

Preparation of Epoxy Resins Containing Ether Ether Sulfone Unit and Thermal Properties

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Received April 30, 2001

Keywords : Epoxy resin, 4-(*p*-Glycidyloxyphenoxy)phenyl sulfone, Amine curing agent, Ether ether sulfone unit.

Epoxy resins are a class of thermosetting polymers that has gained industrial importance as well as academic interest because of the tunable properties of final products and the complicated set of side reactions occurring in any particular network-forming chemistry. The toughening of epoxy resin networks has raised much attention in recent years because epoxy resins possess desirable properties and are ideal candidates for important applications. Reactive rubber, a traditional toughening agent, rubber is incorporated into the epoxy resin to form a multiphase network during the curing process.¹ However, the toughness enhancement is accompanied with a significant sacrifice of properties at elevated temperature. On the other hand, many thermoplastics, such as polysulfone,² polyethersulfone,³⁻⁵ poly(ether ether ketone)^{6,7} and polyetherimide⁸⁻¹² are used as toughening and thermal stabilizing agent. These modified epoxy resin are two-phase systems, in which the phase separations proceed via spinodal decomposition induced by an increase of the molecular weight of the epoxy network during the curing reaction.¹³ The morphology of these systems, which decides the properties of the modified epoxy resins, is the result of the fixation of the phase-separated structure.¹⁴ There is a need for toughened and thermally stable epoxy resins having a thermoplastic unit in the main chain, which maintains toughness and thermal stability without phase separation at elevated temperatures.

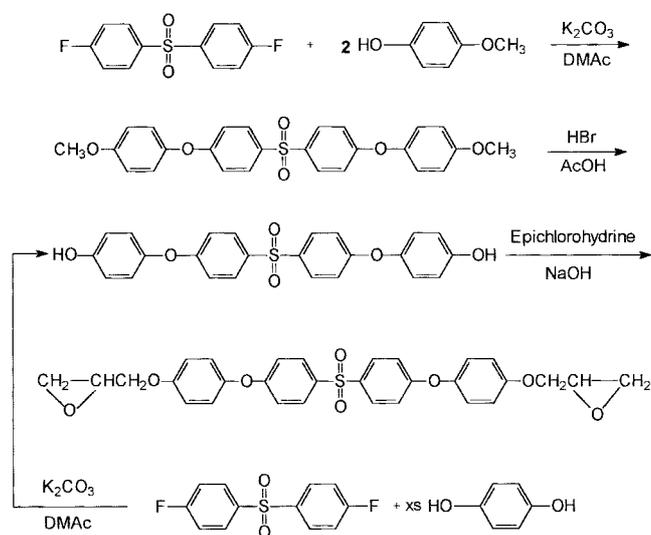
In a previous study, epoxy resin containing an ether ether ketone unit was prepared and its curing behaviors and thermal properties, including thermal stability, were investigated.¹⁵ In this report, 4-(*p*-glycidyloxyphenoxy)phenyl sulfone (GPPS) containing an ether-ether-sulfone (EES) unit was newly prepared, and the curing behaviors and thermal properties of the epoxy system with 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulfone (DDS) are studied by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA).

4-(*p*-Glycidyloxyphenoxy)phenyl sulfone (GPPS) was synthesized *via* a two-step or a three-step route as shown in Scheme 1. 4-(*p*-Hydroxyphenoxy)phenyl sulfone (HPPS) was synthesized from 4-methoxy phenol and 4,4'-difluorophenyl sulfone by aromatic nucleophilic substitution reaction, followed by a deprotection reaction of 4-(*p*-methoxyphenoxy)phenyl sulfone (MPPS) with hydrobromic acid.

GPPS was directly prepared by reacting 4-fluorophenyl sulfone with excess hydroquinone in the presence of potassium carbonate. This method gave a moderate yield (62%) with a good purity, as illustrated in Scheme 1. HPPS was reacted with ten-fold excess epichlorohydrin using tetraethyl ammonium bromide as catalyst, resulting in GPPS in good yield.¹⁶ Diglycidyl compound was purified by recrystallization and characterized in the usual way by IR, NMR spectroscopy and elemental analysis. Due to the high excess of epichlorohydrin used in the synthesis, oligomeric diepoxides were found after purification. The purity was proven by thin layer chromatography and the presence of a band in the IR spectrum between 3300-3500 cm⁻¹, which would show the presence of small amount of hydroxy groups. In the NMR spectrum, the integral values of aromatic protons at 8.1-6.8 ppm and the glycidyl group at 4.2, 3.3 and 2.8 ppm also indicated that glycidyl groups were introduced.

