

Epoxy Resin Based on 4,4'-Dihydroxydiphenylsulfone.

I. Synthesis and Reaction Kinetics with 4,4'-Diaminodiphenylmethane and 4,4'-Diaminodiphenylsulfone

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SYNOPSIS

Epoxy resins based on 4,4'-dihydroxydiphenylsulfone (DGEBS) and diglycidyl ether of bisphenol A (DGEBA) were prepared by alkaline condensation of 4,4'-dihydroxydiphenylsulfone (bisphenol S) with epichlorohydrin and by recrystallization of liquid, commercial bisphenol A-type epoxy resin, respectively. Curing kinetics of the two epoxy compounds with 4,4'-diaminodiphenylmethane (DDM) and with 4,4'-diaminodiphenylsulfone (DDS) as well as T_g values of the cured materials were determined by the DSC method. It was found that the $-\text{SO}_2-$ group both in the epoxy resin and in the hardener increases T_g values of the cured materials. DGEBS reacts with the used hardeners faster than does DGEBA and the curing reaction of DGEBS begins at lower temperature than does the curing reaction of DGEBA when the same amine is used. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic diglycidyl ethers of the bisphenol type forms an important group of epoxy resins. Epoxy resins based on bisphenol A have achieved the greatest significance. Efforts to branch out the application areas of epoxides led to the investigation of other bisphenols as raw materials for the production of epoxy resins. First of all, 4,4'-dihydroxydiphenylmethane (bisphenol F) and bisphenol S were used.

Epoxy resin based on bisphenol S, prepared by condensation of bisphenol S and epichlorohydrin, was described for the first time by Beavers in 1953.¹ It was obtained in the form of white crystalline powder with melting point of 162–163°C.

At present, epoxy resins based on bisphenol S are used, for instance, in castings with good flexural and compressive strength,² in production of laminates with higher toughness,³ for laminates and two-com-

ponent adhesives with good thermal stability and chemical resistance,⁴ for coatings with higher thermal resistance than that of epoxy resins based on bisphenol A,⁵⁻⁷ and for thermoplastic products characterized by relatively high strength at elevated temperatures and high resistance to mechanical shock.⁸

EXPERIMENTAL

Materials Used

Diglycidyl ether of bisphenol A (DGEBA) was obtained in the form of a white crystalline powder by recrystallization of commercial liquid epoxy resin CHS Epoxy 15 (Spolchemie, Czech Republic) from the mixture of ethyl methyl ketone and methanol (1 : 4). The product had an epoxy value of 5.78 equiv/kg and a total chlorine content of 0.03%, and a melting point of 43°C was obtained.

4,4'-Diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulfone (DDS) were products of BASF and Rüttgerswerke, respectively; epichlorohydrin and sodium hydroxide, of Spolchemie; bis-

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phenol S, of Bayer; and isobutyl methyl ketone, of Shell Oil Co.

Synthesis of 4,4'-Dihydroxydiphenylsulfone (DGEBS)

Into a reactor equipped with thermometer, mechanical stirrer, and reflux condenser were charged 200 g (0.8 g mol) of bisphenol S and 370 g (4 g mol) of epichlorohydrin. The stirred mixture was heated under a nitrogen atmosphere to the refluxing temperature. Bisphenol S dissolved completely in epichlorohydrin. The mixture was maintained at the refluxing temperature (100–110°C) for 7 h while 70.4 g (1.76 g mol) of NaOH were added in the form of a 42% aqueous solution.

The excess of epichlorohydrin and water were distilled off at 100°C and 40 kPa. Then, the reaction mixture was dissolved in boiling isobutyl methyl ketone, stirred 30 min, and then filtered. DGEBS was obtained after cooling in the form of white crystalline powder with an epoxy value 4.985 equiv/kg, total chlorine content of 0.21%, and a melting point of 163°C.

Cure Procedure

Samples for T_g measurements were prepared by the following procedure: Melted DGEBA was mixed with DDM or DDS at 120–130°C. Melted DGEBS was mixed with DDS at 170°C. Compositions were stirred until transparent solutions were obtained. The liquids were poured into vertical steel molds and cured. In the case of the DGEBS–DDM system, DGEBS was melted at 170°C and poured into a container with DDM. This mixture was mixed and stirred until the transparent solution was obtained. This liquid was poured into a vertical steel mold and left 15 min at room temperature and then heated at the curing temperature. Curing conditions for the measured systems are given in Table I.

