

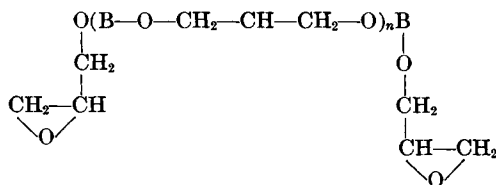
Effect of Molecular Structure on Mechanical Properties of Epoxy Resins

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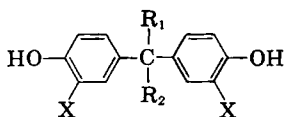
Introduction

Many patents have been issued on the synthesis of various glycidyl ethers.¹⁻⁵ The tests conducted on these polyethers have been confined mainly to such physical properties as softening point, viscosity, and curing time. Comparatively little has been reported on mechanical properties such as the impact and shear strengths of adhesive-bonded joints utilizing the polyethers derived from higher molecular weight dihydric phenols. In this investigation, joints were prepared with epoxy adhesives derived from several series of polyethers represented by the formula:



where B is the hydrocarbon portion of the dihydric phenol and $n = 0$ or more.

In series I and II, the bisphenol is of the general type:



In series I(A), $R_1 = \text{CH}_3$ or C_3H_7 and R_2 varies from CH_3 to C_9H_{19} . In series I(B) the benzhydryl carbon atom is incorporated in a cyclohexane or cyclopentane ring (Table II). The corresponding bisphenols derived from *o*-cresol ($R_1, R_2, X = \text{CH}_3$) as well as from resorcinol were also tested as dihydric phenols (Table III). The shear and impact bond strengths of adhesives based on these compounds were measured.

The bisphenols were all prepared by the Baeyer reaction⁶ which has been used by many investigators.⁷⁻¹³ The resins were made by reacting the

bisphenol with epichlorohydrin in an alkaline medium.

Experimental

The bisphenols described in this paper (Table IV) were prepared by two methods, both modifications of the original Baeyer synthesis. The glycidyl polyethers of these dihydric phenols were prepared using the procedure described by Shokal;⁴ namely, by reacting epichlorohydrin with the bisphenol in an alkaline medium.

Method A. Preparation of Bisphenols Using Aliphatic Ketones

One mole of ketone and 4 moles of phenol were heated with 4 g. concentrated hydrochloric acid, 40 g. anhydrous calcium chloride, and 3 ml. of β -mercaptopropionic acid at 110°C . for 4 hr. The color changed from yellow to a deep red. Excess phenol was removed by vacuum distillation. The product was recrystallized from tetrachloroethane. Yields were 55-86% theoretical.

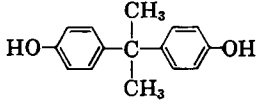
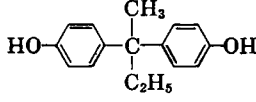
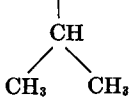
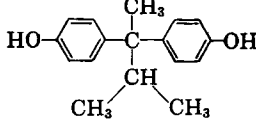
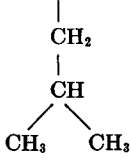
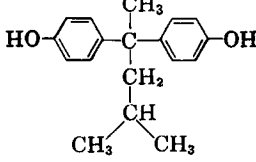
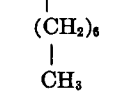
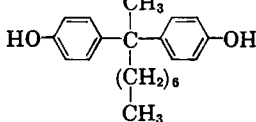
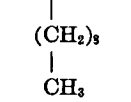
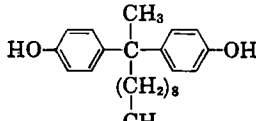
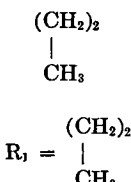
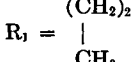
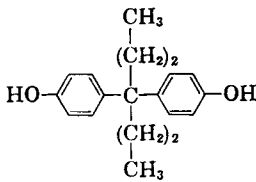
Method B. Preparation of Bisphenols Using Cyclic Ketones

A stream of dry hydrogen chloride gas was passed into a mixture of $1/2$ mole of cyclic ketone, 2 moles of phenol, and 2 ml. of β -mercaptopropionic acid. The temperature of the mixture rose to 50°C . After standing 24 hr., excess phenol was removed by vacuum distillation. The product was recrystallized from tetrachloroethane. Yields were 48-78% of theoretical.

