Preparation of Epoxy Resins Containing Ether Ether Ketone Unit and Their Thermal Properties

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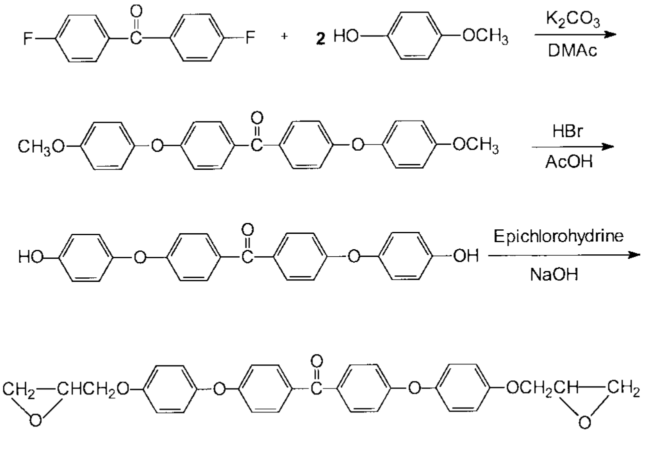
Epoxy resins are among the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fiber composites. Their cured resins have one drawback: they are brittle and have poor resistance to crack propagation. Various kinds of engineering thermoplastics such as poly(ether sulfone)s,[1-3] poly(ether imide)s,[4-7] poly(aryl ether ketone)s[8-10] and poly(phenylene oxide)[11,12] have been examined as modifiers. They were found to be less effective owing to the poor interfacial bonding between the two uncompatibilized phases in the cured resin. There is a need for toughened epoxy resin having an engineering thermoplastic unit in the main chain, which maintains a toughness without phase separation at the elevated temperature.

In this report, 4,4'-bis(*p*-dihydroxyphenoxy)benzophenone diglycidyl ether (DHBPDGE) containing an ether-ether-ketone (EEK) unit was newly prepared and the thermal properties of epoxy system using 4,4'-diaminodiphenylether (DDE), 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulfone (DDS) were examined by DSC and TGA.

DHBPDGE having an EEK unit was synthesized via a three-step route as shown in Scheme 1. 4,4'-Bis(*p*-dihydroxyphenoxy)benzophenone (DHBP) was prepared from 4-methoxy phenol and 4,4'-difluorobenzophenone by aromatic nucleophilic substitution reaction, followed by deprotection of 4,4'-bis(*p*-dimethoxyphenoxy)benzophenone (DMBP) with HBr. DHBP was reacted with epichlorohydrine to result in DHBPDGE in good yield. The integral values of aromatic protons at 7.8 and 7.1 ppm based on diphenyl ketone unit did not change and new signals appeared at 4.2, 3.3 and 2.8 ppm. The results indicate that glycidyl group was introduced to DHBP.



Scheme 1

DHBPDGE was white crystalline solid having melting point of 175 °C and soluble in polar aprotic solvents such as DMF, NMP and *m*-cresol, and slightly soluble in ethanol, THF and 1,2-dimethoxyethane.

Polymers were prepared from DHBPDGE and one of the three different aromatic diamines: DDE, DDM and DDS. The polymers were prepared using epoxy/diamine weight ratio of 1/1, 2/1 and 3/1 to ensure epoxy end groups that could be cross-linked in a further step to three-dimensional networks. The amine-cured DHBPDGE was analyzed by FT-IR spectroscopy. The absorption at 3330-3400 cm^{-1} corresponding N-H stretching band decreased apparently and OH absorption band appeared at 3500 cm^{-1}. The IR result indicates that cross-linking of the DHBPDGE proceeded by thermal curing process.

