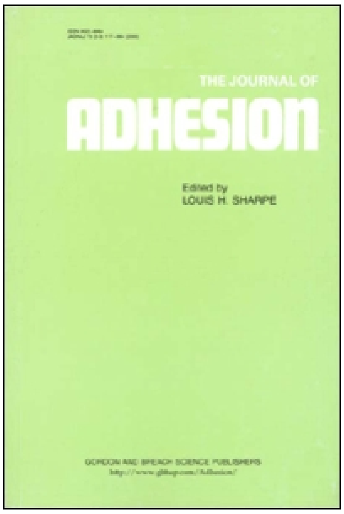


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

The Synthesis of New Epoxy Resins and their Physical Properties

Hiroshi Kakiuchi[a]; Ho Huu Thoi[a]; Thai Van Quang[a]
[a] Department of Applied Chemistry, Yokohama National University, Yokohama, Japan

To cite this Article Kakiuchi, Hiroshi , Thoi, Ho Huu and Van Quang, Thai(1981) 'The Synthesis of New Epoxy Resins and their Physical Properties', The Journal of Adhesion, 11: 4, 291 — 304

To link to this Article: DOI: 10.1080/00218468108078924

URL: http://dx.doi.org/10.1080/00218468108078924

J. Adhesion, 1981, Vol. 11, pp. 291-304
0021-8464/81/1104-0291 $06.50/0

Printed in Great Britain

The Synthesis of New Epoxy Resins and their Physical Properties

HIROSHI KAKIUCHI, HO HUU THOI and THAI VAN QUANG
Department of Applied Chemistry, Yokohama National University, Yokohama, Japan

(*Received November 10, 1978; in final form November 4, 1980*)

A series of homologous bisphenols was synthesized by the reaction of potassium *p*-hydroxybenzoate with dichloroalkanes or by the esterification of *p*-hydroxybenzoic acid with glycols. The studies of the synthesis of the diglycidyl ethers from these bisphenols were carried out by variation of the reaction conditions. The diglycidyl ethers synthesized were cured with hexahydroxyphthalic anhydride or with 4,4′-diaminodiphenylmethane. The effects of chemical structure of the cured resins on their mechanical, thermal, electrical, and adhesive properties were investigated. The results show that there is a good correlation between chemical structure and physical properties of the cured resins. The more the number of oxyethylene units ($-O-CH_2-CH_2-$) that are incorporated into the bisphenol portion of the network, the more flexible and polar the cured resins become. The increase in the flexibility of the cured resins is manifested by the decrease in the deflection temperature, elastic modulus and the enhancement of the elongation of the resins. The increase in the polarity of polymer results in the enhancement of the electric constant and the better adhesive properties.

INTRODUCTION

Epoxy resins, one of the most important thermosetting resins available today, are being used in many fields of industry [1,2] such as, coating, adhesive, reinforced plastic, electrical potting etc. . . . Most of the commercial epoxy resins now available are mixtures of polyglycidyl ethers made by the reaction of bisphenol A, 2,2-bis(4′-hydroxyphenyl)propane, with epichlorohydrin in the presence of alkali. The versatility of the epoxy resins has attracted the attention of a number of researchers, as evidenced by many reports in the literature which dealt with the synthesis,[1-4] formulation,[1,2,5,6] and curing reaction[1,2,7-10] of epoxy resins.

Recently, one of the most interesting problems in the field is the study of the effects of chemical structure and crosslink density between the networks on the physical properties of cured resins. The effects of crosslink density on the dynamic mechanical properties have been investigated by several workers by using a series of oligomers of diglycidyl ethers from bisphenol A[11,12] or by variation of the ratio of the diglycidyl ether to hardener.[13,14] Kwei[15] and Pogany[12] have investigated the effects of chemical structures on the mechanical properties of the diglycidyl ether of bisphenol A cured with a series of α,ω-diamines. The mechanical and adhesive properties of diglycidyl ethers of ethylene glycol and its homologues cured with aliphatic amines have been evaluated by Shimbo and Ochi.[16] These results are summarized as follows: the values of tensile modulus of the resins are affected in the rubbery region by their chemical structures and crosslink densities and those of each resin are constant or change slightly in the glassy and rubbery region but drastically in the transition region.

However, one of the demerits of the resin from bisphenol A is that it is too brittle. In an attempt to improve this demerit we have prepared a series of disphenols containing different numbers of the flexible segments of oxyethylene. The diglycidyl ethers from these bisphenols were cured with hardners and the effects of chemical structures on the physical properties of the cured resins have been investigated.

