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Synthesis and Characterization of a Novel Silicon-Containing Epoxy Resin

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Abstract: A novel silicon-containing epoxy resin, the diglycidylether of bisphenol A-silicon (DGEBA-Si), was synthesized and characterized. The properties of the DGEBA-Si epoxy resin cured with 4,4-diaminodiphenyl methane (DDM), including its cure behavior, glass transition temperature, thermal stability, and mechanical strength were investigated. The char yield of the DGEBA-Si/DDM system was higher than that of a commercial DGEBA/DDM system, indicating that the DGEBA-Si epoxy resin showed good flame-retardance. The cured DGEBA-Si/DDM specimens possessed lower glass transition temperatures and higher mechanical properties than DGEBA/DDM specimens. These features were attributed to the introduction of siloxane groups into the main chain of the epoxy resin, which resulted in the improved flexibility of the cured DGEBA-Si/DDM system.

Keywords: synthesis, silicon, epoxy, thermal properties, mechanical properties.

Introduction

Epoxy resins based on diglycidylether of bisphenol-A (DGEBA) are widely used in advanced composites, coatings, structural adhesives, and microelectronics because of their good thermal stabilities, high modulus, good electrical properties, and outstanding adhesion.[1] However, the epoxy resins cannot successfully satisfy field applications that require higher toughness and flame resistance. Therefore, many attempts have been made to improve toughness and flame-retardant of the epoxy resins.

There are two methods to improve the toughness of the epoxy. One is the introduction of impact modifier into the epoxy resins to increases the ductile properties in the epoxy network, and another is the modification of epoxy structure by introduction of functional groups into the main or side chain of the epoxy. As an impact modifier, liquid rubbers and thermoplastics, such as carboxyl-terminated butadiene acrylonitrile (CTBN), amine-terminated butadiene acrylonitrile (ATBN), polysulfone, polyamide copolymer, and poly(ether ether ketone), have been previously used.[2-6] By changing the chemical structure of the epoxy, higher-performance physical properties can be obtained.[7] For example, the introduction of sulfone group into the main chain leads to an increases of flexibility of the epoxy resins.[8] Incorporation of phosphorus and silicon into the backbone of the epoxy leads to an increase of flame-retardant properties.[9,10] The silicon groups in the epoxy matrix can act as a toughening agent in the epoxy networks and improve impact strength.[11,12] Among these functional groups, silicon-containing chemical units are more advantageous modifiers, which possess some excellent properties, such as low-temperature flexibility, high-temperature stability, and flame-retardant.[13]

In this study, a novel silicon-containing epoxy resin has been synthesized from commercial DGEBA and dichlorodiphenyl silane and characterized by means of FT-IR, ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis.[11,12] The curing behaviors, glass transition temperature, thermal stabilities, mechanical properties, and fracture morphologies of the epoxy resin are evaluated by using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), a universal test machine (UTM), and scanning electron microscope (SEM).

Experimental

Materials. Diglycidylether of bisphenol-A (DGEBA) as an epoxy resin used in this study was supplied from Kukdo Chem. (YD-128), which had an epoxide equivalent weight (EEW) of 185-190 g/eq and a density of about 1.16 g/cm^3 at 25 °C. Dichlorodiphenyl silane (DCDPS), triphenylphosphine (TPP), and 4,4′-diaminodiphenyl methane (DDM) were supplied from Aldrich Chem. The chemical structures of DGEBA, DCDPS, and DDM were shown in Figure 1.

Synthesis of DGEBA-Si Epoxy Resin. DGEBA (152 g,

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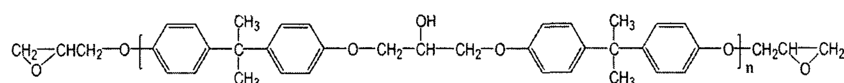
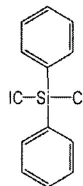
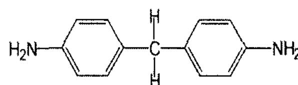


Diglycidylether of bisphenol A (DGEBA)



Dichlorodiphenyl silane (DCDPS)



4,4′-diaminodiphenyl methane (DDM)

Figure 1. The chemical structures of DGEBA, DCDPS, and DDM.