The curing behaviors of DHBPDGE with aromatic diamines were examined under nitrogen by DSC at a rate 10 °C/min to determine the optimum curing conditions. Typical DSC thermograms of DHBPDGE using various curing agents are shown in Figure 1. Table 1 also shows the results of the curing behavior of DHBPDGE. There are obvious differences between the three curing systems. They exhibited endotherms at different temperatures in Figure 1. This phenomenon associated with the melting temperature of curing agent as well as the miscibility of curing agents in DHBPDGE. The maximum exothermic temperature of curing was in the order of DDS > DDE > DDM for DHBPDGE/diamine = 2/1. As shown in Figure 1, all the diamine curing agents exhibit different reactivity to DHBPDGE. BHBPDGE/DDE system started the exothermic reaction just after the endothermic melting transition of both epoxy and curing agent. Compared with other curing agents, DDE show lower reactivity than DDM and higher reactivity than DDS. This phenomenon can be in part explained by the low melting temperature of 90 °C for DDM. The variation in reactivity

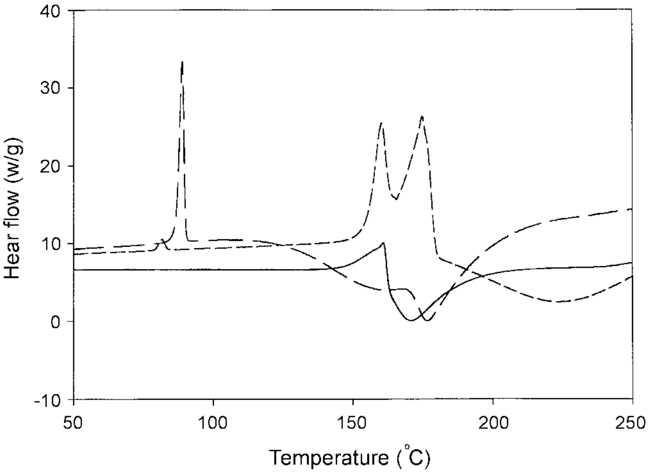


Figure 1. DSC thermograms of (——) DHBPDGE/DDE, (—) DHBPDGE/DDM and (---) DHBPDGE/DDS at a heating rate of 10 °C/min in nitrogen.

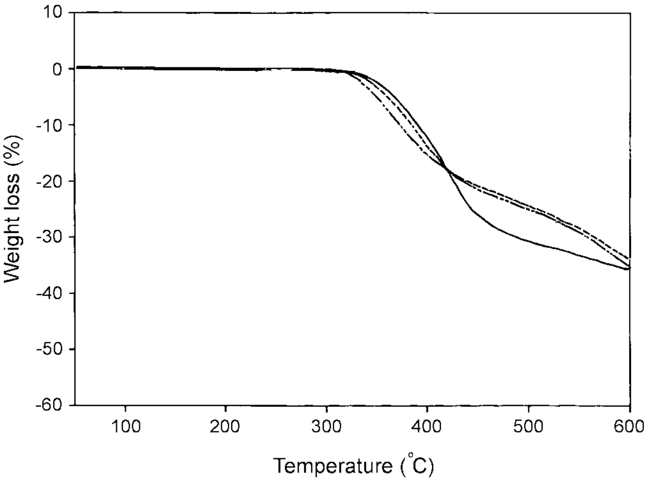


Figure 2. TGA thermograms of (---) DHBPDGE/DDE=2/1, (—) DHBPDGE/DDM=2/1 and (——) DHBPDGE/DDS=2/1 at a heating rate of 10 °C/min under nitrogen.

could be also due to the electronic effect. An electron-donating group in the amine compound, for example, the methylene group in DDM, would enrich the electron density of the amine group and therefore increase the reactivity of amine toward oxirane ring. On the other hand, DDS, which contains a strong electron-withdrawing group, shows lower reactivity.[13]

The maximum temperature of curing was 155 °C for DHBPDGE/DDM = 1/1. For DHBPDGE/DDM = 2/1 and 3/1, the DSC profiles show two exothermic peaks, which is based on the concentration and the phase of curing agent. It is believed that in the former system DHBPDGE/DDM = 1/1 the polymer would be cross-linked loosely or linear in the earlier stages of curing, because of the higher concentration of curing agent compared with the latter system. The first and second exothermic peaks for DHBPDGE/DDM = 2/1 and 3/1 systems were corresponding to the reaction of primary and secondary amine with epoxy groups, respectively.