EXPERIMENTAL

Synthesis of bisphenols

Ethylene bis(*p*-hydroxybenzoate), EGB, and tetramethylene bis(*p*-hydroxybenzoate), TMGB, were prepared by the reaction of potassium *p*-hydroxybenzoate with dichloroethylene and dichlorotetramethylene, respectively. The mixture of 0.5 mol of potassium *p*-hydrobenzoate, 0.25 mol of dichloroalkane, and 250 ml of DMF was refluxed for 2 hr. Then, the solution of reaction mixture was concentrated, poured into water and the resulting bisphenol was obtained as precipitate. Yields were 77% for EGB and 90% for TMGB.

Bisphenols diethylene glycol (DEGB), propylene glycol (PGB) and triethylene glycol (TEGB) were prepared by the esterification of *p*-hydroxybenzoic acid with the corresponding glycols using *p*-toluenesulfonic acid as a catalyst. *p*-Hydroxybenzoic acid (0.5 mol), glycol (0.25 mol) and catalyst (1 g) were dissolved in a mixture of toluene and nitrobenzene. The reaction mixture was refluxed at 125–130°C for 20 hr and the water formed was removed by means of a Dean–Stark trap. The reaction mixture was chilled to 0°C, the precipitate was washed with benzene to remove nitrobenzene and with a sodium bicarbonate solution to remove the unreacted acid.

The yields were more than 60% in all the cases. The bisphenol from nonaethylene was prepared by heating the mixture of *p*-hydroxybenzoic acid, nonaethylene glycol and catalyst at 150–160°C for 20 hr. The unreacted reactants were removed by washing with sodium bicarbonate solution.

All the bisphenols were identified by NMR and molecular weight measurements.

Preparation of diglycidyl ethers from the bisphenols

With some necessary modifications, the general method of preparation used was described in the literature.[3,4] Epichlorohydrin (1.5 mol) was heated to the desired temperature and benzyltrimethylammonium chloride, BTA (4 g) was added. Bisphenol (0.1 mol) was dissolved in an aqueous solution of sodium hydroxide (0.2 mol in 40 ml water) at 0°C (to avoid the possible occurrence of the saponification of bisphenol). The cold solution obtained was added drop-by-drop during the desired time, and then the mixture was heated for additional 45 minutes. The organic phase was washed with water. The excess epichlorohydrin was removed by use of a rotary evaporator. Toluene was added to the residue, and the trace of remaining epichlohydrin was removed as the toluence azeotropes.

Description of technique and specimen preparation for testing and physical properties of the cured resins

The stoichiometric composition of resin and hexahydrophthalic anhydride (HHPA) was mixed at 80°C, and benzyldimethylamine (BDMA) was added to the mixture. Air bubbles contained in the mixture were removed. The resulting mixture was cast into a mold which had been previously treated with a mold release agent. The prepared resin was then cured in an air oven for 2 hr at 100°C and then for 15 hr at 150°C. The resin cured in such a way was used for the measurement of mechanical, thermal, and electrical properties.

The tensile properties were measured with an universal tensilon type UTM_1 of Toyo Measuring Instrument Co. according to the method outlined in ASTM D638-58T.

Deflection temperature was measured according to the ASTM D648-56 test procedure. The width and depth of the specimen were 1.2 × 1.2 cm.

The hardness of resin was determined by a durometer, Shore type, using the method described in ASTM D2240-64T.

The thermal shock resistance was measured according to Olyphant's method.[1] A $\frac{1}{4}$ in thick washer was used in this experiment. The thermal cycle was conducted according to Shell's standard method.

Details for the thermogravimetry experiments are as follows. About 5 mg of the cured resin samples were heated under nitrogen atmosphere at programmed rate of 5°C/min in a thermobalance. Two variables, temperature of the sample and weight loss, were recored.

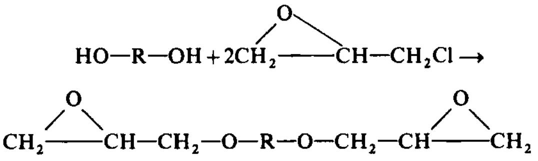
Dielectric constant was determined by the method described in ASTM D150–65T. The thickness of the test specimen was 0.3 mm, the applied voltage was 100 volts, and the diameter of electrode was 38 mm.

The adhesive properties were determined according to the method outlined in ASTM D1002–64. The steel panel used was 15 cm in length and 1.5 cm in width. The panels were degreased with trichloroethylene.

