received great attention for their features and potential as novel properties. For example, it was reported that polyamidoamine dendrimer was synthesized by repeating two processes<sup>13–16</sup>: (1) Michael addition of acrylic ester, such as methyl acrylate, to amino groups as initiator core, and (2) terminal amidation of the resulting ester moieties with an alkyl diamine.

On the other hand, the functionalization of terminal amino groups of polyamidoamine dendrimer has been reported. For example, it was reported that the ring-opening polymerization of  $\alpha$ -amino acid *N*-carboxy anhydride was achieved from terminal amino groups of polyamidoamine dendrimer.<sup>17</sup> In addition, Tomalia et al. reported that by using polyamidoamine dendrimer having terminal pivalate groups, zero-valent copper nanoclusters could be synthesized.<sup>18</sup>

In a previous article we reported on the surface modification of ultrafine silica surface by grafting hyperbranched polyamidoamine onto the surface using dendrimer synthesis methodology<sup>19</sup> as follows: (1) Michael addition of methyl acrylate to amino groups introduced onto silica surface and (2) terminal amidation of the resulting ester moieties with ethylenediamine. The propagation of dendrimer from the silica surface was not achieved theoretically, however, and hyperbranched polyamidoamine was grafted onto the surface because of steric hindrance of the grafted dendrimer.

In the present work, in order to functionalize the terminal amino groups of hyperbranched polyamidoamine grafted on ultrafine silica surface, we investigated the curing of epoxy resin by hyperbranched polyamidoamine-grafted ultrafine silica. In addition, the mechanical properties of the curing product were also examined.

## EXPERIMENTAL

### Materials and Reagents

Aerosil 200, the ultrafine silica used, was obtained from Nippon Aerosil Company, Ltd., Ja-

pan. The silica was dried *in vacuo* at 110°C for 48 h before use. The properties of the ultrafine silica are shown in Table I. The silanol group content was determined by volumetrically measuring the amount of ethane evolved by reaction with triethyl aluminum.<sup>20</sup>

### Reagents

The following four reagents were obtained from Kanto Chemical Company, Inc., Japan:  $\gamma$ -aminopropyltriethoxysilane (APS) and the boron trifluoride diethyl ether complex were used without further purification; methyl acrylate (MA) was distilled under reduced pressure; and ethylenediamine (EDA) was refluxed over sodium and distilled just before use. Other reagents and solvents were purified by the ordinary methods before use.

### Epoxy Resin

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

### Grafting of Hyperbranched Polyamidoamine onto Ultrafine Silica Surface using Dendrimer Synthesis Methodology

Grafting reaction and propagation of hyperbranched polyamidoamine from the silica surface was achieved by use of the methodology of polyamidoamine dendrimer synthesis, which repeats two processes: (1) Michael addition of MA to amino groups on the surface and (2) amidation of terminal ester groups with EDA. The detailed procedure is described in a previous article.<sup>19</sup>

### Determination of Percentage of Grafting

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

**Table I** Properties of Ultrafine Silica

Silica	Specific Surface Area (m <sup>2</sup> /g)	Particle Size (nm)	OH Groups (mmol/g)
Aerosil 200	200	12	1.37

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

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

### Complexation of Terminal Amino Groups of Hyperbranched Polyamidoamine on Silica with $\text{BF}_3$

Complexation of the terminal amino groups of the hyperbranched polyamidoamine on the silica surface was carried out by the reaction of those terminal amino groups with boron trifluoride diethyl ether complex.<sup>21</sup> A typical example is as follows: In a 100-mL flask were charged 0.10 g of hyperbranched polyamidoamine-grafted silica, 0.15 g of boron trifluoride diethyl ether complex, and 10 mL of diethyl ether as solvent. The mixture was stirred with a magnetic stirrer for 24 h at 0°C. After the reaction the solvent and the unreacted boron trifluoride diethyl ether complex were removed by evaporation, and the silica obtained was repeatedly washed with diethyl ether.

