Synthesis of Epoxy Resin–Silica Nanocomposites Provided from Perhydropolysilazane as a Curing Reagent and the Precursor of Silica Domain

Reiko Saito, Yosuke Fujii, Tohru Kumagai

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan

Correspondence to: R. Saito (E-mail: rsaito@polymer.titech.ac.jp)

ABSTRACT: Epoxy resin–silica nanocomposites with spherical silica domains with 29.0 nm in diameter in an epoxy resin matrix were synthesized from Bisphenol-A type epoxide monomer, 2,2-*bis*(4-glycidyloxyphenyl)propane (DGEBA), and perhydropolysilazane (PHPS, —$[Si_2$—$NH]_n$—). The volume fraction of silica domain in the composite varied from 5.4 to 37.8 vol % by varying the feed ratio of PHPS to the epoxide monomer. The reaction mechanism of epoxy group and PHPS was investigated by using glycidyl methacrylate as a model compound of the epoxy monomer by ^{1}H-nucular magnetic resonance and Fourier transform infrared spectrometry. Ammonia gas provided by the decomposition of PHPS with moisture converted PHPS to silica and cured the epoxy monomer. The curing of epoxy monomer preferably proceeded than the conversion of silica. The addition of 1,4-diaminobutane drastically accelerated the rate of curing; white and hard epoxy resin–silica nanocomposites were obtained. The good thermal stability of the composite prepared with DGEBA/PHPS/1,4-diaminobutane was observed by thermogravimetric analysis. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Epoxy resin, which is well applied to the coating and electrical insulation materials because of its good transparency, high mechanical strength, and good electrical insulating properties, has relatively low thermal stability[1–3] and poor water-vapor barrier properties.[4–7] The increases of glass transition temperature and mechanical strength of the epoxy resin by blend of the silica materials, such as montmorillonite and silica beads, during the curing of epoxy resin have been reported.[8–13] In the most cases, the surface of the silica materials was modified with organic compound containing the reactive group with epoxide group to increase the affinity between the silica and the epoxy resin.[14–20] The most important advantage of addition of the silica materials is that the shape and size of the isolated silica domains in the composites are well controlled. On the other hand, it is difficult to change the shape and the size of the silica domains from the silica materials blended to the system.

Sol–gel method is a predominant method to provide the continuous silica domain in the composites.[21,22] Generally, porous silica is formed from alkoxysilanol by the sol–gel method. In contrast, the silica glass with less lattice defects is obtained from perhydropoly-

silazane (PHPS), which is a preceramic material with the repeating unit of (SiH$_2$—NH), by sol–gel method by curing at lower than 100°C (Figure 1). The formation of the composite with PHPS and poly(*tert*-butyl methacrylate-*co*-2-hydroxymethyl methacrylate) or poly(*tert*-butyl methacrylate-*co*-trimethylsilyloxy ethyl methacrylate) improved the water-vapor barrier properties of poly(*tert*-butyl methacrylate).[23] The high reactivity of monosilanyl and silanyl groups of PHPS and hydroxy group resulted in the immediate grafting of PHPS onto the organic polymer with hydroxy group by blending of PHPS and the polymer. The casting and curing the graft copolymer on a substrate at below 100°C provided the organic–silica nanocomposites on the substrate.[24] During the calcinations of PHPS, steam acted as a catalyst.
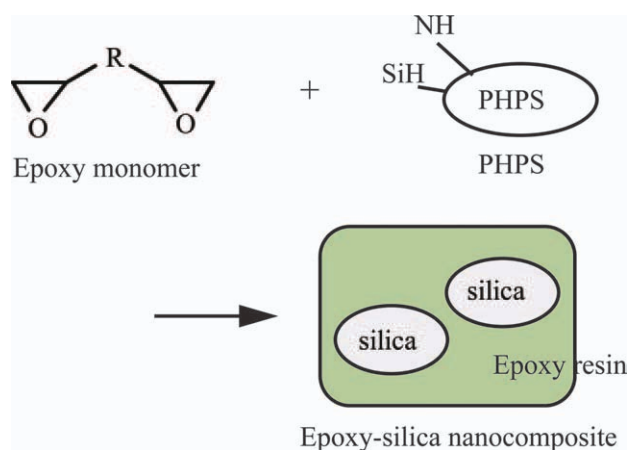
PHPS contains primary and secondary amine groups, which may be reactive with epoxy group. The epoxy resin–silica nanocomposite is expected by curing the blend solution of PHPS and an epoxy monomer. The most interesting feature of this method is that PHPS will act both the preceramic material and a curing reagent. Neither the synthesis of epoxy–silica nanocomposite with PHPS nor the reaction of epoxy group and PHPS has been investigated. Figure 2 shows the general scheme of
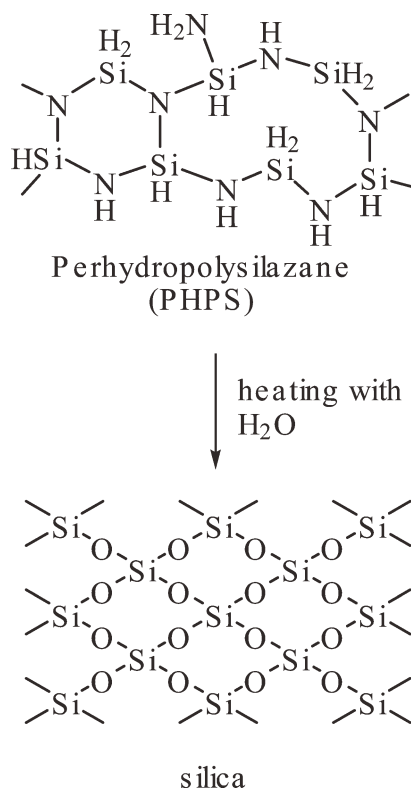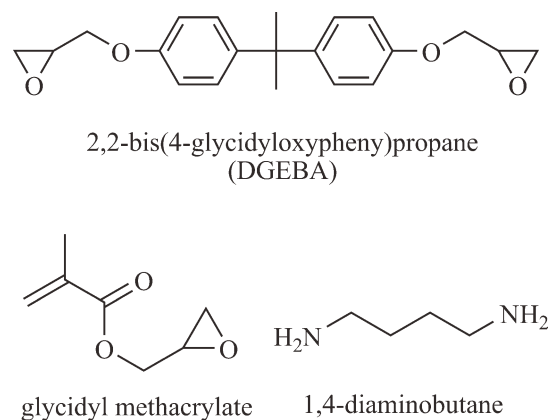
Figure 1. Chemical structure of PHPS and its conversion to silica.