RESULTS AND DISCUSSION

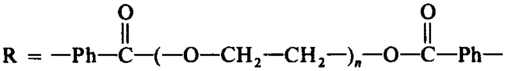
1. Synthesis of epoxy resins from bisphenols and epichlorohydrin

The reactions of bisphenols with epichlorohydrin in the presence of alkali form diglycidyl ethers of bisphenols whose structure is suggested as (I)



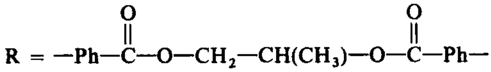
(I)

if



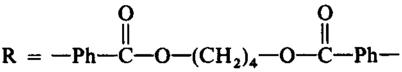
$$R = -Ph-\overset{\overset{O}{\|}}{C}-(-O-CH_2-CH_2-)_n-O-\overset{\overset{O}{\|}}{C}-Ph-$$

(I) stands for diglycidyl ethers of biphenols from ethylene glycol (n = 1, DGEGB), diethylene glycol (n = 2, DGDEGB), triethylene glycol (n = 3, DGTEGB), and nonaethylene glycol (n = 9, DGNEGB); if



$$R = -Ph-\overset{\overset{O}{\|}}{C}-O-CH_2-CH(CH_3)-O-\overset{\overset{O}{\|}}{C}-Ph-$$

(I) stands for diglycidyl ether of bisphenol from propylene glycol (DGPGB); if

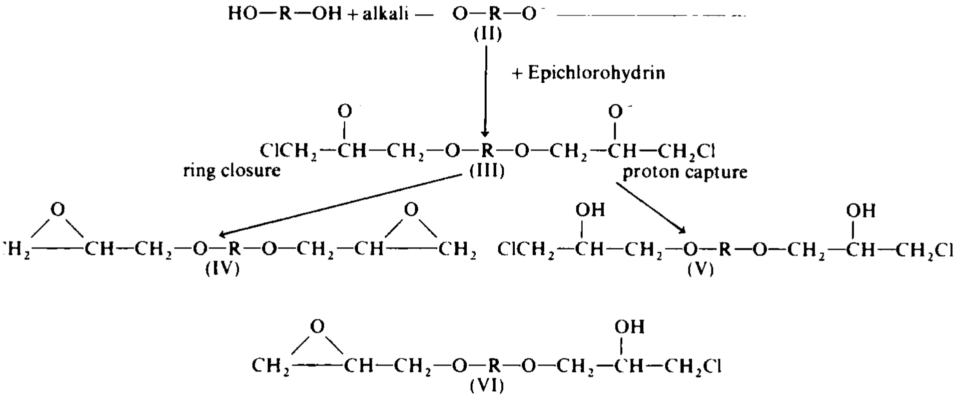


$$R = -Ph-\overset{\overset{O}{\|}}{C}-O-(CH_2)_4-O-\overset{\overset{O}{\|}}{C}-Ph-$$

(I) stands for diglycidyl ether of bisphenol from tetramethylene glycol (DGTMGB).

We suggest the following scheme to explain the reactions of bisphenols and epichlorohydrin under alkaline conditions

Scheme I



The initial step involves the formation of phenoxide anion (II) from the reaction of base with bisphenol. At the reaction temperature phenoxide (II) may react with epichlorohydrin to form dialkoxide (III) or may undergo the saponification. Resulting dialkoxide (III) may undergo ring closure reaction yielding diglycidyl ether (IV) or capture two protons giving dichlorohydrin (V) or both of the reactions may occur to form monoepoxy compound (VI). Diglycidyl ether (IV) may react further with phenoxide anion yielding oligomers.

In order to find out the most suitable reaction conditions for the preparation of diglycidyl ethers from the bisphenols, we have carried out a systematic study of the synthesis of DGEGB by variation of temperature, dehydrohalogenating agent, and catalyst.