### Curing of Epoxy Resin

Curing of epoxy resin in the presence of hyperbranched polyamidoamine-grafted silica was carried out as follows. Into a sampling tube were charged 0.1 g of hyperbranched polyamidoamine-grafted silica (or silica having  $\text{BF}_3$ -amine complex groups) and 0.5 g of epoxy resin. The mixture was uniformly milled by a three-roll mill (Inoue MFG., Inc.) and then poured on a Teflon sheet and heated at 120°C and 170°C in an electric oven.

After the reaction the product was extracted with THF using a Soxhlet apparatus until no more epoxy resin could be extracted. The resulting product from the above procedure was dried *in vacuo* at 100°C. The gel fraction was determined by the following equation:

$$\text{Gel fraction (\%)} = [(B - C)/(D - C)] \times 100$$

where  $B$  is the weight (g) of curing material after extraction,  $C$  is the weight (g) of silica charged, and  $D$  is the weight (g) of curing material before extraction.

### Pencil Scratch Test of the Curing Product of Epoxy Resin

The scratch hardness of the curing product of epoxy resin by hyperbranched polyamidoamine-grafted silica was estimated under constant stress with a pencil according to the Japanese Industrial Standards (JIS) pencil scratch test.<sup>22</sup> A film of the curing product was cast on a stainless plate, and the surface of the film was scratched with a pencil varying the hardness from B (soft) to 9H (hard). The limitation of scratch resistance was measured as the scratch hardness.

### Infrared Analysis

The infrared spectra were recorded on a Shimadzu Infrared Spectrophotometer using KBr pellet.

## RESULTS AND DISCUSSION

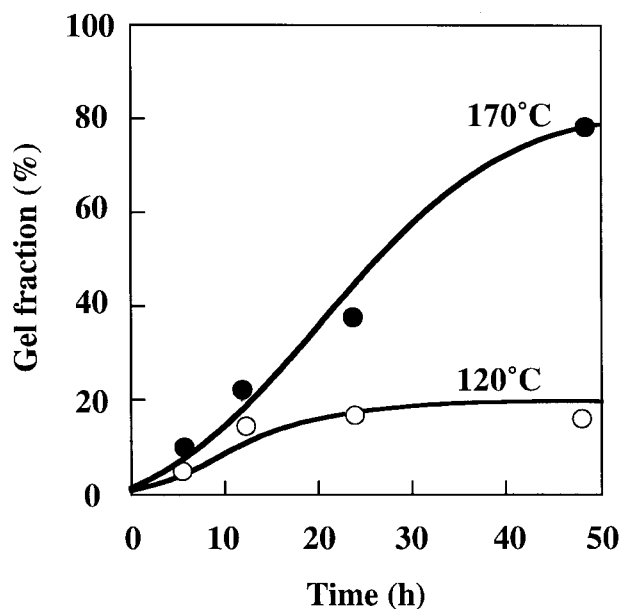
### Grafting of Hyperbranched Polyamidoamine onto Ultrafine Silica Surface using Dendrimer Synthesis Methodology

Table II shows the results of hyperbranched polyamidoamine grafting unto silica surface using

**Table II Percentage of Grafting and Amino Group Content of Modified Silica Using Dendrimer Synthesis Methodology**

Generation	Grafting (%)	Amino Groups (mmol/g)	Theoretical	
			Grafting (%)	Amino Groups (mmol/g)
2nd	15.5	1.0	54.7	3.2
4th	24.1	1.5	273.6	12.8
6th	47.7	2.1	797.5	51.2
8th	80.2	2.6	4651.2	204.8

Amino groups of initiator core (0.8 mmol/g).



**Figure 1** Effect of temperature on the curing of epoxy resin by hyperbranched polyamidoamine-grafted silica: Epoxy resin, 0.50 g; hyperbranched polyamidoamine-grafted silica, 0.10 g.

dendrimer synthesis methodology. Silica having 0.80 mmol/g of amino groups was used as an initiator site.