0.2 mol), DCDPS (22.8 g, 0.09 mol), TPP (2.6 g), and toluene (100 g) were placed in a 500 mL four-neck round flask equipped with mechanical stirrer, thermometer, and reflux condenser. The mixture was reacted at 55 °C for 24 h. After the reaction was completed, the crude product was filtered and washed with distilled water. The toluene and water were distilled off at 130 °C and 70 kPa. The obtained DGEBA-Si epoxy resin was a viscous liquid: yield 81%, EEW 349g/eq.

IR (KBr): 1249 (C-O-C), 1121 (Si-O), 915 (epoxide group), 771 cm^{-1} (C-Cl). ^{1}H NMR (acetone-d$_6$): δ=6.7~7.4 (m, 8H, aromatic protons), 4.0~4.2 (m, 4H, C-$\underline{H_2}$-O), 3.6~3.9 (m, 4H, C$\underline{H_2}$Cl), 2.6~3.0 (m, 3H, oxirane ring protons). ^{13}C NMR (acetone-d$_6$): δ=41.6 (CH_2Cl), 68.7, 51.9, 43.9 (epoxide group). $(C_{90}H_{98}O_{14}SiCl_2)_n$: Calcd. C 71.95%, H 6.53%, O 14.92%; Found C 71.39%, H 6.72%, O 13.79%.

Sample Preparation. The DGEBA or DGEBA-Si epoxy resin was preheated in an oil bath at 100 °C for 1 h and then the stoichiometric amount of DDM was added to the epoxy resin. The mixtures were fully stirred and degassed in a vacuum oven before measuring. The preparation of the specimens for the mechanical tests was as follows: bubble-free mixtures were poured into a stainless mold and cured at 110 °C for 1 h, at 140 °C for 2 h, and at 170 °C for 1 h in a convection oven.

Characterization and Measurements. FT-IR measurement on epoxy resin was performed with a Bio-Rad Co. digilab FTS-165 by using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were obtained by a BRUKER Co. DRX300 spectrometer operation at 300 MHz using acetone-d$_6$ as a solvent. Elemental analyzer (CE EA-1110) was used for elemental analyses (C, H, O) of the epoxy resin. The epoxy equivalent weight (EEW) of the epoxy resin was determined by the pyridinium chloride titration method.

The cure behaviors were investigated with a differential scanning calorimeter (Perkin Elmer, DSC 6) at the temperature ranged from 30 to 300 °C at a heating rate of 10 °C/min under the nitrogen flow of 30 mL/min. Dynamic mechanical analysis (DMA) was measured using a dynamic mechanical analyzer (RDS-II, Rhemetrics Co.) in a frequency of 1 Hz and the temperature range from 30 to 250 °C at a heating rate of 5 °C/min. Thermogravimetric analyses were performed with a du Pont TGA-2950 analyzer to investigate the thermal degradation of the cured epoxy at the temperature ranged from 30 to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

The critical stress intensity factor (K_{IC}) was measured by single edge notched (SEN) three-point flexural test, which was conducted on a universal test machine (Instron Model 1125 mechanical tester) according to ASTM E-399. For a SEN beam fracture toughness test, the K_{IC} value was calculated from the following equation:[14]