Quaternary ammonium salt has been used as a catalyst in the reaction of sodium salts of fatty acid with epichlorohydrin[4, 17] to improve the reaction yield and to diminish the chlorohydrin by-product. It has been also found to be as a catalyst for some interfacial reactions. The effects of BTA catalyst are shown in Table I. The products obtained without catalyst have a high chlorohydrin equivalent. We believe that the main component of the products is monoepoxy compound (VI) since the values of epoxy equivalent, chlorohydrin equivalent and molecular weight of the products are very close to the theoretical value for (VI). The theoretical values of epoxy equivalent,

TABLE I

Reaction of Ethylene Glycol bis(*p*-hydroxybenzoate) with Epichlorohydrin. Effects of the Catalyst

Exp[a]	Catalyst BTA(g)	Molecular weight[b]		Chlorohydrin[c] equivalent	Epoxide[d] equivalent		Yield[e]
		obsd.	calcd.		obsd.	calcd.	%
1	4	425	414	0.080	275	207	95
2	none	445	414	0.165	435	207	98

[a] Reaction temperature, 65°C; time, 4 hr; dehydrohalogenating agent, NaOH, 0.2 mol; ethylene glycol bis(*p*-hydroxybenzoate), 0.1 mol; epichlorohydrin, 1.5 mol.

[b] Determined by VPO in dioxane.

[c] Chlorohydrin equivalent is defined as the number of gram equivalents of chlorine which are contained in 100 g of resin.

[d] Epoxide equivalent is defined as the weight of resin in grams which contains one gram equivalent of epoxy.

[e] Based on the assumption that one mole bisphenol reacts with two moles of epichlorohydrin.

chlorohydrin equivalent, and molecular weight for monoepoxy (VI) are 450, 0.222, and 450, respectively. The role of BTA in the reaction is not known clearly, however, maybe there are exchanges between Na cations and ammonium cations. The ammonium salt of bisphenol is soluble in epichlorohydrin and the reaction of phenoxide anion with epichlorohydrin may take place in epichlorohydrin phase. Consequently, the chance for proton capture from water is less and thus BTA promotes the dehydrohalogenation.

The data on the effects of reaction temperature in Table II show that the most suitable reaction temperature is 65°C. The epoxide equivalent, chlorohydrin equivalent and molecular weight of the products obtained at low temperature are greater than their corresponding theoretical values, *i.e.*, the

TABLE II

Synthesis of Epoxy Resin from Ethylene Glycol bis(*p*-hydroxybenzoate). Effects of the Reaction Temperature

Exp.[a]	Temp. °C	Molecular weight		Epoxide equivalent		Chlorohydrin	Yield
		obsd.	calcd.	obsd.	calcd.	equivalent	%
3	50	445	414	305	207	0.095	93
1	65	425		275		0.080	95
4	75	405		290			100
5	85	365		335			108

[a] Ethylene glycol bis(*p*-hydroxybenzoate), 0.1 mol; epichlorohydrin, 1.5 mol; NaOH, 0.2 mol; BTA, 4 g; reaction time, 4 hr.

TABLE III

Synthesis of Epoxy Resin from Ethylene Glycol bis(*p*-hydroxybenzoate) and Epichlorohydrin. Effects of the Dehydrohalogenating Agents.

Exp.[a]	Dehydrohalogenating agent	Molecular weight (obsd.)	Epoxide equivalent (obsd.)	Yield %
1	NaOH	425	275	95
6	KOH	450	330	98
7	MeONa	275	250	92

[a] Ethylene glycol bis(*p*-hydroxybenzoate), 0.1 mol; epichlorohydrin, 1.5 mol; dehydrohalogenating agent 0.2 mol; reaction temperature, 65°C; time, 4 hr; 4 g of BTA was used for reactions 1 and 6.

portion of chlorohydrins (V) and (VI) increased. This may be due to the decrease in rate for the ring closure reaction with lowering of the temperature which is at the same time sufficient to allow the proton capture and thus leads to the formation of chlorohydrin compound. At higher reaction temperature (see exp. 4 and 5) the increase both in the yield and the epoxide equivalent and the decrease in molecular weight of resins can be explained by the formation of oligomers from epichlorohydrin which is negligible at low temperature. In order to ascertain the formation of the oligomers from epichlorohydrin, the reaction described in experiment 5 was carried out without bisphenol. We obtained a resinous material of the oligomers of epichlorohydrin with the molecular weight of 290 and epoxide equivalent of 1200.

The results in Table III show that sodium hydroxide is the most suitable dehydrohalogenating agent. The value of molecular weight and of epoxide equivalent of the resin obtained using potassium hydroxide as dehydrohalogenating agent, are much higher than their theoretical values. This can be explained by the increase in the yield of oligomers formed by the reaction of the initially formed glycidyl ether with potassium phenoxide. On the other hand, when sodium methoxide was used the molecular weight of the resin obtained was much lower than the theoretical value. The results can be attributed to the occurrence of the saponification of the ester function in the bisphenol. By calculating the number of protons of ethylene glycol and of aromatic ring in the NMR of the diglycidyl ether, we were able to show that the saponification was negligible when potassium or sodium hydroxide was used.