As shown in Table I, the percentage of grafting and amino group content of the resulting silica increased with an increase in the number of generations. The percentage of grafting and amino group content at every generation, however, was considerably smaller than that of the theoretical value described in a previous article.<sup>19</sup> The results indicate that the propagation of polyamidoamine dendrimer is very inefficient. This may be because the Michael addition and amidation are carried out in a heterogeneous system and because the grafted chains on the surface interfere with the propagation of polyamidoamine from the surface because of steric hindrance.<sup>19</sup>

#### Curing of Epoxy Resin by Silica Modified by Grafting of Hyperbranched Polyamidoamine

It has been reported that functional groups such as carboxyl and phenolic hydroxyl groups on a carbon-black surface play an important role in the curing (gelation) of epoxy resins.<sup>23</sup> On the other hand, it is well known that amines have the ability to cure various epoxy resins. Therefore, an investigation was done of the curing of epoxy resin by use of terminal amino groups of silica

**Table III** Pencil Scratch Hardness of Curing Products

Silica	Grafting (%)	Curing Time <sup>a</sup> (h)	Pencil Hardness
Treated with APS	—	48	× <sup>b</sup>
Polyamidoamine-grafted	47.4	48	B
Polyamidoamine-grafted	80.2	24	5 H
Polyamidoamine-grafted	80.2	48	8 H

<sup>a</sup> Epoxy resin/silica: 9/1; Temperature: 170°C.

<sup>b</sup> Not cured at all.

modified by grafting of hyperbranched polyamidoamine as a curing agent.

Figure 1 shows the effects of temperature and reaction time on the curing of epoxy resin by hyperbranched polyamidoamine-grafted silica (eighth generation). In both the presence of untreated silica and the absence of silica, epoxy resin hardly cured at 170°C even after 48 h. On the contrary, the curing of epoxy resin successfully proceeded in the presence of silica modified with hyperbranched polyamidoamine at 170°C. However, when the curing reaction was carried out at 120°C, the curing of epoxy resin was insufficient in the presence of modified silica even after 48 h.

The percentage of gel fraction at 170°C increased with increasing reaction time. These results indicate that the reaction of epoxy resin with the terminal amino groups of hyperbranched polyamidoamine-grafted silica was accelerated with increasing reaction time and temperature.

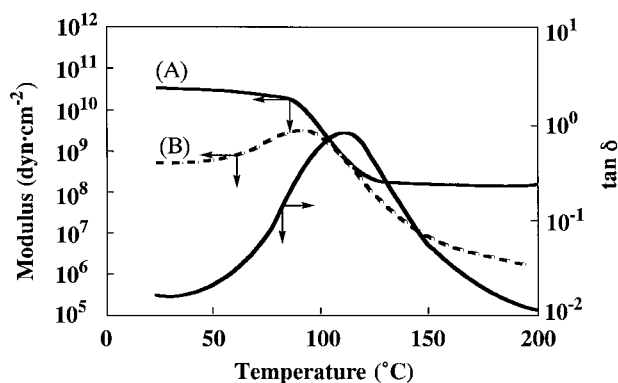
Furthermore, the limited scratch resistance of the curing product cured by hyperbranched polyamidoamine-grafted silica was examined by the pencil scratch test. The results are shown in Ta-

**Table IV** Curing of Epoxy Resin by Hyperbranched Polyamidoamine-Grafted Silica

Generation	Grafting (%)	Gel Fraction (%)
Untreated	—	Trace
γ-APS	—	6.5
2nd	15.5	12.6
4th	24.1	16.3
6th	47.7	39.4
8th	80.2	77.0

Epoxy resin/silica: 9/1; Temperature: 170°C; Time: 48 h.





**Figure 2** DMA curves of epoxy resin cured by hyperbranched polyamidoamine-grafted silica as curing agent: (a) Dynamic modulus, (b) Loss modulus.

ble III. The scratch hardness of the curing product, which was cured for 24 h at 170°C, was 5 H, but for the product cured for 48 h, the product was attained after 8 H. The results also indicate that the curing reaction was almost sufficient by curing at 170°C for 48 h.

Table IV shows the effect of dendrimer grafting onto a silica surface on the curing of epoxy resin at 170°C. The curing of epoxy resin scarcely proceeded in the presence of untreated silica and of silica treated with APS. In the presence of silica with a lower percentage of grafting, the curing of epoxy resin was insufficient. On the contrary, in the presence of hyperbranched polyamidoamine-grafted silica the curing reaction of epoxy resin proceeded with a higher percentage of grafting. The percentage of gel fraction increased with an increasing percentage of hyperbranched polyamidoamine grafting because amino groups increased with an increasing percentage of grafting. These results indicate that the terminal amino groups of hyperbranched polyamidoamine-grafted silica have an ability to cure epoxy resin.