GPPS was a white crystalline solid having a melting point of 83 °C and miscible in diglycidyl ether of Bisphenol A (DGEBA) and soluble in common organic solvents, such as *N,N*-dimethylformamide, *N*-methylpyrrolidinone, *m*-cresol, ethanol, tetrahydrofuran and 1,2-dimethoxyethane.

4,4'-Diaminodiphenylmethane (DDM) and 4,4'-diamino-



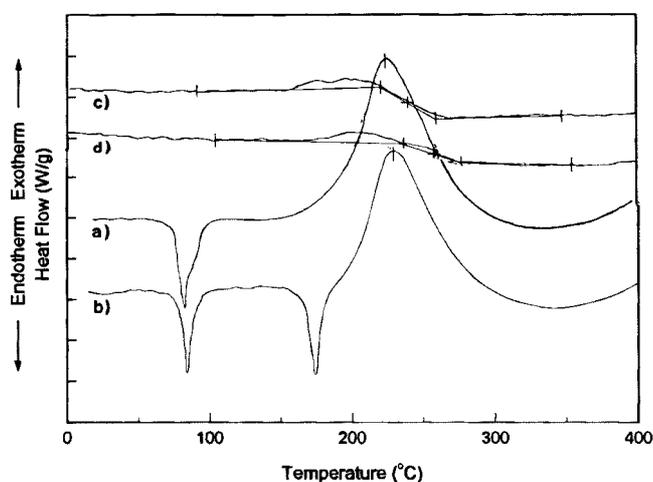
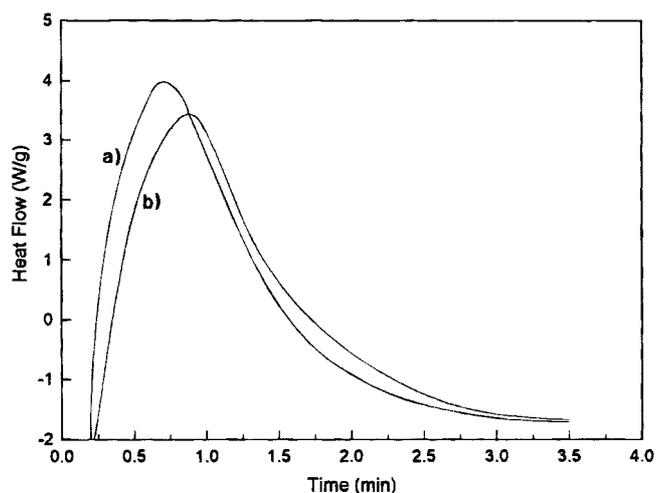
Scheme 1

Table 1. Thermal Properties of GPPS/DDS and DDS System

Curing Agents	mp (°C)	GPPS/Curing agent	T_g (2nd)	T_{Endo}	T_{Exo}
			(°C)		
DDM	89-91	2/1	241	82-90	220
		3/1	228	82-90	220
DDS	175-177	2/1	256	84, 176	225
		3/1	237	83, 180	228

diphenylsulfone (DDS) were used as curing agent. The epoxy resins were cured by using an epoxy/diamine weight ratio of 2/1 and 3/1. The curing behavior of GPPS was examined at 10 °C/min under nitrogen by DSC to obtain the optimum curing conditions for preparing diamine-cured epoxy networks. GPPS was cured with DDM or DDS in DSC pan. Table 1 summarizes the results of the curing behavior of GPPS. There are similar curing properties between the two curing systems. Figure 1 shows the dynamic scan of the GPPS-DDM and DDS mixtures. At 80-90 °C DDM/GPPS melts (Figure 1(a)), and at about 175 °C, DDS melts, as shown in Figure 1 (b); at about 200 °C the curing reaction starts, with a maximum of the exothermic peak at 220 °C. At about 270 °C the cure is complete, as can be inferred from the analysis of the second heating scan, where the absence of exotherms indicates no post-cure in the resin. A second dynamic DSC scan of GPPS/DDM, performed on the cured sample, revealed a glass transition temperature of 241 °C. Commercial epoxy resin obtained from tetraglycidyl-4,4'-diaminodiphenylmethane and DDS have a lower glass transition temperature, although a high cross-link density is expected.¹⁷ During the isothermal reaction of the GPPS/DDM performed at 250 °C, an exothermic peak appeared. This result indicates that the reaction proceeded without change of the reaction rate.