Table I Curing Conditions of Epoxide Compositions

System	Curing Procedure (h/°C)
DGEBS/DDM	2/140 + 2/160 + 2/180 + 2/200 2/160 + 2/180 + 2/200 + 1/220
DGEBS/DDS	+ 1/230
DGEBA/DDM	2/130 + 4/180
DGEBA/DDS	2/130 + 2/180 + 2/200 + 1/220

Table II T_g Values of the Cured DGEBS and DGEBA

System	T_g (°C)
DGEBS/DDM	172
DGEBS/DDS	201
DGEBA/DDM	163
DGEBA/DDS	183

DSC Method

T_g measurements and kinetic parameters of the curing process were determined using a Perkin-Elmer differential scanning calorimeter DSC-2 in a stoichiometric ratio of epoxy resin and diamine. T_g measurements were taken at 50–377°C with a heating rate 10°C/min. Calculation of T_g values was performed by the Richardson and Savill method.⁹

The activation energy of the curing process was calculated by Kissinger's method.¹⁰ Measurements were taken at various heating rates, 5, 10, 20, 40, and 80°C/min, in a nitrogen atmosphere. The $S(m, n)$ kinetic model was used for the formal kinetic description of the curing process [eq. (1)]:

$$(dx/dt) = k \cdot x^m \cdot (1 - x)^n \quad (1)$$

where k is the rate constant; x , the conversion; and m and n , the kinetic exponents of the $S(m, n)$ model.

RESULTS AND DISCUSSION

T_g Measurements

The influence of the central —SO₂— group both in the epoxy resin and in the hardener on the T_g of the cured samples is evident from Table II. The maximum curing temperature of each system was significantly above the T_g found, so we suppose that the maximum conversion at the functional groups was reached.

As is obvious, T_g values increase significantly in the range of DGEBA/DDM < DGEBS/DDM < DGEBA/DDS < DGEBS/DDS. We can say that the —SO₂— group both in the hardener and in the epoxy resin raises the T_g of the cured material. The difference between the two boundary compositions DGEBA/DDM and DGEBS/DDS is nearly 40°C. It was not surprising because similar differences between T_g values of epoxy resins cured with

DDM and DDS were found formerly.¹¹⁻¹³ The increase of T_g values after curing was found also when the central $-\text{SO}_2-$ group instead of the alkyl group was in the epoxy resin. Kamon¹⁴ found that the T_g values of diglycidyl ethers cured with DDM increase in the range of DGEBF (T_g value is 150°C) < DGEBA (180°C) < DGEBS (200°C).

Similar results were found for diglycidyl ethers cured with methylhexahydrophthalic anhydride.¹⁴ In the case of tetraglycidyl ethers based on DDM or DDS cured with DDS,¹⁵ a higher T_g value was also found for the composition with the central $-\text{SO}_2-$ group. Reinking¹⁶ studied the influence of different bisphenols in poly(hydroxy ethers) and Johnson¹⁷ in poly(aryl ethers). It was found that central group between two benzene rings influences the T_g in a similar way as in the above-mentioned cases. Higher T_g values were found at polymers with highly polar groups $-\text{SO}_2-$ and $-\text{CO}-$ in comparison with the $-\text{C}(\text{CH}_3)_2-$ group. Similar results were found even in the case of copolymers

Table III Peak Temperatures (T_m) at Various Curing Rates

System	Heating Rate ($^\circ\text{C}/\text{min}$)				
	5	10	20	40	80
DGEBS/DDM	129	145	162	179	205
DGEBS/DDS	197	210	230	251	277
DGEBA/DDM	157	172	180	216	239
DGEBA/DDS	212	228	255	276	304

based on bisphenol A, bisphenol S, and their diglycidyl ethers.¹⁸

Reaction Kinetics

Dependence of the heat capacity on the temperature for the followed systems is evident from Figure 1.