The thermal stability of the cured epoxy resins was evaluated by thermogravimetric analyses (TGA) under nitrogen. Figure 2 shows the TGA thermograms of DHBPDGE. While being heated under nitrogen, the amine-cured epoxy system showed a two-stage weight loss behavior. In the case of aromatic amine-cured resins, the decomposition of the epoxy resins was not so cleanly distinguishable from the decomposition of epoxy itself or curing agent units. All of the diamine-cured DHBPDGE resins showed residual weight percent 87-88% at 400 °C and 67-78% at 500 °C.

Table 1. The Thermal Properties of Epoxy Resins Synthesized by EDHBPDGE and Aromatic Diamines (Heating Scan)

Curing agents	mp (°C)	DHBPDGE/ Curing agent	Endo (°C)	Exo (°C)
DDM	89-91	1/1	90	155
		2/1	90	156, 176
		3/1	90	157, 184
DDE	190-192	1/1	157	167
		2/1	162	171
		3/1	157	169
DDS	175-177	1/1	162, 169	207
		2/1	162, 176	225
		3/1	164, 180	241

Weight loss of diglycidyl ether of Bisphenol A (DGEBA) epoxy system begins at around 309-321 °C and then gives a rapid weight loss at about 400 °C, to result in an one-stage weight loss. Although some of the initial weight loss temperatures of DHBPDGE-based resin were a little lower than that of DGEBA-based resin, 10% weight loss and residual weight at 400 and 500 °C indicates the increase in thermal stability of DHBPDGE-based resins as shown in Table 2. The thermal stability was due to the more thermally stable rigid aromatic moiety.

In conclusion, new EEK-containing epoxy compound DHBPDGE was synthesized. DDM, DDE and DDS were used as curing agents for DHBPDGE epoxy resins. The curing features were examined by DSC analysis and well-

Table 2. Thermal Stability of Epoxy Resins Synthesized by EDHBPDGE and Aromatic Diamines

Epoxy/Curing agents		I DT[a] (°C)	10% wt Loss (°C)	Residual Weight (%)	
				400 °C	500 °C
DHBPDGE/DDM	1/1	301	371	88.3	77.5
	2/1	317	378	87.6	77.4
	3/1	311	386	89.1	74.1
DHBPDGE/DDE	1/1	309	381	88.7	78.6
	2/1	327	384	87.3	76.9
	3/1	316	387	88.7	70.7
DHBPDGE/DDS	1/1	345	401	89.7	70.8
	2/1	329	412	89.3	69.7
	3/1	324	391	87.2	67.9
DEGEBA/DDM	2/1	312	359	68.2	35.3
DEGEBA/DDE	2/1	321	356	66.7	38.7
DEGEBA/DDS	2/1	309	361	69.3	40.6

[a]initial decomposition temperature

mixed resin powder was cured at 120 °C for 30 min and 180 °C for 2 hr. The resulting epoxy resins showed high residual weight 87-89% at 400 °C and 67-78% at 500 °C implying their good thermal stability.

Experimental Section

Chemicals and Instruments. Epichlorohydrine (Aldrich Chem. Co.) was used without purification. DDE was purified by sublimation at 170 °C under vacuum. DDM and DDS were recrystallized in benzene and 95% ethanol, respectively. Diglycidylether of Bisphenol A (DGEBA) was obtained from Kukdo Chem. Co. (YD-128S, epoxy equivalent weight 205-225 g/eq).

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer. FT-IR spectra were taken on a Midac model M-1200 spectrometer. Elemental analysis data were obtained with Yanaco-MT-3 CHN analyzer. Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC 7 under nitrogen at a heating rate of 10 °C/min. TGA measurements were carried out on a Shimadzu TGA 50 thermal analyzer at a heating rate of 10 °C/min under nitrogen.