### Properties of Curing Products

The elastic modulus and glass-transition temperature of curing products was estimated by using dynamic mechanical analysis (DMA). The results are shown in Figure 2 and Table V. As can be seen in Figure 2, the modulus of elasticity was found to be about  $10^{10}$  dyn/cm<sup>2</sup>, and this value was lower than that of curing products using a conventional curing agent such as ethylenediamine. The glass-transition temperature was about 105°C, a value nearly equal to curing products using a conventional curing agent.

Figure 3 shows the result of the measurement of heat resistance of curing product by TGA. The 10% weight loss temperature of the curing product using hyperbranched polyamidoamine-grafted silica and ethylenediamine as curing agents in the presence of untreated silica was determined to be 360°C and 300°C, respectively. This indicates that the heat resistance of the curing product using the modified silica was superior to that using ethylenediamine.

These results suggest the terminal amino groups of hyperbranched polyamidoamine-grafted silica act as an effective curing agent of the epoxy resins, and it can be reckoned that hyperbranched polyamidoamine-grafted silica is incorporated uniformly with chemical bonds in epoxy resin. In addition, it is speculated that in such a curing material with hyperbranched polyamidoamine-grafted silica, the density of the network is high in the vicinity of the silica surface and decreases going away from the surface because the curing reaction proceeds from surface amino groups in a heterogeneous system.

### Curing of Epoxy Resin by Terminal BF<sub>3</sub>-Amine Complex Groups on Silica Surface

It is well known that amines react easily with boron trifluoride diethyl ether complex to produce BF<sub>3</sub>-amine complex.<sup>21</sup> In general, boron trifluoride amine complex is known as a latent curing agent.<sup>24</sup> Therefore, BF<sub>3</sub>-amine complexation of terminal amino groups of hyperbranched polyamidoamine-grafted silica was achieved by the treatment of hyperbranched polyamidoamine-grafted silica with boron trifluoride diethyl ether complex.

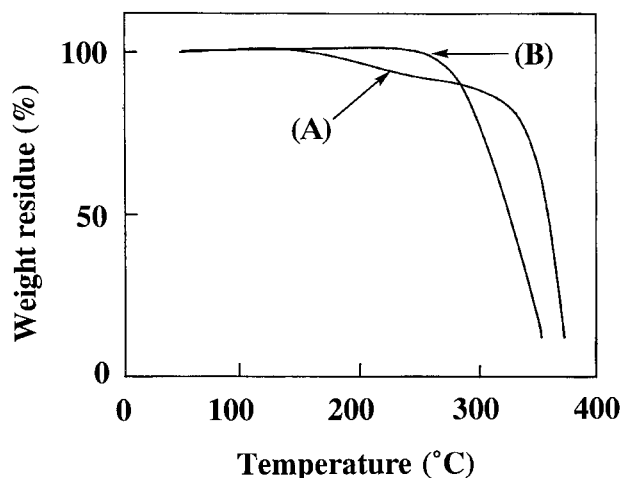
Figure 4 shows the IR spectrum of hyperbranched polyamidoamine-grafted silica treated

**Table V** Properties of Epoxy Resin Cured by Hyperbranched Polyamidoamine-Grafted Silica (8th Generation) and Ethylenediamine in the Presence of Untreated Silica

Curing Agent	$T_g$ (°C)	Elastic Modulus (mPa)	Heat Resistance (°C)
Ethylene diamine <sup>a</sup>	95–124	3400–3700	300
Polyamidoamine-grafted silica <sup>b</sup>	105	1000	360

<sup>a</sup> Epoxy resin/silica/ethylenediamine: 90/10/1.