2. Preparation of the other diglycidyl ethers

By using the most suitable reaction conditions which have been found in the study of the synthesis of DGEGB, we have synthesized the diglycidyl

TABLE IV

Data on Diglycidyl Ethers of DEGB, TEGB, NEGB, TMGB, and PGB

Exp.[a]	Bisphenol	Yield %	Molecular weight calcd.	Molecular weight obsd.	Epoxide equivalent calcd.	Epoxide equivalent obsd.
8	DEGB	92	458	460	229	280
9	TEGB	89	502	500	251	310
10	NEGB	91	752	670	376	430
11	TMGB[b]	83	442	480	221	276
12	PGB	90	428	420	214	280

[a] Reaction temperature, 65°C; time, 5 hr; bisphenol, 0.1 mol; epichlorohydrin, 1.5 mol; NaOH, 0.2 mol; catalyst, 4 g of BTA.

[b] KOH was used instead of NaOH.

ethers from DEGB, TEGB, TMEGB, PGB, and NEGB. The results are shown in Table IV.

3. Physical properties of the cured resins

Mechanical Properties The epoxy resin systems were cured using hexahydrophthalic anhydride (HHPA) as a hardener with benzyldimethylamine (BDMA) as a catalyst. The curing reaction was carried out in two stages. The first stage was conducted at relatively lower temperature in order to minimize the shrinkage. The temperature was then raised in the second stage to minimize the epoxide residue in the cured resin. The mechanism of the curing reaction of epoxy compounds and HHPA to form a crosslinking structure polymer has been proposed by Kakiuchi *et al.*[7,8] The gel times of the systems increase in the order of

$$\text{DGEGB}\,(0.57) < \text{DGDEGB}\,(1.10) < \text{DGTEGB}\,(1.35) < \text{DGNEGB}\,(2.10)$$

where the values in the parentheses express the gel time in minutes at 150°C. These results may be attributed to the increase in epoxide equivalent of epoxy resins in this order.

The stress-strain curves for the cured resins are shown in Figure 1. The curve for the cured resin from diglycidyl ether of bisphenol A (DGBA) shows that this resin is brittle and hard. When the segment of oxyethylene was introduced into the resin molecule, the decrease of the slope of its curve was observed. In contrast to the conventional epoxy systems, DGNEGB containing nine units of oxyethylene in its molecule behaved as a rubber-like material at room temperature.

The mechanical properties of the cured resins are shown in Table V. Since all of the diglycidyl ethers were cured by the same hardener and under

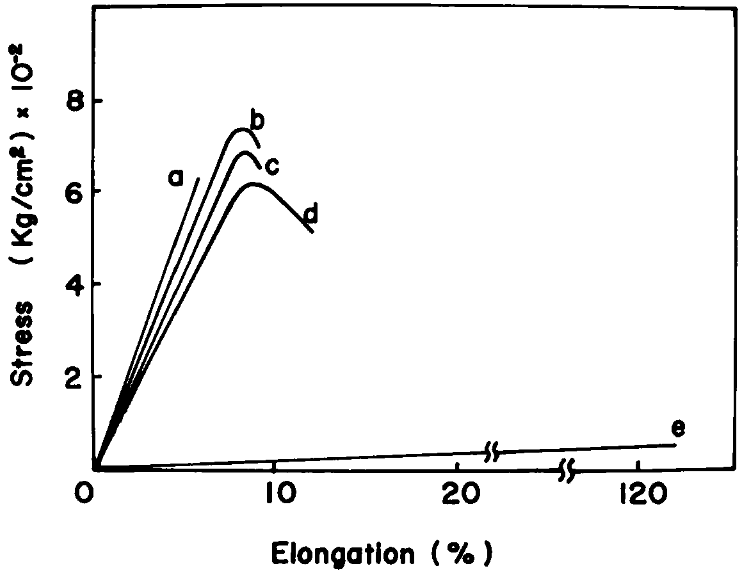


FIGURE 1 Stress-strain curves for the cured epoxy resins from: (a), DGBA (epikote 828); (b), DGEGB; (c), DGDEGB; (d), DGTEGB; (e), DGNEGB.