Figure 2. Synthesis of epoxy resin–silica nanocomposite with PHPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. Chemical structures of glycidyl methacrylate, DGEBA, and 1,4-diaminobutane.

synthesis of epoxy resin–silica nanocomposite. If the epoxy group opens by PHPS, PHPS and the epoxy resin will be covalently bonded via hydroxy group of epoxy resin and monosilanyl and silanyl groups of PHPS. The silica domain will be formed from PHPS in the composite. The covalent bonds of Si—C formed with Si—H and hydroxy groups are stable at high temperature. As a result, the epoxy resin–silica nanocomposite will be obtained from the blend solution of epoxide monomer and PHPS. The development of the epoxy resin–silica nanocomposite as the coating material will be useful for the solar cell technology and other coating technologies.

However, the followings are concerned. (1) Whether the primary and secondary amine groups of PHPS reacts with the epoxide group. (2) Whether the PHPS decomposes during the reaction with the epoxide monomer. In a solution, the concentrations of epoxy and amine groups are high. This means a lot amount of hydroxy groups are formed in the solution. The high concentration of hydroxy group often causes the decomposition of PHPS rather than the formation of the covalent bond.

In this study, we aimed to synthesize the epoxy resin–silica nanocomposite with PHPS and to clarify the reaction mechanism of PHPS and epoxy group. For the analysis of reaction mechanism, glycidyl methacrylate, a monofunctional epoxide was used. For the composite synthesis, 2,2-*bis*(4-glycidyloxyphenyl)propane (DGEBA) was chosen as the monomer. The addition of 1,4-diaminobutane as a cocuring reagent was also investigated. The chemical structures of glycidyl methacrylate, DGEBA, and 1,4-diaminobutane are shown in Figure 3. The reaction was analyzed by [1]H-nuclear magnetic resonance (NMR) and Fourier transform infrared spectrometry (FTIR). The morphologies of the microphase separation were observed by transmission electron microscopy. Thermal stability of the composites was measured by thermogravimetic analysis (TGA).

EXPERIMENTAL

Materials

Glycidyl methacrylate (Kanto Chemical, Tokyo Japan, 96.0%) was purified by distillation under vacuum. Xylene (Kanto Chemical, Tokyo Japan, 85.0%) was dried over calcium hydride (Kanto Chemical, Tokyo Japan, >95.0%) for 24 h, and distilled under vacuum. PHPS/xylene solution (NN-110, AZ electronic materials, Tokyo Japan, 20 wt % of PHPS, average-number molecular weight of PHPS: 700 with −[SiH$_2$NH$_{0.57}$]$_{15.7}$−), DGEBA (TCI, Tokyo Japan, 85%), 1,4-diaminobutane (Kanto Chemical, Tokyo Japan, 97.0%), and chloroform-d (Kanto Chemical, Tokyo Japan, 98.0%) were used as received.

Preparation of Composite by Method A

Certain amounts of DGEBA and NN-110 were mixed and stirred at room temperature for 24 h in nitrogen atmosphere. Then, the solution was cast on a Teflon dish and heated at

Table I. Conditions and Results of Epoxy Resin–Silica Composites and Epoxy Resin C

Code	DGEBA[a] (g)	NN-110[a] (mL)	DAB[a] (mL)	Method[b]	[NH] of PHPS/[epoxy] (mol/mol)	[NH] of DAB/[epoxy] (mol/mol)	Content of silica (vol %)	Conversion of epoxy group[c] (mol%)	Conversion of PHPS[d] (mol%)
A-1	1.00	14.3	0.00	Method A	5.80	0.00	37.8	98.9	68.9
A-2	1.00	5.77	0.00	Method A	2.34	0.00	28.5	98.8	93.4
A-3	1.00	3.70	0.00	Method A	1.50	0.00	23.2	94.3	97.9
A-4	1.00	2.33	0.00	Method A	0.94	0.00	17.7	94.6	100.0
A-5	1.00	1.36	0.00	Method A	0.55	0.00	12.2	72.4	99.9
A-6	1.00	0.54	0.00	Method A	0.22	0.00	5.7	34.7	100.0
B-1	1.00	1.59	0.063	Method B	0.64	0.43	13.1	97.7	100.0
B-2	1.00	1.19	0.071	Method B	0.48	0.48	10.5	100.0	100.0
B-3	1.00	0.56	0.112	Method B	0.23	0.76	5.4	97.5	100.0
C	1.00	0.00	0.147	Method C	0.00	0.99	0.0	100.0	–

[a] DGEBA: 2,2-*Bis*(4-glycidyloxyphenyl)propane. NN-110: a perhydropolysilazane (PHPS)/xylene solution with 20 wt % of PHPS. DAB: 1,4-diaminobutane, [b] Method A: The mixture of DGEBA and NN-110 stirred for 24 h in nitrogen was heated for 100 h at 120°C in an oven with steam. Method B: The mixture of DGEBA, NN-110, and 1,4-diaminobutane (DAB) stirred for 24 h in nitrogen was heated for 3 h at 120°C in the oven with steam. Method C: The mixture of DGEBA and DAB was stirred for 6.5 h at room temperature in air, [c] Determined by FTIR by using the absorption peak at 914 cm^{-1}, [d] Determined by FTIR by using the absorption peaks at 1080 and 2160 cm^{-1}.