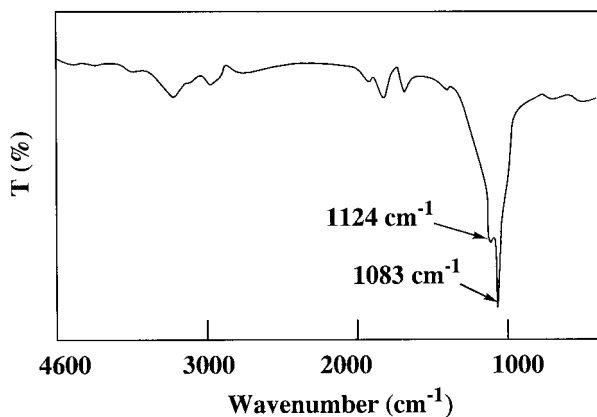
<sup>b</sup> Epoxy resin/polyamidoamine-grafted silica: 5/1.



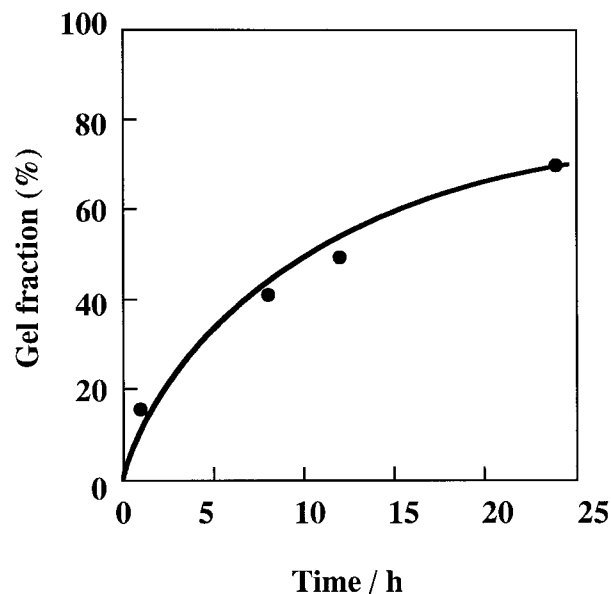
**Figure 3** TGA curves of epoxy resin cured by (a) hyperbranched polyamidoamine-grafted silica and (b) ethylenediamine as curing agent.

with boron trifluoride diethyl ether complex. In the IR spectrum of hyperbranched polyamidoamine-grafted silica treated with boron trifluoride diethyl ether complex can be observed new absorptions, at  $1083\text{ cm}^{-1}$  and  $1124\text{ cm}^{-1}$ , which are characteristic of  $\text{BF}_3$ -monoethylamine group. This result suggests that the terminal amino groups of hyperbranched polyamidoamine-grafted silica have reacted with boron trifluoride to produce  $\text{BF}_3$ -amine complex groups on the silica surface.

The result of the investigation of curing epoxy resin by silica having terminal  $\text{BF}_3$ -amine complex groups is shown in Figure 5. The curing of epoxy resin also proceeded in the presence of hyperbranched polyamidoamine-grafted silica hav-



**Figure 4** IR spectrum of hyperbranched polyamidoamine-grafted silica having  $\text{BF}_3$ -amine complex groups.



**Figure 5** Curing of epoxy resin by terminal  $\text{BF}_3$ -amine complex of hyperbranched polyamidoamine-grafted silica at  $120^\circ\text{C}$ : Epoxy resin, 0.50 g; hyperbranched polyamidoamine-grafted silica having terminal  $\text{BF}_3$ -amine complex groups, 0.10 g.

ing terminal  $\text{BF}_3$ -amine complex groups. The gel fraction reached 68.2% at  $120^\circ\text{C}$  for 24 h. This indicates that the curing reaction was accelerated by trifluoroboration of the terminal amino groups of hyperbranched polyamidoamine-grafted silica.

## CONCLUSIONS

1. The terminal amino groups of hyperbranched polyamidoamine-grafted ultrafine silica prepared by use of dendrimer synthesis methodology act as effective curing agents of epoxy resin. The curing activity increased with an increasing percentage of hyperbranched polyamidoamine grafting.
2. In the presence of hyperbranched polyamidoamine-grafted silica having  $\text{BF}_3$ -amine complex groups, the curing of epoxy resin was accelerated and the curing of epoxy resin was achieved at a lower temperature.
3. It was expected that ultrafine silica would be incorporated uniformly with chemical bonds into epoxy resins matrix by use of hyperbranched polyamidoamine-grafted silica as a curing agent.

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