the same conditions, the difference in the mechanical properties of the cured resins are attributed to the difference in the structure of diglycidyl ethers. It can be seen in Table V that when the length of glycol portion increases, the modulus, hardness, and tensile strength fall off while the value of elongation at break increases. This means that the flexibility of the cured resins increases with increasing number of oxyethylene units. However, except for the case of DGNEGB in which the temperature of measurement is lower than

TABLE V

Data on the Physical Properties of Cured Resins[a]

Exp.	System	Hardness Barcol (type D)	Tensile strength kg/cm^2	Elongation at break %	Elastic modulus kg/cm^2	Deflection[b] temperature °C	Cracking
13	DGEGB	80–82	750	9	10,600	89	2.5
14	DGPGB	80–82	760	9	10,700	84	3.0
15	DGDEGB	79–81	690	9	10,200	70	3.5
16	DGTMGB	77–79	690	10	10,400		
17	DGTEGB	77–79	610	12	9,600	45	9.3
18	DGNEGB	34–37	18	122	15	<R.T	14.0
19	DGBA	85–86	670	6	11,000	127	0.0

[a] Curing condition: 100°C for 2 hr and then 150°C for 15 hr; hardener, HHPA (stochiometric quantity); catalyst BDMA. The tests were conducted at 23 ± 2°C.

its glass temperature, the magnitudes for these changes are not drastic. In this connection, Shimbo and Ochi[16] have studied the dynamic mechanical properties of diglycidyl ether of glycols (mono-, di-, tetra-, and nonaethylene glycol) cured by triethylene tetramine. They concluded that the values of tensile strength and modulus of the resins changed slightly in the glassy region but drastically in the transition region.

It can be seen in Table V that the effects of the length of glycol portion in the diglycidyl ether on deflection temperature are more significant than its effects on the modulus. The deflection temperature decrease considerably with increase in the number of oxyethylene units. The results can be explained by the consideration that the deflection temperature may be related to the motion of (—O—CH —CH —) sequences which is expected to occur at lower temperature when the number of such sequences is larger. The similar effect of chain stiffness on the glass transition temperature was observed by Kwei[15] and Pogany[14] for the systems of DGBA cured by a series of alphatic amines and by Shimbo and Ochi[16] for the series of diglycidyl ethers. By comparing the deflection temperature of DGEGB and of DGPGB, we note that the methyl group attached to the backbone decreases the deflection temperature about 5°C. This can be explained by the less compactness of chains of cured resins due to the methyl substituent.

The results of the thermal resistance of the cured resins show that the more the number of oxyethylene units are incorporated into the chain of crosslink, the better the thermal shock resistance of the resins are. Note that the thermal shock resistance increases with the increase in the value of cracking index.

As can be seen in Figure 2, the thermal stability of the cured resins falls off with the number of oxyethylene being introduced into the resin molecule. The decomposition of the cured resins of DGBA, DGEGB, DGDEGB, and DGTEGB begins respectively around 300, 170, 170, and 150°C and the temperatures at which 10% of the total weight loss was attained are 355, 365, 370, and 390°C, respectively. The results can be attributed in part to the incorporation of aliphatic ether portions containing the weak C—O bond as well as to the difference in the crosslinking density of the resins.

Electrical Properties of the Cured Resins The effects of temperature on the dielectric constants for the cured resins are shown in Figure 3. In the glass region the dielectric constant increases slightly with the increase in temperature, but it increases considerably in the transition region. We explain the results as follows. The mechanism of the deformation of the resin by the electric field below the glass transition temperature is thought to be predominantly by the stretching of covalent and Van Der Waals bonds and some motion of localized chain segments; however, in the transition region,