120°C for 10 h in an oven with steam. The conditions are summarized in Table I.

Preparation of Composite and Epoxy Resin by Method B
Certain amounts of DGEBA, 1,4-diaminobutane, and NN-110 were mixed and were stirred at room temperature for 24 h in nitrogen atmosphere. Then, the solution was cast on the Teflon dish and heated at 120°C for 3 h in the oven with steam. In the case of epoxy resin C, GDEBA (1.0 g, 2.94 mmol) and 1,4-diaminobutane (0.147 mL, 1.42 mmol) were mixed and the mixture was stirred for 6.5 h at room temperature in air. The conditions are summarized in Table I.

Characterization
^{1}H-Nuclear Magnetic Resonance. Glycidyl methacrylate (0.12 mL, 0.912 mmol) was dissolved in 0.5 mL of CDCl$_3$ in an NMR tube. For the measurement under nitrogen atmosphere, NN-110 (0.2 mL, PHPS: 36.8 mg, 0.053 mmol) was added to the solution under dry nitrogen. Then, the tube was sealed under nitrogen. For the measurement in air, the tube was sealed in air. The ^{1}H-NMR measurement was carried out with a ^{1}H-NMR spectrometer (JEOL, Tokyo Japan, GLX-400 400MHz) at room temperature using the signal of the deuterated solvent as lock and the internal standard for chemical shift data in the δ-scale relative to TMS.

Fourier Transform Infrared Spectrometry. The reaction of epoxy group and conversion of PHPS to silica were measured by an FTIR spectrometer (Jasco, Tokyo Japan, FTIR-4100). The specimen was placed on a KBr plate for KBr method, or placed on Aluminum mirror for grazing angle refraction accessory (Jasco, Tokyo Japan, RAS-PRO410 B) with an incident angle for 80°. To analyze the reaction of epoxy group and PHPS, the absorption peaks of epoxy group at 914 cm^{-1} and monosilanyl and silanyl groups at 2160 cm^{-1} were used.

Transmission Electron Microscopy. A drop of blend solutions of DGEBA/NN-110 or DGEBA/NN-110/1,4-diaminobutane was cast on a copper microgrid coated with a carbon substrate. The grid was heated at 120°C for 10 h in the oven with steam and dried completely under vacuum at room temperature. The microphase separation of the specimen was observed by a transmission electron microscope (HITACHI, Tokyo Japan, H-7100) at 50 kV without staining.

Thermogravimetric Analysis. TGA was performed with a thermogravimeter (Shimazu, Kyoto Japan, TGA-50) in a rage of 50–900°C at a heating rate of 5.0 K min^{-1} under nitrogen with flow rate 20 mL min^{-1}.

RESULTS AND DISCUSSION
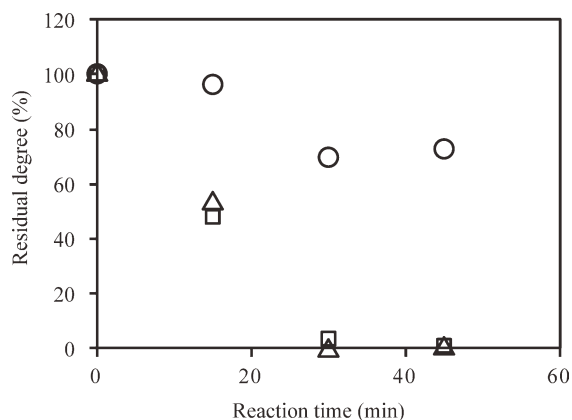
The Reaction of PHPS and Epoxy Group
First, the reaction of PHPS and epoxy group was investigated by ^{1}H-NMR. Figure 4 shows the ^{1}H-NMR spectra of the mixture of glycidyl methacrylate and the PHPS/xylene solution (the solution NN-110). The molar ratio of glycidyl methacrylate to PHPS was 18.2. Taking account of the chemical structure of PHPS, —[SiH$_2$NH$_{0.57}$]$_{15.7}$—,[25] the molar ratio of [NH]/[epoxy group] was 0.5. The initial concentration of glycidyl methacrylate was normalized by using the resonance of vinyl group at 5.62 and 6.17 ppm. PHPS is highly reactive with the moisture and oxygen in air. Especially, the moisture in air is a catalyst of PHPS to convert it to silica. Thus, the reaction was carried out in nitrogen atmosphere. The epoxy ring was observed at in a range of 2.7–3.2 ppm. The broad peaks of Si—H and Si—H$_2$ groups were observed at 4.4 and 4.7 ppm and agreed well with the literature.[26] These peaks did not change by heating at 80°C for 24 h in nitrogen. It was found that the glycidyl type epoxy group did not react with PHPS in nitrogen atmosphere. In other words, the primary and secondary amine groups of PHPS did not open the epoxy ring. Figure 4(c) shows the ^{1}H-NMR spectra of the mixture of glycidyl methacrylate and the PHPS/xylene solution
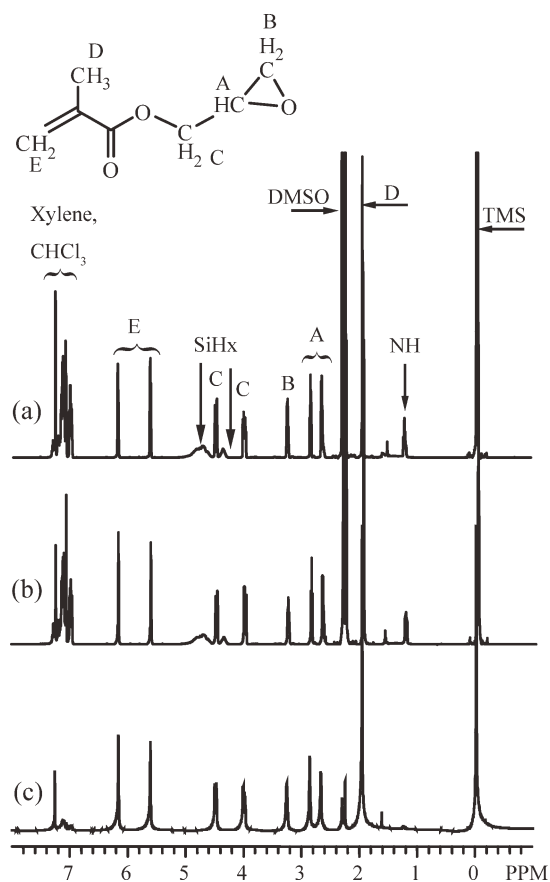
Figure 4. ^{1}H-NMR spectra of NN-110/glycidyl methacrylate solution with [NH]/[epoxy group] = 0.5 measured in DMSO-d$_6$. (a) At time 0, (b) stirred at 80°C for 24 h in nitrogen atmosphere, and (c) stirred for 3 h at 80°C in air.