The onset temperature of the exotherms for GPPS/DDS started just after the endothermic melting transition temperature of the curing agent. The onset of the exothermic starting temperature of GPPS/DDM was similar to that of the

**Figure 1.** DSC thermograms of (a) GPPS/DDM = 1/2, (b) GPPS/DDS = 2/1, (c) GPPS/DDM = 1/2 (2nd scan) and (d) GPPS/DDS = 1/2 (2nd scan) at a heating rate of 10 °C/min in nitrogen.**Figure 2.** DSC isothermal scans of (a) GPPS/DDM = 2/1 and (b) GPPS/DDS = 2/1 mixture at 250 °C.

GPPS/DDS system. The reactivity of DDS was lower than that of DDM, as shown in Figure 2(b). The melting points for DDM and DDS were 90 and 176 °C, respectively. This phenomenon is directly associated with the melting temperature of DDS in GPPS. The variation in reactivity could also be due to the electronic effect. An electron-donating group in the amine compound would enrich the electron density of the amine group. On the other hand, DDS, which contains a strong electron-withdrawing group, showed lower reactivity.

The thermal properties of the cured epoxy resins were evaluated by thermogravimetric analyses (TGA) under nitrogen. From the TGA thermograms in Figure 3, stability parameters for the epoxy resin cross-linked with aromatic diamines were calculated. Data are summarized in Table 2. The decomposition onset temperature (T_{onset}), the temperature with 10% weight loss ($T_{10\%}$) and the residual weight of GPPS and the DGEBA/GPPS system were higher than those of the DGEBA system. The maximum weight loss temperature (T_{max}) and the rate of weight loss (dW/dt) at temperature T_{max} were obtained. The dW/dt values were between

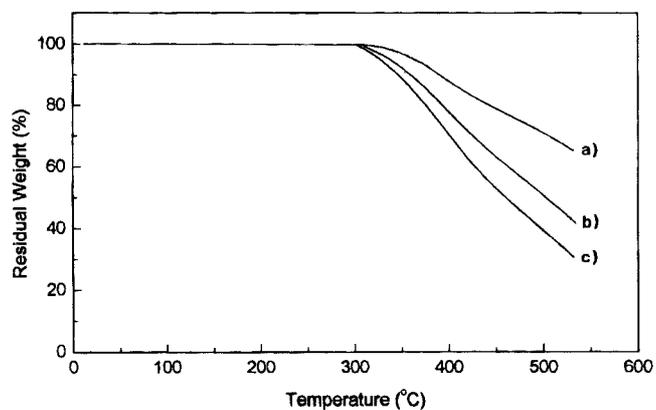
**Figure 3.** TGA thermograms of (a) GPPS/DDS = 2/1, (b) DGEBA/GPPS/DDS = 8/2/3.3 and (c) DGEBA/DDS = 2/1 at a heating rate of 10 °C/min under nitrogen.