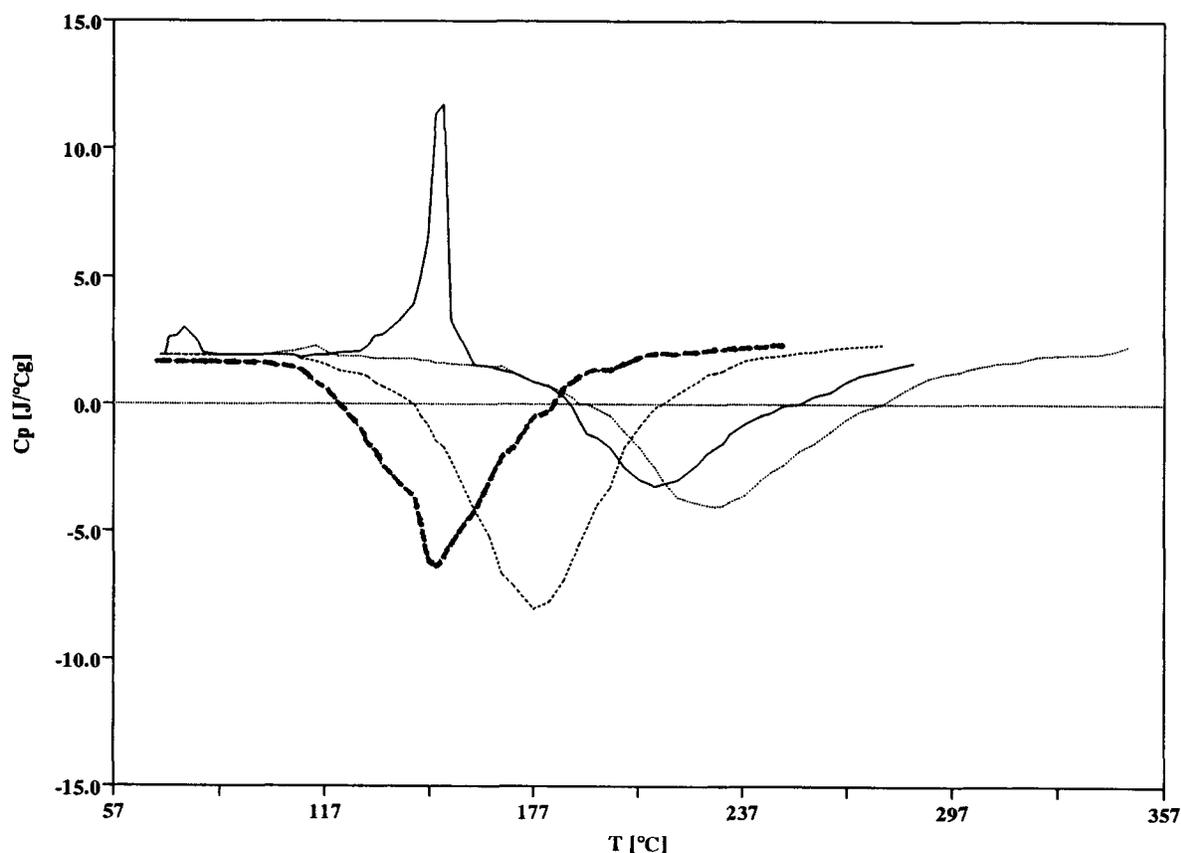


Figure 1 Dependence of the heat capacity (C_p) on the temperature: (---) DGEBA/DDM; (·····) DGEBA/DDS; (-·-·-) DGEBS/DDM; (—) DGEBS/DDS.

Table IV Kinetic Parameters of the Curing Process, Rate Constants, and Kinetics Exponents of the $S(m, n)$ Kinetic Model for Measured Systems

System	E (kJ/mol)	k (150°C) (s ⁻¹)	n	m	ln A (s ⁻¹)
DGEBS/DDM	50.0	$4.38 \cdot 10^{-2}$	1.60	0.88	11,090
DGEBS/DDS	64.8	$1.30 \cdot 10^{-3}$	1.36	0.38	11,782
DGEBA/DDM	51.4	$8.30 \cdot 10^{-3}$	1.40	0.69	9,824
DGEBA/DDS	60.0	$8.55 \cdot 10^{-4}$	1.43	0.57	9,997

The curing reaction of the used epoxy resins with DDM begins at a lower temperature than does the same reaction with DDS. On the contrary, if the $-\text{SO}_2-$ group is in aromatic diglycidyl ether (DGEBS), the curing reaction begins at a lower temperature in comparison with DGEBA containing a central alkyl group, when the same amine is used. It is in agreement with the peak temperatures T_m , which are seen from Table III. T_m was used also for the calculation of the activation energy (E) and frequency factor (A) by Kissinger's method.¹⁰

Kinetic parameters of the curing process, rate constants, and exponents of the $S(m, n)$ kinetic model for the measured systems are shown in Table IV. It was found that DDS reacts with epoxy resins much more slowly than does DDM. The reason is in the lower basicity and electron density on the nitrogen in DDS in comparison with DDM ($-M$ effect of the central $-\text{SO}_2-$ group). Rate constant ratios of the reactions of DDM and DDS were found to be