in air at 3 h at 80°C. Interestingly, the peaks of epoxy group and Si—H and Si—H$_2$ groups decreased. It suggests that the air was needed for the reaction between PHPS and epoxy group.

To clarify the reaction mechanism of PHPS and epoxy group, the content changes of the N—H group, Si—H, and Si—H$_2$

Figure 5. Time dependence of the contents of N—H group (square), Si—H, and Si—H$_2$ group (circle), and epoxy group (triangle) heated at 80°C in air at the molar ratio of [NH]/[epoxy group] = 0.5.
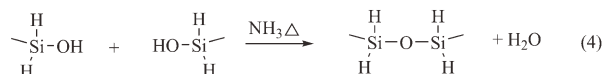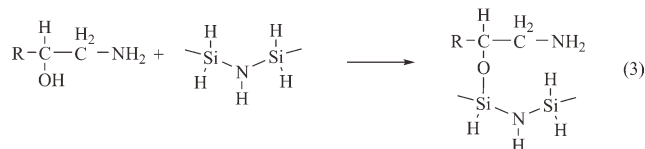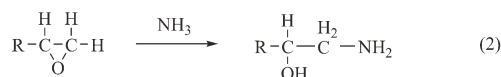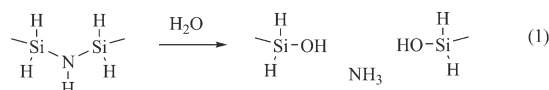
Figure 6. Proposed reaction mechanism of PHPS and DGEBA with water in air. (1) The ammonia gas and silanol group were formed by decomposition of PHPS. (2) Hydroxy group was provided by the reaction between epoxy group and ammonia gas. (3) The epoxy resin and PHPS were covalently connected by the reaction of hydroxy group and Si—H or Si—H$_2$ groups of PHPS. (4) The condensation of silanol occurred with the ammonia gas.

groups and epoxy group by heating were measured by ^{1}H-NMR in air. Figure 5 shows the degrees of residual of N—H, Si—H, and S—H$_2$, and epoxy groups in the system. During the reaction, the strong smell of ammonia was detected. In early stage, N—H bonds decreased owing to the decomposition of PHPS with water in air and ammonia gas was formed. However, the quantitative measurement of ammonia gas was not carried out. As the quick release of the gas was required to void the storage of monosilane gas, which was a flammable with air. Then, the epoxy group and Si—H and Si—H$_2$ groups decreased. We have already reported that the excess amounts of water and alcohol to PHPS provided the ammonia gas and silanol groups.[24] Dargère et al. reported the curing mechanism of hydridosilazane with water as the formation of ammonia gas and silanol group by decomposition and the condensation of silanol and Si—H$_2$ groups with ammonia gas as a catalyst.[27] Therefore, the following reaction mechanism of PHPS and epoxy group is proposed and is shown in Figure 6. (1) The ammonia gas and silanol group were formed by decomposition of PHPS. (2) Hydroxy group was provided by the reaction between epoxy group and ammonia gas. (3) The epoxy resin and PHPS were covalently connected by the reaction of hydroxy group and Si—H or Si—H$_2$ groups of PHPS. (4) The condensation of silanol occurred with the ammonia gas. Here, the reactions 2 and 4 are competitive. In this study, epoxy group, which is well cured with basic catalyst, existed in the system. Thus, not only the calcinations of PHPS to silica but also the curing of epoxy group was carried out with ammonia gas. In conclusion, the epoxy group was not cured with the amine groups of PHPS but the ammonia gas provided by the decomposition of PHPS in air.
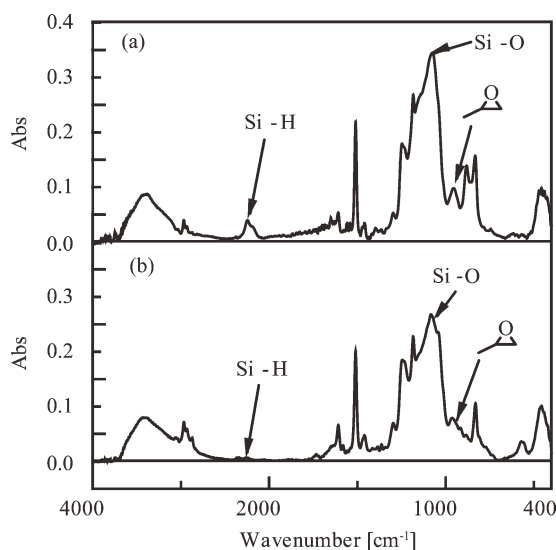
Figure 7. FTIR spectra of the composite A-4 with [NH]/[epoxy group] = 0.94. (a) Before heating. (b) After heating at 120°C for 3 h.