Preparation of 4,4'-Bis(*p*-dihydroxyphenoxy)benzophenone Diglycidyl Ether (DHBPDGE). A 250 mL three neck round-bottom flask equipped mechanical stirrer and thermometer, was charged with BDHPBP (13.05 g, 33 mmol), ethanol (100 mL), NaOH (2.62 g, 66 mmol), epichlorohydrin (ECH, 40.00 g, 432 mmol) and was heated to 90 °C for 6 hr with vigorous stirring. Then a solution of NaOH (2.76 g, 69 mmol) dissolved in distilled water (20 mL) was added dropwise for 1 hr at 60 °C, and the reaction mixture was heated to 80 °C and maintained for 2 hr.[14] Then mixture was poured into methanol and filtered. The crude reaction product was dissoved in DMAc and precipitated into methanol. The final product was washed with methanol and water, and dried at 60 °C under vacuum to give white powdery product. The epoxy equivalent value of DHBPDGE was 295-300 g/eq.

DHBPDGE: yield 86%, mp 175 °C. FT-IR (KBr) 3113-3016 (aromatic C-H), 2961-2836 (aliphatic C-H), 1607-1503 (C=C), 1650 (C=O), 1242-1036 (C-O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.7 (d; 4H, aromatic protons), 7.1 (m; 12H, aromatic protons), 4.2 (m; 4H 2-O-C$\underline{H_2}$-), 3.3 (m; 4H, 2 oxirane -C$\underline{H_2}$-O-), 2.8 (m; 2H, 2 oxirane -CH-O-).

Representative Curing Procedure of DHBPDGE with Diamines. DHBPDGE and aromatic diamine DDE (1/1, 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 PTFE mold and cured at 120 °C for 30 min and then post-cured at 180 °C for 2 h. Other curing agents DDM and DDS cured epoxy systems and Bisphenol A epoxy system was also cured by a procedure similar to the method described above.

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References

1. Bucknall, C.; Partridige, I. K. *Polymer* **1983**, *24*, 639.
2. Raghara, R. S. *J. Polym. Sci., Part B, Polym. Phys.* **l987**, *25*,1097.
3. Ragahava, S. J. *Polym. Sci. Part B: Polym. Phys.* **1988**, *26*, 65.
4. Bucknall, C. B.; Gilbert, A. H. *Polymer* **1989**, *30*, 213.
5. Bauer, R. S.; Stenzenberger, H. D.; Romer, W. *Natl. SAMPE Symp.* **1989**, *34*, 899.
6. Gilbert, A. H.; Bucknall, C. B.; *Makromol. Chem., Macromol. Symp.* **1991**, *45*, 289.
7. Murakami, A.; Saunder, D.; Oishi, K.; Yoshii, T.; Saito, M.; Watanabe, O.; Takezawa, M. *Nippon Setchaku Gakkaishi* **l99l**, *27*, 364.
8. Jang, B. Z.; Lian, J. Y.; Hwang, L. R.; Shih, W. K. *J. Reinf. Plast.* **l989**, *8*, 3l2.
9. Iijima, T.; Tochimoto, T.; Tomoi, M. *J. Appl. Polym. Sci.* **199l**, *43*, l685.
10. Bennet, G. S.; Farris, R. J.; Thompson, S. A. *Polymer* **1991**, *32*, l637.
11. Pearson, R. A.; Yee, A. F. *Polymer* **l993**, *34*, 3658.
12. Venderbosch, R. W.; Nelissen, J. G. L.; Meijer, H. E. H.; Lemstra, P. *J. Makromol. Chem. Macromol. Symp.* **l993**, *75*, 73.
13. Parekh, J. K.; Patel, R. G. *Die Angew. Macromol. Chem.* **1995**, *227*, 1.
14. Jung, J. C.; Lee, S. H. *Polymer (Korea)* **1990**, *14*, 481.