Table 2. Thermal Stability of Cured Epoxy System

Epoxy/Curing agents	T _{onset}	T _{10%}	T _{max}	Residual Weight (%)		
				400 °C	500 °C	
GPPS/DDM	2/1	328	384	431	83.3	70.2
	3/1	329	379	423	85.1	73.8
GPPS/DDS	2/1	327	394	437	88.1	71.4
	3/1	331	389	431	84.2	75.6
DEGEBA/DDM	2/1	312	310	379	67.1	35.2
DEGEBA/DDS	2/1	309	321	387	68.1	40.3
DGEBA/GPPS/DDM	9/1/3.3	317	328	396	72.2	49.4
DGEBA/GPPS/DDM	8/2/3.3	321	336	394	75.8	51.2
DGEBA/GPPS/DDS	9/1/3.3	318	331	393	73.1	51.8
DGEBA/GPPS/DDS	8/2/3.3	323	342	392	78.1	52.7

-12 and -10%/min, and the char yield at 400 and 500 °C are also collected in the same Table. The GPPS epoxy system showed a 15-30% higher residual weight than that of the typical DGEBA epoxy resin. The DGEBA/GPPS mixed epoxy system also showed improved thermal stability. While being heated under nitrogen, DGEBA from DDS curing agents showed a one-stage weight-loss behavior. As observed for GPPS, weight loss begins at around 330 °C and then gives 83-88wt% residual weight loss at about 400 °C. The first stage weight loss was caused by the pyrolysis of the aliphatic unit. However, for DDM and DDS cured resins the decomposition of the epoxy resins was not so cleanly distinguishable from the decomposition of the polymer backbone.

The cured GPPS sample was also analyzed by FT-IR spectroscopy. The N-H characteristic absorbance at 3330-3400 cm⁻¹ was decreased and the O-H stretching band around 3500 cm⁻¹ was increased. The IR result also indicates that cross-linking of the GPPS proceeded almost quantitatively by the thermal curing process.

In conclusion, new ether ether sulfone containing epoxy compound GPPS was prepared from 4-(*p*-hydroxyphenoxy)-phenyl sulfone and epichlorohydrin. The use of glycidyl terminated molecule with rigid sulfonyl group was found to lead to improved thermal properties and better performances at high temperature compared with conventional epoxy resins. The studies of mechanical properties are in progress and will be reported elsewhere.

Experimental Section

Chemicals and Instruments. 4-Fluorophenyl sulfone (Fluka Chem. Co.), 4-methoxyphenol (Aldrich Chem. Co.), hydrobromic acid (48 wt. % in water) and epichlorohydrin were used without further purification. Toluene, methanol, ethanol, chloroform, 1,2-dichloroethane, acetic acid, ethyl acetate, sodium hydroxide and potassium hydroxide were used as received. Hydroquinone was purified by sublimation under vacuum. *N,N'*-dimethylacetamide (DMAc) was purified by vacuum distillation after drying by azeotropic distillation with benzene using a Dean-Stark separator. DDM and DDS

were recrystallized in benzene and 95% ethanol, respectively. DGEBA was a commercial epoxy resin based on Bisphenol A, namely YD-128S (Kukdo Chem. Co., Seoul), with an epoxy equivalent weight of 205-225 g/eq.

¹H NMR spectra were recorded on a Varian Gemini 2000 spectrometer. Fourier-transform infrared (FT-IR) spectra were taken on a Midac model M-1200 spectrometer. Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC 7 under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) measurements were carried out on a Shimadzu TGA 50 thermal analyzer at a heating rate of 10 °C/min under nitrogen.

Preparation of 4-(*p*-Methoxyphenoxy)phenyl Sulfone (MPPS). In a round-bottomed flask (500 mL) equipped with a Dean-Stark separator were placed 4-fluorophenyl sulfone (8.15 g, 32 mmol), 4-methoxyphenol (8.36 g, 67 mmol), potassium carbonate (18.52 g, 134 mmol), dry DMAc (80 mL) and toluene (30 mL). The solution was maintained at 120 °C for 12 hr and was refluxed at 160 °C for 1 hr to eliminate water. After the reaction was completed, the reaction mixture was poured into ice water to precipitate the reaction product. The solid product was filtered and washed with water/ethanol (1/2), and recrystallized from ethanol to yield a brownish crystalline product.

MPPS: Yield 87%. mp 185 °C. FT-IR (KBr) 3125-3001 (aromatic C-H), 2994-2805 (aliphatic C-H), 1615-1532 (C=C), 1240-1035 (C-O), 1135 (S=O), 625 (S-C) cm⁻¹. ¹H NMR (CDCl₃) δ 7.8 (d; 4H, aromatic protons), 6.9 (m; 12H, aromatic protons), 3.8 (s; 6H, -OCH₃).