Synthesis of the Composites

The composites were prepared by two different methods. The conditions and results are summarized in Table I. All specimens were prepared in air. In the case of method A, DGEBA and the PHPS/xylene solution were mixed in air, and then the mixtures were cured at 120°C. The feed ratio of N—H bond of PHPS to epoxy group, [NH]/[epoxy], varied from 5.80 to 0.22. Blending of the PHPS/xylene solution to DGEBA resulted in the foaming and increasing of the solution viscosity, indicating that PHPS reacted with DGEBA. After forming, incomplete curing occurred. The DGEBA–PHPS composites were soft solid with sticky surface. Then, the samples from A-1 to A-4 were postcured by heating at 120°C. They became hard solid without sticky surface.

Figure 7(a) shows the FTIR spectra of A-4 before heating. The [NH]/[epoxy] of A-4 in feed was 0.94. The reaction of epoxy group did not complete with PHPS. After the blending with PHPS, the epoxy group was detected at 914 cm^{-1}. In contrast, PHPS partially converted to silica. The Si—H and Si—O groups were detected at 2160 and 1080 cm^{-1}, respectively. It is normal that the PHPS readily converted to silica in air at room temperature. Figure 7(b) shows the FTIR spectra of A-4 after the heating at 120°C. The Si—H peak at 2160 cm^{-1} completely vanished, the Si—O peak at 1080 cm^{-1} increased, and the epoxy ring peak at 914 cm^{-1} decreased by heating. The conversions of PHPS to silica and DGEBA to epoxy resin determined by FTIR were 100 and 94.6 mol %, respectively. Subsequently, the DGEBA–PHPS composites were converted to the epoxy resin–silica composites by heating at 120°C for 10 h.

The conversions of epoxy group and PHPS are summarized in Table I. The conversion of DGEBA strongly depended on the content of PHPS. The conversion of DGEBA increased with the increase of PHPS content and was saturated at ca. 99% at over [NH]/[epoxy group] = 2.34. The amount of ammonia gas provided from PHPS increased by increase of the PHPS content. The high conversion of DGEBA was owing to the high concentration of ammonia gas provided from PHPS. In contrast, the

conversion of PHPS to silica decreased by decreasing the content of DGEBA. As described above, ammonia gas provided from PHPS was theoretically used both the curing of DGEBA and the condensation of silanol groups. The reaction of epoxy group and ammonia, however, is more preferable than the condensation of silanol. The hydroxy group, which is highly reactive with Si—H group, was preferentially formed by the reaction between epoxy group and ammonia. Therefore, the complete conversion of PHPS to silica was observed at high DGEBA content. On the other hand, the conversion of PHPS in the matrix of organic polymer without hydroxy group was relatively slow.[28] The low DGEBA content did not enhance the conversion of PHPS because of low hydroxy group in the system. In conclusion, PHPS acts as the curing reagent of DGEBA by providing the ammonia gas during its conversion to silica. At the same time, the epoxy group enhanced the conversion of PHPS to silica by the formation of hydroxy group.