$$K_1 = (k_{\text{DGEBA/DDM}}/k_{\text{DGEBA/DDS}}) = 9.71$$

$$K_2 = (k_{\text{DGEBS/DDM}}/k_{\text{DGEBS/DDS}}) = 33.69$$

The rate constant ratio, K_1 , is in accordance with our previous results, where reaction kinetics were followed isothermally at 80°C using IR spectroscopy.¹⁹ In this work, K_1 was found to be 12.5. The epoxy resin DGEBS reacts with the used hardeners faster than does DGEBA. The central $-\text{SO}_2-$ group in the molecule of DGEBS is more electro-negative than is the $-\text{C}(\text{CH}_3)_2-$ group in DGEBA. It is the reason for the higher δ^+ charge on the end carbon atom of the epoxy group in DGEBS. Similar results were found, e.g., for the reaction of phenylglycidyl ether (PGE) and *N*-methylglycidyl aniline with dibutylamine,²⁰ where the higher δ^+ charge on the end carbon atom of the epoxy group in PGE causes higher reaction rate. Rate con-

stant ratios of the reactions of the DGEBS and DGEBA with the amines used were found to be

$$K_3 = (k_{\text{DGEBS/DDM}}/k_{\text{DGEBA/DDM}}) = 5.28$$

$$K_4 = (k_{\text{DGEBS/DDS}}/k_{\text{DGEBA/DDS}}) = 1.52$$

It was found that the hardener has only a slight influence on the values of the exponents of the $S(m, n)$ kinetic model.

CONCLUSIONS

The central $-\text{SO}_2-$ group both in the epoxy resin and in the hardener increases T_g values of the cured materials significantly as expected from the structure. The epoxy resin with this group reacts faster and the curing reaction begins at lower temperature than in the case of DGEBA when the same amine is used. On the contrary, the hardener with this group (DDS) reacts much more slowly than does DDM.

REFERENCES

1. E. M. Beavers, U.S. Pat. 2,765,322 (1953) (to Rohm & Haas Co.); *Chem. Abstr.*, **51**, 5119g (1957).
2. J. E. Singley and G. P. Whittle, U.S. Pat. 3,060,151 (1962) (to Tennessee Corp.).
3. H. Stutz, H. Tesch, P. Neumann, and G. Schaefer, DE 3,523,318 A1 (1987) (to BASF A.-G.); *Chem. Abstr.*, **106**, 139326m (1987).
4. E. Griebisch and H. Hilgert, DE 1,106,072 (1961) (to Schering Aktiengesellschaft); *Chem. Abstr.*, **55**, 26534 (1961).
5. M. F. Sorokin, E. L. Gershanova, Z. A. Mikhitarova, L. I. Volkova, and S. A. Ivanov, *Lakokras. Mater. Ikh. Primen.*, **5**, 11 (1981).
6. M. F. Sorokin, E. L. Gershanova, L. I. Volkova, and S. G. Kirillova, *Lakokras. Mater. Ikh. Primen.*, **4**, 16 (1982).

7. M. F. Sorokin, E. L. Gershanova, L. I. Volkova, and E. Yu. Gatinskaya, *Lakokras. Mater. Ikh. Primen.*, **5**, 2 (1984).
8. R. W. F. Kreps, A. Klootwijk, and J. M. Goppel, U.S. Pat. 3,364,178 (1968) (to Shell Oil Co.); *Chem. Abstr.*, **111**, 116287 (1989).
9. M. J. Richardson and N. G. Savill, *Polymer*, **16**, 753 (1975).
10. H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).
11. V. Bellenger and J. Verdu, *J. Appl. Polym. Sci. Part B Polym. Phys.*, **25**(6), 1219-1234 (1987).
12. P. G. Babayevsky and J. K. Gillham, *J. Appl. Polym. Sci.*, **17**, 2067 (1973).
13. M. Fischer, F. Lashe, and R. Schmid, *Makromol. Chem.*, **181**, 1251 (1981).
14. T. Kamon, *Kobunshi Ronbunshu*, **34**, 833 (1977); *Chem. Abstr.*, **88**, 51465e (1978).
15. T. Iijima, H. Hiraoka, M. Tomoi, and H. Kakiuchi, *J. Appl. Polym. Sci.*, **41**, 2301 (1990).
16. N. H. Reinking, A. E. Barnabeo, and W. F. Hale, *J. Appl. Polym. Sci.*, **7**, 2135 (1963).
17. R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale, and C. N. Merriam, *J. Polym. Sci. Part A-1*, **5**, 2375 (1967).
18. H. V. Hoorn, *J. Appl. Polym. Sci.*, **12**(4), 871 (1968).
19. I. Dobáš, J. Eichler, and J. Klaban, *Coll. Czech. Chem. Commun.*, **40**, 2989 (1975).
20. V. Špaček, J. Pouchlý, and J. Biroš, *Eur. Polym. J.*, **23**, 377 (1987).

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