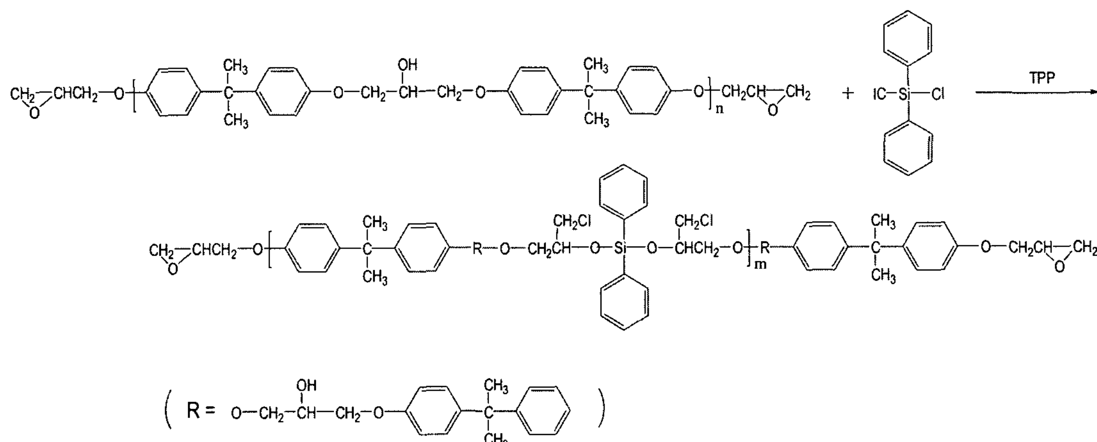
$$K_{IC} = \frac{P \cdot L}{b \cdot d^{3/2}} \cdot Y \tag{1}$$

where P is the rupture force, L the span between the supports, b the specimen width, d the specimen thickness, and Y the geometrical factor.

The flexural properties were measured on the three-point bending test with an Instron Model 1125 according to ASTM D-790. The flexural strength (σ_f) and elastic modulus in flexure (E_b) were calculated from the following equations:[15]

$$\sigma_f = \frac{3PL}{2bd^2} \tag{2}$$

$$E_b = \frac{L^3}{4bd^3} \cdot \frac{\Delta P}{\Delta m} \tag{3}$$



Scheme I. Synthetic route of DGEBA-Si epoxy resin.

where P is the applied load, L the span length, b the width of specimen, d the thickness of the specimen, ΔP the change in force in the linear portion of the load-deflection curve, and Δm the change in deflection corresponding to ΔP.

Each mechanical property value was obtained by averaging the five experimental values. The fractured surfaces were examined with scanning electron microscope (SEM).

Results and Discussion

Synthesis of the Epoxy Resin. Silicon-containing epoxy resin, diglycidylether of bisphenol A-silicon (DGEBA-Si), was prepared by the addition reaction of DGEBA with DCDPS using TPP as catalyst at 55 °C for 24 h. The synthetic route of DGEBA-Si epoxy resin is shown in Scheme I. The structure of resulting DGEBA-Si epoxy resin was characterized by means of FT-IR, ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis.

Figure 2 shows IR spectra of the DGEBA-Si epoxy resin, in which absorption peaks at 1249 and 915 cm^{-1} are due to the C-O-C and epoxide groups, respectively. The characteristic absorption of the new Si-O and C-Cl peaks at 1121 and 771 cm^{-1} emerged after the addition reaction, respectively.[16,17]

For ^{1}H NMR spectra (acetone-d_6), the corresponding proton signals at 6.7~7.4, 4.0~4.2, and 3.6~3.9 ppm due to aromatic ring, C-CH_2-O, and CH_2Cl protons, respectively. The chemical shift at 2.6~3.0 ppm corresponds to protons of the epoxide groups. For ^{13}C NMR spectra (acetone-d_6), chemical shift at 41.6 ppm belongs to the CH_2Cl groups and chemical shift at 68.4, 50.1, 44.6 ppm corresponds to the epoxide groups.[16,18]

For elemental analysis, $(C_{90}H_{98}O_{14}SiCl_2)_n$: Calcd. C 71.95%, H 6.53%, O 14.92%; Found C 71.39%, H 6.72%, O 13.79%. The elemental analysis data are in good agreement with calculated values. The EEW of the DGEBA-Si epoxy resin was found to be 349 g/eq and thus higher than that of DGEBA epoxy resin.