Next, to increase the conversion of DGEBA at low PHPS content, 1,4-diaminobutane was added to the system (method B). The conversions of epoxy group and PHPS are summarized in Table I. For all cases, the equimolecular amounts of whole N—H bonds and epoxy group were mixed. After 17 h, the mixtures became thickened. This indicates that the curing of DGEBA proceeded with 1,4-diaminobutane. Then, white and hard composites were obtained by heating for 3 h at 120°C in air. Figure 8 shows a photograph of B-2 after heating as a typical case. The addition of 1,4-diaminobutane greatly improved the conversions of epoxy group without decreasing the high conversion of PHPS. This supports that the insufficient ammonia gas at low PHPS content resulted in the low conversion of DGEBA. The conversions of DGEBA of all cases by method B (>97.5 mol %) were larger than that of A-5 at [NH]/[epoxy] = 1.5 by method A (94.3 mol %). In the cases by method B, DGEBA was cured with 1,4-diaminobutane, and ammonia gas was used as a catalyst for the conversion of PHPS to silica. PHPS was more weak curing reagent than 1,4-diaminobutane ageist DGEBA.
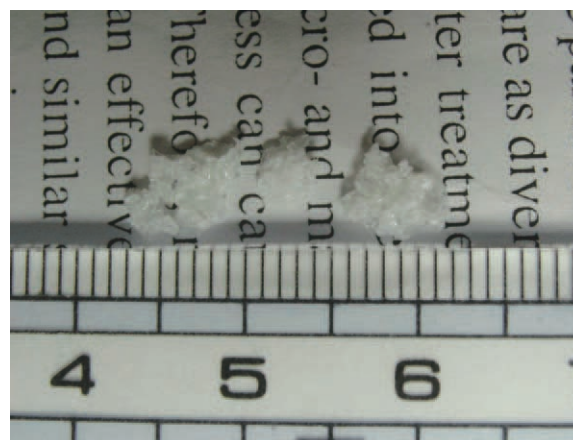
Figure 8. The photograph of the composite B-3 after heating at 120°C for 3 h. [NH of PHPS] : [epoxy group][1,4-diaminobutane] of B-3 = 0.23 : 1.0 : 0.38. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
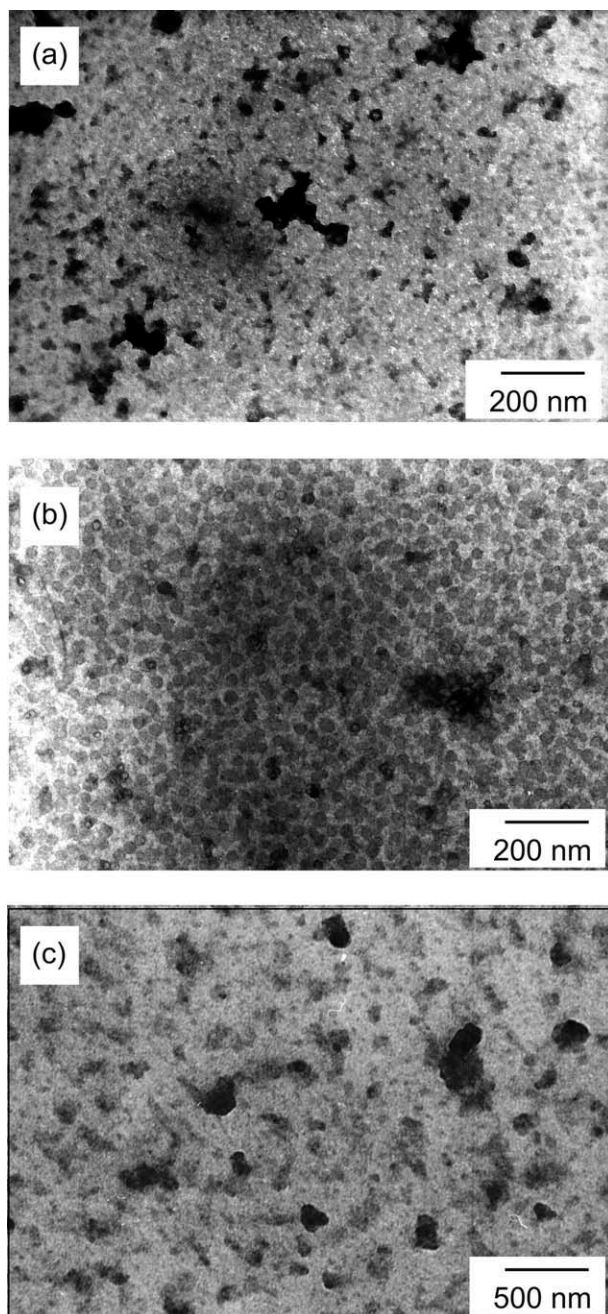
Figure 9. Transmission electron micrographs of the composites synthesized by method B. (a) B-1 with 13.3 vol % of silica. (b) B-2 with 10.5 vol % of silica. (c) B-3 with 5.4 vol % of silica.

Observation of Microphase Separation

As DGEBA and PHPS were individually cured with mainly 1,4-diaminobutane and ammonia gas, respectively, the clear microphase separation was expected for the composites prepared by method B. Additionally, the reaction between Si—H group and hydroxy group provided by the ring opening of epoxy group will increase the homogeneity of the microphase separation and decrease their sizes. Figure 9 shows the transmission electron micrographs of the as cast films of composites B-1, B-2, and B-3. It was impossible to prepare ultra-thin films of the compo-

sites because of the soft epoxy-resin domains and hard silica domains in the composites. The dark regions are silica-rich domains. For all cases, spherical silica domains were microscopically dispersed in an epoxy-resin matrix. Thus, the composites prepared by method B were nanocomposites. Based on the Molau's law, it was natural that the morphologies of the composites were silica spheres in the epoxy resin in the range of the silica content <20 vol %. Interestingly, their silica domain sizes strongly depended on the silica content. It was owing to the segregation behavior of PHPS/silica depended on the content, as well as in the cases of the block or graft copolymers. The change of the silica domains size suggests that the graft copolymer with epoxy polymer backbone having PHPS branches had formed during the reaction. The verification of silica domains size by varying the silica content was the typical feature of the composite synthesized with PHPS. However, the systems of this study were more complicated than the system of general graft copolymer. The segregation between the epoxy resin and the PHPS domain and the formation of covalent bond between the epoxy resin and the PHPS were competitive. In the composite B-1 with 13.1 vol % of silica [Figure 9(a)], the reaction between hydroxy group and PHPS was preferable because of the high
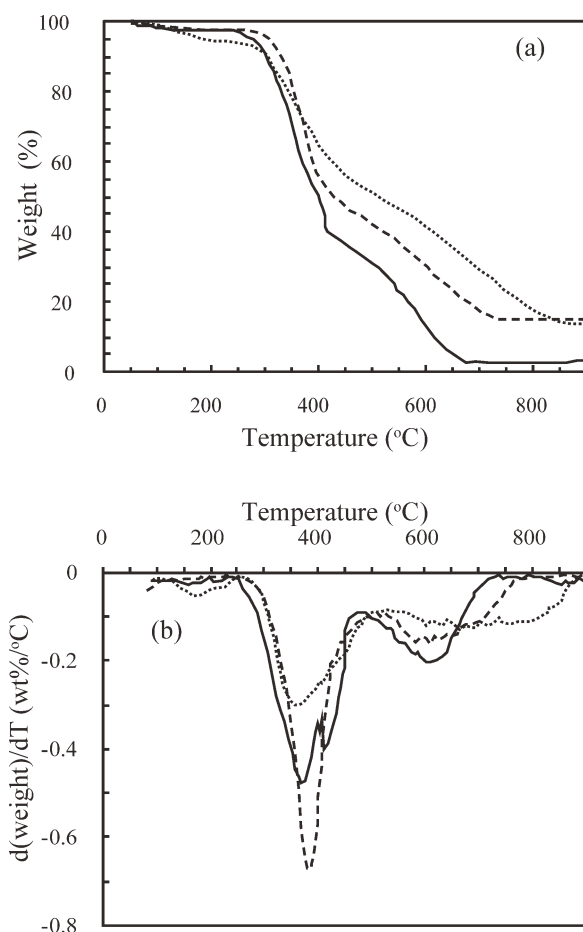
Figure 10. TGA (a) and DTG (b) profiles of the composite A-5 with 12.2 vol % of silica synthesized by method A (dash line), B-2 with 10.5 wt % of silica synthesized by method B (dotted line), and the epoxy resin C (solid line).