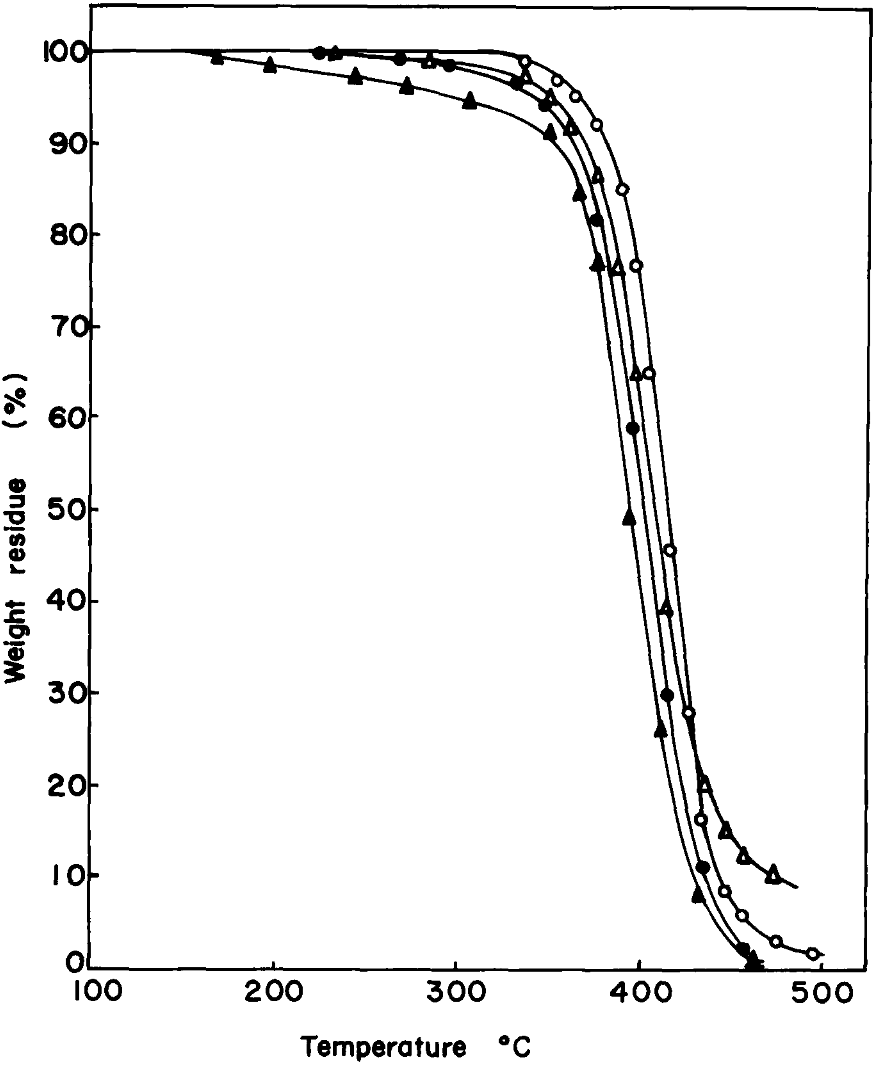


FIGURE 2 Weight residue of cured epoxy resins heated at a rate of 5°C per minute: (○) DGBA, (△) DGEGB, (●) DGDEGB, (▲) DGTEGB.

extensive molecular motion also occurs. The sharp breaks of the curves of dielectric constant *vs.* temperature at 60 cycles/sec were observed around 145, 110, 85 and 55°C for DGBA, DGEGB, DGDEGB, and DGTEGB, respectively. The values of dielectric constant of the resins at a given temperature increase with the increase in the number of oxyethylene units in the resin molecule. The result can be expected since the increase of the oxyethene

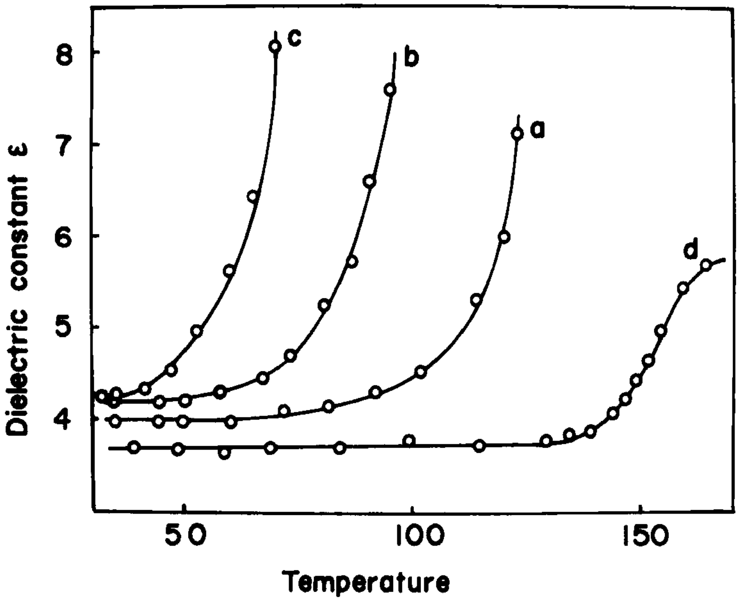


FIGURE 3 The dependence of dielectric constant on temperature for the cured resins at frequence of 60c: (a) DGEGB, (b) DGDEGB (c) DGTEGB, (d) DGBA.

unit, which is polar, will result into an enhancement in the polarity of the resins. The difference in the dielectric constant for these resins is slight in the glassy region but becomes considerable in the transition region.