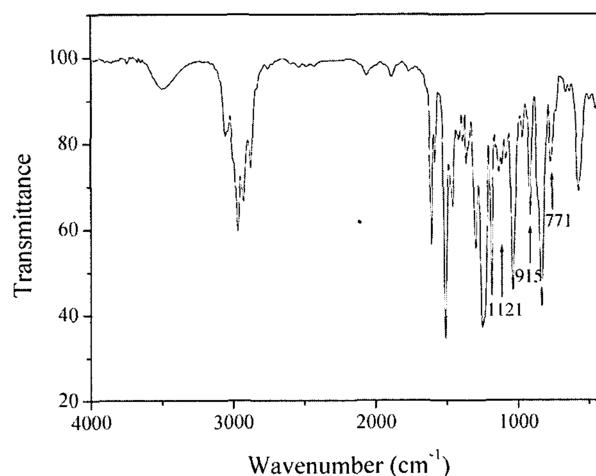


Figure 2. FT-IR spectra of the DGEBA-Si epoxy resin.

Cure Behaviors. The curing behaviors of the DGEBA-Si epoxy resin cured with DDM were evaluated and compared with commercial DGEBA epoxy resin by means of DSC. Figure 3 shows the typical DSC thermograms for DGEBA and DGEBA-Si epoxy resins cured with DDM at a heating rate of 10 °C/min. The peak maximum temperature and the reaction enthalpy (ΔH) of the DGEBA/DDM and DGEBA-Si/DDM systems are summarized in Table I. The results indicate that the DGEBA-Si/DDM and DGEBA/DDM systems have a similar peak maximum temperature, whereas ΔH of the DGEBA-Si/DDM system is significantly lower than that of the DGEBA/DDM system. The lower reaction enthalpy of the DGEBA-Si/DDM system is probably due to the higher EEW, i.e., the low content of oxirane ring groups, of DGEBA-Si epoxy resin.[18]

The conversions of epoxides were calculated by integrating the peak areas of epoxides in the IR spectrum before and after cure. Table I shows the results of conversion, which indicates that the conversion of the DGEBA-Si/DDM sys-

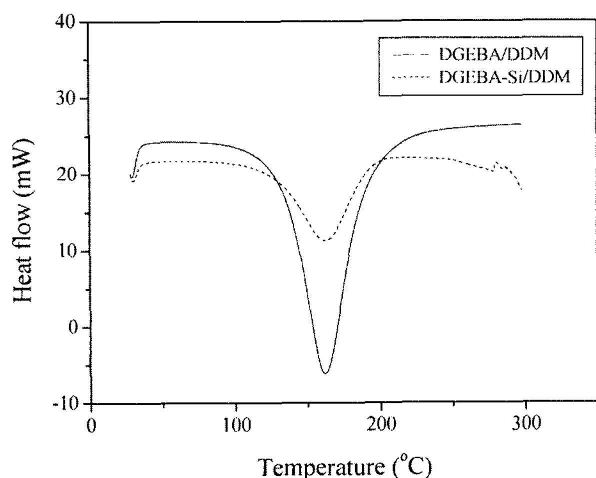


Figure 3. Dynamic DSC thermograms of the DGEBA/DDM and DGEBA-Si/DDM systems as a function of temperature.

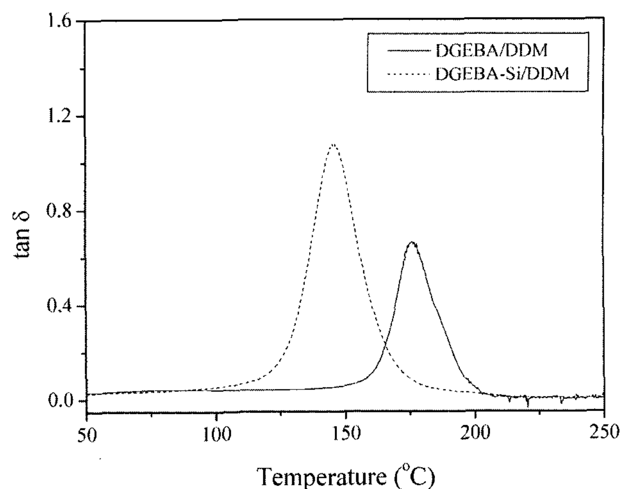


Figure 4. tan δ of the DGEBA/DDM and DGEBA-Si/DDM systems as a function of temperature.