PHPS concentration in feed. The dark silica domains were dispersed in a light gray matrix. The interface between the silica domains and the matrix was not clear. The light gray matrix and unclear interface indicate that the Si atoms were homogeneously dispersed in the matrix. In the composite B-1, PHPS was tightly bonded to the epoxy resin via many hydroxy groups formed by the reaction of DGEBA and 1,4-diaminobutane. As a result, not only segregated silica domains but also the matrix containing silica was formed. In the composite B-2 with 10.5 vol % of silica [Figure 9(b)], the uniform spherical silica domains with 29.0 nm in diameter and 1.05 of polydispersity index were homogeneously dispersed in the epoxy resin. In this case, the rates of curing of DGEBA and conversion of PHPS were optimized, and the grafting of PHPS onto the epoxy resin would ideally proceed. In the composite B-3 with 5.4 vol % of silica [Figure 9(c)], the segregation of organic and silica domains was preferable than the bond formation. The small spherical silica domains of 15 nm in a diameter and large agglomerates were observed. Inhomogeneous and large agglomerates indicate that the strong segregation of the PHPS occurred in the composite. In the case of B-3, DGEBA was mainly cured with 1,4-diaminobutane in early state of the curing. The change of solubility parameter of DGEBA by curing enhanced the phase separation of PHPS and organic domains. Therefore, the microphase separation of epoxy resin–silica nanocomposite strongly depended on the addition of 1,4-dimaninobutane. By optimization of the feed, the homogeneous microphase separation was obtained.

Thermal Stability of the Composites

As described above, the high thermal stability was expected for the composites prepared by method B. Figure 10 shows TGA and DTG profiles of the composites A-5 and B-2 and the epoxy resin C prepared with DGEBA. First, the epoxy resin was partially confined by the silica domains. The char residue of the composites was slightly larger than their silica contents, 13.6 and 11.8 wt % for A-5 and B-2, respectively. Second, the decomposition behavior of all cases was similar to that of the epoxy resin in the literature,[29–32] whereas the first session at below 250°C occurred at N—C bonding with curing reagent, and the second session at over 400°C was breaking bisphenol A units into a variety of small molecules such as phenol, isopropyl phenol, bisphenol A, and their associated compounds. The blend of silica provided from PHPS improved the thermal stability of the epoxy resin. The first decomposition temperature of the composite was 255°C, whereas that of the epoxy resin C was 220°C. The second decomposition temperature of the composites was higher than 500°C. The decomposition of B-2 at 140 °C would be owing to the loss of excess 1,4-diaminobutane. Especially, in the case of B-2, the pyrolysis was not completed at 800°C. These composites showed better thermal stability than the epoxy–silica composites prepared with silica beads[33] and with POSS.[34] Again, in the composite B-2, the spherical silica domains were homogeneously dispersed in the matrix of epoxy resin, as well as the composites with silica beads and with POSS. The incomplete of decomposition of B-2 at 800°C would be owing to that the strong bonding silica and epoxy domains by covalent bonds. The homogeneous nanostructure of the composite by optimization of reaction rates of curing of

DGEBA with 1,4-diamnimobutane and the covalent bonding of PHPS and DGEBA resulted in the enhancement of thermal stability of the epoxy resin–silica composite. In conclusion, the thermal stability of epoxy resin was greatly improved by blending of silica provided from PHPS and 1,4-diaminobutane by method B.

CONCLUSION

PHPS acted as a weak curing reagent of epoxy monomer by the decomposition with moisture in air. Reaction mechanism composed of three steps. The first step: the decomposition of PHPS and providing of ammonia gas and silanol groups, the second step: the curing of epoxy group and condensation of silanol groups with ammonia gas as the catalyst, and the third step: the reaction of Si—H group and hydroxy group prepared by opening of epoxy ring. The hard and white solid composites were obtained by blending of PHPS and DGEBA and heating at 120°C. 1,4-Diaminobutane preferably reacted to epoxy monomer, whereas ammonia gas from PHPS reacted to both epoxy monomer and PHPS; the addition of 1,4-diaminobutane to the mixture improved both conversions of epoxy monomer and PHPS even at low silica content. The spherical silica domains with narrow size distribution were homogeneously dispersed in the epoxy-resin matrix by optimization of the contents of DGEBA, 1,4-diaminobutane, and PHPS. The thermal stability of the composite greatly improved by combining PHPS and the epoxy resin with 1,4-diaminobutane because of its homogeneity of microphase separation and the covalent bonding between the epoxy resin and the silica domains.