The Adhesive Properties of the Cured Resins It can be seen in Table VI that the value of tensile shear strength of the resins increases with the increase in the number of oxyethylene units. In general, the adhesive properties of resins are known to be affected by the polarity and the flexibility of resins. The adhesive forces are expected to arise from Van Der Waals interactions between the applied resins and surfaces of the steel panels used

TABLE VI

Adhesive Properties of the Resins Cured with 4,4'-diaminodiphenylmethane[a]

System	DGTEGB	DGDEGB	DGEGB	DGBA
Tensile shear strength[b] (kg/cm^2)	101	83	43	40

[a] Cured at 130°C for 4 hr.

[b] The average value for five test specimens. Test panels, stainless steel; measured at 23 ± 2°C.

in the test, so that the forces will increase when the polarity of resins increases. On the other hand, Erich and Bodnar[18] have reported that the local stresses in the glue line of the joint, which are a negative function of modulus, reduce considerably the bonding strength of an adhesive. Therefore, the observed order of increasing tensile shear strength for the cured resins from DGBA to DGTEGB can be attributed to the increase in the polarity and the decrease in modulus of these systems when we go from DGBA to DGTEGB. In this connection, Sandler[19] has reported that the resin containing the ester group, being polar, has good adhesive properties.

CONCLUSIONS

A series of diglycidyl ethers from new bisphenols containing different numbers of oxyethylene units in the molecule was synthesized. The study of the physical properties of the cured resins from these diglycidyl ethers shows that by selecting the chemical structure of the segments between the crosslinks, it is possible to effect a great change in their physical properties. The incorporation of oxyethylene segments into the network results in an increase in the flexibility and polarity of the cured resins. The increase in the flexibility of the cured resins is manifested by the decrease in deflection temperature, elastic modulus and the improvement of the thermal shock resistance. The enhancement of the polarity of the cured resins is manifested by the increase in the electric constant and tensile shear strength.

Acknowledgements

We wish to thank Dr. W. Fukuda of Yokohama National University, and Mr. M. Murata, Somaru, Ltd., for their valuable discussions. One of the authors (H. H. Thoi) also expresses his thanks to the Japanese Ministry of Education for carrying out this investigation.

References

1. H. Lee and K. Neville, *Handbook of Epoxy Resins* (McGraw-Hill, New York, 1967).
2. H. Kakiuchi, *Epoxy Jushi (Epoxy Resins)* (Shokodo, Tokyo, 1968). In Japanese.
3. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry* (Interscience, New York, 1968), p. 465.
4. G. Maerker, J. F. Carmichael, and W. S. Port, *J. Org. Chem.* **26**, 781 (1961).
5. R. Schmid, *et al. J. Polym. Sci., Part C,* **30**, 339 (1970).
6. A. Noshay and L. M. Robeson, *J. Polym. Sci. Al* **12**, 689 (1974).
7. Y. Tanaka and H. Kakiuchi, *J. Appl. Polym. Sci.* **7**, 1063 (1963).
8. Y. Tanaka and H. Kakiuchi, *J. Appl. Polym. Sci.* **7**, 1951 (1963).
9. Y. Tanaka, M. Tomio and H. Kakiuchi, *J. Macromol. Sci. Chem. Al*, 2471 (1967).
10. K. Dusek and M. Bleha, *J. Polym. Sci. Chem. Ed.* **15**, 2393 (1977).
11. J. P. Bell, *J. Polym. Sci. A2* **6**, 417 (1970).

12. M. Shimbo, M. Iwakoshi and M. Ochi, *J. Adhesion Socy. Japan* **10,** 161 (1974).
13. T. Murayama and J. P. Bell, *J. Polym. Sci. A2* **8,** 437 (1970).
14. G. A. Pogany, *Eur. Polym. J.* **6,** 343 (1970).
15. T. K. Kwei, *J. Polym. Sci. A2* **4,** 943 (1966).
16. M. Shimbo and M. Ochi, *Nippon Kagaku Zasshi* **10,** 2006 (1974).
17. M. Inano, *Kogyo Kagaku Zasshi* **70,** 92 (1967).
18. W. Erich and M. J. Bodnar, *J. Appl. Polym. Sci.* **3,** 296 (1960).
19. S. R. Sandler, *J. Appl. Polym. Sci.* **11,** 465 (1967).