Table I. Curing Characteristics of the DGEBA-Si/DDM and DGEBA/DDM Systems

System	Peak Maximum Temperature (°C)	ΔH (J/g)	Conversion (%)[a]
DGEBA/DDM	162	532	96.2
DGEBA-Si/DDM	163	255	95.3

[a]Conversion was calculated by integrating the peak areas of epoxides in the IR spectrum.

tem is similar to that of the DGEBA/DDM system.

Dynamic Mechanical Analysis. Glass transition temperature (T_g) of the cured epoxy resin was determined by DMA measurement. Figure 4 shows the temperature dependence of tan δ for the cured specimens. T_g value was taken as a maximum value of the tan δ curve. The T_g of the cured DGEBA-Si/DDM specimen is 146 °C, whereas for the cured DGEBA/DDM specimen T_g is 176 °C. The results can be interpreted in terms of the DGEBA-Si possess relatively high EEW value and thus reduced the cross-linking density of the epoxy network, resulting in decreasing the T_g in the DGEBA-Si/DDM system. The low T_g of the DGEBA-Si/DDM system may be also resulted from the flexible linkage of Si-O-C in the backbone of the epoxy resin.[18]

Thermal Stabilities. The thermal degradation behaviors of the cured DGEBA/DDM and DGEBA-Si/DDM specimens were studied with TGA at a heating rate of 10 °C/min in a nitrogen atmosphere and the TGA thermograms are shown in Figure 5. From the TGA thermograms, the thermal stability factors and char yields of the systems can be determined.[19,20]

The results of the thermal stability factors and the residues at 800 °C of the systems under nitrogen atmosphere are listed in Table II. As observed, the DGEBA-Si/DDM specimen was degraded at a lower temperature than that of the DGEBA/DDM specimen, which is probably due to the decomposition of the silane groups.[21] However, the degradation temperature of the DGEBA-Si/DDM specimen is higher than that of the DGEBA/DDM specimen at above 30% weight loss. The decomposition of silane groups in backbone is capable of forming a silane-rich residue after the initial stage of thermal degradation, which prevents further decomposition of the resin, resulting in raising the decomposition temperature in the DGEBA-Si/DDM system.[21] The char yield value of the DGEBA-Si/DDM specimen at 800 °C under nitrogen was 23.9%, while the DGEBA/DDM specimen was 13.2% under the same test conditions. This result can be attributed to the silicon migration to char surface and the formation of silicon-protecting layer in the char surface, resulting in preventing the weight loss of the DGEBA-Si/DDM system.[22]

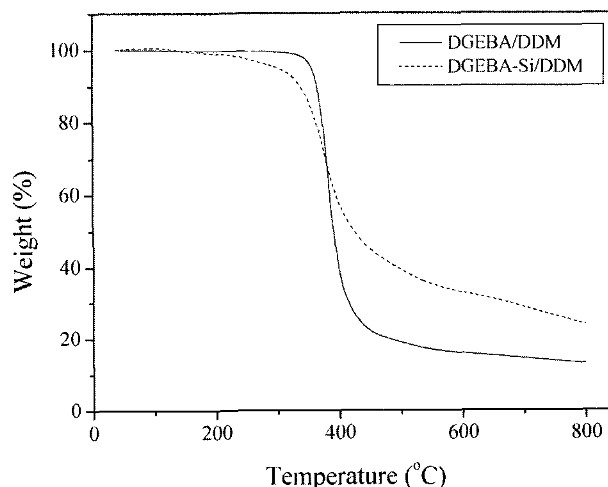


Figure 5. TGA thermograms of the DGEBA/DDM and DGEBA-Si/DDM systems.