REFERENCES

1. Grayson, M. A.; Wolf, C. J. *J. Polym. Sci. Part A-1: Polym. Chem.* **1984,** *22*, 1897.

2. Bornmann, J. A. *J. Polym. Sci. Part C: Polym. Lett.* **1988,** *26*, 409.

3. El Gouri, M.; El Bachiri, A.; Hegazi, S. E.; Rafik, M.; El Harfi, A. *Polym. Degrad. Stab.* **2009,** *94*, 2101.

4. Frisch, H. L.; Foreman, R.; Schwartz, R.; Yoon, H.; Klempner, D.; Frisch, K. C. *Polym. Eng. Sci.* **1979,** *19*, 294.

5. Feng, J.; Berger, K. R.; Douglas, E. P. *J. Mater. Sci.* **2004,** *39*, 3413.

6. Mittal, V. *J. Comp. Mater.* **2008,** *42*, 2829.

7. Guadagno, L.; Vertuccio, L.; Sorrentino, A.; Raimondo, M.; Naddeo, C.; Vittoria, V.; Iannuzzo, G.; Calvi, E.; Russo, S. *Carbon* **2009,** *47*, 2419.

8. Unsworth, J.; Li, Y. *J. Appl. Polym. Sci.* **1992,** *46*, 1375.

9. Adachi, T.; Araki, W.; Nakahara, T.; Yamaji, A.; Gamou, M. *J. Appl. Polym. Sci.* **2002,** *86*, 2261.

10. Kwon, S. C.; Adachi, T. *J. Mater. Sci.* **2007,** *42*, 5516.

11. Lakshmi, M. Suguna; Narmadha, B.; Reddy, B. S. R. *Polym. Degrad. Stab.* **2008,** *93*, 201.

12. Mahrholz, T.; Stängle, J.; Sinapius, M. *Compos. A* **2009,** *40*, 235.

13. Hsieh, T. H.; Kinloch, A. J.; Masania, K.; Sohn Lee, J.; Taylor, A. C.; Sprenger, S. *J. Mater. Sci.* **2010,** *45*, 1193.

Applied Polymer
JOURNAL OF
SCIENCE

14. Myslinski, P.; Lazowski, Z. *Mater. Chem. Phys.* **1993,** *33*, 139.

15. Miyagawa, H.; Drzal, L. T. *J. Adhes. Sci. Technol.* **2004,** *18*, 1571.

16. Wichmann, M.H. G.; Cascione, M.; Fiedler, B.; Quaresimin, M.; Schulte, K. *Compos. Interfaces* **2006,** *13*, 699.

17. Lew, C.; Chowdhury, F.; Hosur, M. V.; Netravali, A. N. *J. Adhes. Sci. Technol.* **2007,** *21*, 1407.

18. Olmos, D.; Baselga, J.; Mondragon, I.; González-Benito, J. *J. Adhes. Sci. Technol.* **2008,** *22*, 1443.

19. Di Gianni, A.; Amerio, E.; Monticelli, O.; Bongiovanni, R. *Appl. Clay Sci.* **2008,** *42*, 116.

20. Chemtob, A.; Croutxé-Barghorn, C.; Soppera, O.; Rigolet, S. *Macromol. Chem. Phys.* **2009,** *210*, 1127.

21. Weng, W.-H.; Chang, C.-C.; Chen, H. *Compos. Interfaces* **2005,** *11*, 631.

22. Branda, F.; Tescione, F.; Ambrogi, V.; Sannino, D.; Silvestri, B.; Luciani, G.; Costantini, A. *Polym. Bull.* **2011,** *66*, 1289.

23. Saito, R.; Nakagawa, D. *Polym. Adv. Technol.* **2009,** *20*, 285.

24. Saito, R.; Kobayashi, S.; Hayashi, H.; Shimo, T. J. *Appl. Polym. Sci.* **2008,** *109*, 1498.

25. Saito, R.; Kobayashi, S.; Hayashi, H.; Shimo, T. J. *Appl. Polym. Sci.* **2007,** *104*, 3388.

26. Kawamoto T.; Kikuta, K.; Hirano, S. J. *Mater. Res.* **1998,** *13*, 353.

27. Dargère, N.; Bounor-Legaré, V.; Boisson, F.; Martin, G.; Spnntag, P.; Garios, N.Frontiers in Polym Sci, Proceedings, 2011 May 31, Lyon France, in association with the journal Polymer, P.3.123.

28. Saito, R.; Kuwano, K.; Tobe, T. J. *Macromol. Sci. Pure Appl. Chem.* **2002,** *39A*, 171.

29. Grassie, N.; Guy, M. I.; Tennent, N. H. *J. Degrad. Stab.* **1985,** *12*, 65.

30. Grassie, N.; Guy, M. I.; Tennent, N. H. *J. Degrad. Stab.* **1985,** *13*, 11.

31. Grassie, N.; Guy, M. I.; Tennent, N. H. *J. Degrad. Stab.* **1986,** *14*, 125.

32. Erickson, K. L. *J. Therm. Anal. Cal.* **2007,** *89*, 427.

33. Jin, H.-Y.; Yang, Y.-Q.; Xu, L.; Hou, S.-E.J. *Appl. Polym. Sci.* **2011,** *121*, 648.

34. Wu, K.; Kandola, B. K.; Kandare, E.; Hu, Y. *Polym. Comp.* **2011,** *32*, 378.