Preparation of 4-(*p*-Hydroxyphenoxy)phenyl Sulfone (HPPS). In a round-bottomed flask (250 mL), was added MPPS (12.5 g, 29.30 mmol) dissolved in acetic acid (100 mL) and hydrobromic acid (30 mL). The solution was maintained at 110 °C for 48 hr. After the reaction was completed, the reaction mixture was precipitated into distilled water. The precipitated solid was filtered and washed with water several times. The solid product was recrystallized in ethylene dichloride/ethyl acetate (80/20) to give white powdery product in 71% yield.

Another Method of Synthesis of HPPS. HPPS was directly prepared from 4-fluorophenyl sulfone and hydroquinone in the presence of potassium carbonate. In a round-bottomed flask (500 mL) equipped with a Dean-Stark separator were placed 4-fluorophenyl sulfone (8.15 g, 32 mmol), hydroquinone (28.19 g, 256 mmol), potassium carbonate (8.85 g, 64 mmol), dry DMAc (250 mL) and toluene (40 mL). The solution was maintained at 120 °C for 12 hr and was refluxed at 160 °C for 1 hr to eliminate water. After the reaction was completed, the reaction mixture was poured into distilled water to precipitate the reaction product. The solid product was filtered and washed with methanol/water (70/30) several times, and recrystallized from 1,2-dichloroethane/ethyl acetate (80/20) to obtain white crystalline product in 62% yield.

HPPS: mp. 172 °C. FT-IR (KBr) 3390 (O-H), 3121-3010 (aromatic C-H), 1615-1535 (C=C), 1245-1032 (C-O), 1140 (S=O), 621 (S-C) cm⁻¹. ¹H NMR (acetone-*d*₆): δ 8.6 (s; 2H,

aromatic -OH), 7.9 (d; 4H, aromatic protons), 6.9 (m; 4H, aromatic protons).

Preparation of 4-(*p*-Glycidyloxyphenoxy)phenyl Sulfone (GPPS). In a 250 mL three neck round-bottom flask equipped with a mechanical stirrer and a thermometer, were placed DHPS (9.03 g, 21 mmol), ethanol (100 mL), sodium hydroxide (1.66 g, 42 mmol) and epichlorohydrin (80 mL). The reaction mixture was heated to 90 °C for 12 hr with vigorous stirring. Then a solution of sodium hydroxide (2.89 g, 72.20 mmol) dissolved in distilled water (20 mL) was added drop-wise for 1 hr at 60 °C, and the reaction mixture was raised to 80 °C and maintained for 2 hr. The reaction mixture was extracted with tetrahydrofuran and evaporated. The crude reaction product was washed with methanol and water, and dried at 60 °C under vacuum to give a white powdery product. The epoxy equivalent value of GPPS was 302-305 g/eq.

GPPS: Yield 84%, mp 83 °C. FT-IR (KBr) 3100-3016 (aromatic C-H), 2961-2842 (aliphatic C-H), 1607-1503 (C=C), 1242-1036 (C-O), 1650 and 1280 (S=O), 622 (S-C) cm⁻¹. ¹H NMR (CDCl₃): δ 7.8 (d; 4H, aromatic protons), 6.9 (m; 4H, aromatic protons), 4.1 (m; 4H -O-CH₂-CH-), 3.7 (m; 2H oxirane -CH-O-), 2.7 (m; 4H oxirane -CH₂-O-).

Curing Procedure of GPPS with Diamines. GPPS and aromatic diamine DDM (2/1, and 3/1 wt) as curing agent were mixed and milled at ambient temperature to obtain the well-mixed resin powder. The resin powder was placed in a DSC pan and PTFE mold, and cured at 180 °C for 1 hr and then post-cured at 220 °C for 4 hr. DDS cured DGEBA epoxy system was also cured by a procedure similar to the method described above. A mixture of GPPS (4.42 g), YD-128S (17.68 g) and DDS (7.35 g) was in a mill at moderate

temperature to give a thermosettable viscous liquid epoxy resin. The resin was cured in a mold at 180 °C for a period of 1 hr and then post-cured at 220 °C for 4 hr to obtain a cured specimen for thermal stability.

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