Table II. Thermal Properties of the Cured DGEBA/DDM and DGEBA-Si/DDM Specimens

Sample	Temperature at Characteristic Weight Loss (%)						Residue (%) at 800 °C
	5%	10%	20%	30%	40%	50%	
DGEBA/DDM	355	364	373	379	385	391	13.2
DGEBA-Si/DDM	300	337	363	379	395	424	23.9

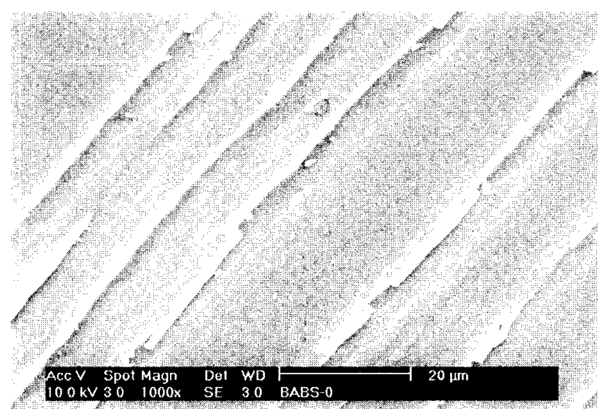
Table III. Mechanical Properties of the Cured DGEBA/DDM and DGEBA-Si/DDM Specimens

Specimen	K_{IC} (MPa·m$^{1/2}$)	σ_f (kPa)	E_b (GPa)
DGEBA/DDM	3.53±0.11	118±2.4	2.9±0.22
DGEBA-Si/DDM	4.48±0.1	151±2.7	4.1±0.25

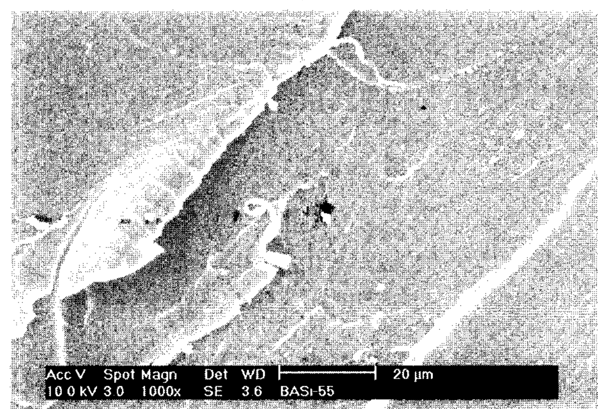
Mechanical Properties. The mechanical properties of the cured DGEBA/DDM and DGEBA-Si/DDM specimens are determined in terms of the fracture toughness and flexural strength. The critical stress intensity factor (K_{IC}), flexural strength (σ_f), and elastic modulus in flexure (E_b) were determined based on the three-point bending test.

The results of mechanical properties are summarized in Table III. The DGEBA-Si/DDM specimen shows remarkably higher K_{IC}, σ_f, and E_b values than those of the DGEBA/DDM specimen. The introduction of soft siloxane segment into the main chain of epoxy resin leads to an increase of flexible properties of the epoxy network, resulting in increasing the mechanical properties of the DGEBA-Si/DDM system.[11]

Figure 6 shows the morphology on fractured surfaces of the specimens after K_{IC} tests. In Figure 6(a), the SEM micrograph of the DGEBA/DDM specimen shows regulative cracks on the fracture surfaces. However, the micrograph of the DGEBA-Si/DDM specimen shows tortuous cracks and exhibits many ridges, as shown in Figure 6(b). This is why the DGEBA-Si/DDM system exhibits higher mechanical properties than those of the DGEBA/DDM system.



(a)



(b)

Figure 6. SEM micrographs of the DGEBA/DDM (a) and DGEBA-Si/DDM (b) systems after K_{IC} tests (magnification of 1000).

Conclusions

In summery, the silicon-containing DGEBA-Si epoxy resin was synthesized and characterized to investigate the cure behaviors, glass transition temperature, thermal stabilities, and mechanical properties. The char yield of the cured DGEBA-Si epoxy resin was higher than that of commercially available DGEBA, which was due to the silicon migration to char surface and the formation of silicon-protecting layer. The DGEBA-Si/DDM specimen showed a lower glass transition temperature and higher mechanical properties than those of the DGEBA/DDM specimen. The results could be attributed to the introduction of soft silicon segment into the main chain of the epoxy resin, resulting in increasing the flexibility in the DGEBA-Si/DDM system.

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