Preparation of Glycidyl Polyethers

To a mixture of $1/2$ mole of the bisphenol, 7 moles of epichlorohydrin, and 3 ml. of water was added 1.2 moles of sodium hydroxide over a period of 2 hr. The reaction mixture was stirred at $95-100^\circ\text{C}$. for 2 additional hours. When cool, the excess epichlorohydrin was removed and the residue

TABLE I
Effect of Molecular Structure on Bond Strengths of Epoxy Adhesives Derived From Different Bisphenols
(Series I(A): Phenol derivatives where R₂ is aliphatic)

Compound	R ₂	Structure of bisphenol	Cure	Average shear strength (5 values), psi		Impact strength (5 values), ft.-lb./0.5 sq. in.			
				73.5° F.	160° F.	73.5°F.		-65°F.	
						Avg.	Range	Avg.	Range
Bisphenol A	CH ₃		14 days at 73°F.	1060	830	4.4	2.3-6.4	4.7	2.6-7.5
2,2'-Bis(4-hydroxyphenyl)butane	C ₂ H ₅		Overnight at 73°F.; then 3 hr. at 160°F.	1370	580	6.1	2.6-7.6	1.9	1.3-2.3
2,2'-Bis(4-hydroxyphenyl)isopentane			Overnight at 73°F.; then 3 hr. at 160°F.	1210	350	2.9	1.9-5.5	1.2	1.1-1.4
2,2'-Bis(4-hydroxyphenyl)isohexane			Overnight at 73°F.; then 3 hr. at 160°F.	2040	230	3.9	2.0-5.6	2.7	1.9-4.2
2,2'-Bis(4-hydroxyphenyl)nonane			14 days at 73°F.	2110	140	5.1	2.5-7.1	2.0	1.8-2.4
2,2'-Bis(4-hydroxyphenyl)undecane			Overnight at 73°F.; then 3 hr. at 160°F.	960	100	1.6	1.5-1.7	1.2	1.1-1.4
4,4'-Bis(4-hydroxyphenyl)heptane	 R ₁ = 		Overnight at 73°F.; then 3 hr. at 160°F.	980	760	1.3	1.2-1.5	1.2	1.1-1.4

treated with 250 ml. benzene. The benzene solution was evaporated and the product heated to 170°C. at 25 mm. The product was an amber-colored viscous liquid in each case.

Mechanical Testing

The mechanical properties of the epoxy adhesives are shown in Tables I-III. In using the resins as adhesives, diethylene triamine (DETA) curing

agent was thoroughly mixed with the epoxy compound. The adhesive was then brushed onto the bonding surfaces of 1 × 4 × 1/8 in. thick steel panels. The coated surfaces were joined immediately to form 1/2 in. lap shear specimens. The adhesive bonded joints were then cured prior to testing. All shear specimens were tested in tensile shear in the Tinius Olsen Plastiversal Testing Machine in the 2000 lb. range at a constant rate of load increase of 600-700 psi/min. in accordance with

TABLE II

Effect of Molecular Structure on Bond Strengths of Epoxy Adhesives Derived From Different Bisphenols
(Series I(B): Phenol derivatives where the benzhydryl carbon atom is incorporated in a cyclohexane or cyclopentane ring)

Compound	R ₂	Structure of Bisphenol	Cure	Average shear strength (5 values), psi		Impact strength (5 values), ft.-lb./0.5 sq. in.			
				73.5° F.	160° F.	73.5°F.		-65°F.	
						Avg.	Range	Avg.	Range
1,1'-Bis(4-hydroxyphenyl)-cyclopentane			14 days at 73°F.	1330	700	1.9	1.7-2.2	1.7	1.3-2.2
1,1'-Bis(4-hydroxyphenyl)-cyclohexane			14 days at 73°F. Overnight at 73°F.; then 3 hr. at 160°F.	770	970	3.3	2.3-6.3	2.1	1.7-3.0
1,1'-Bis(4-hydroxyphenyl)-4-methyl-cyclohexane			14 days at 73°F.	530	320	2.2	1.8-2.6	1.7	1.3-2.1
1,1'-Bis(4-hydroxyphenyl)-3-methyl-cyclohexane			14 days at 73°F.	470	40	1.0	0.8-1.1	0.90	0.8-1.0

TABLE III

Effect of Molecular Structure on Bond Strengths of Epoxy Adhesives Derived From Different Bisphenols
(Series II. *o*-Cresol. Series III. Resorcinol derivatives)

Compound	R ₂	Structure of Bisphenol (or Phenol)	Cure	Average shear strength (5 values), psi		Impact strength (5 values), ft.-lb./0.75 sq. in.			
				73.5° F.	160° F.	73.5°F.		-65°F.	
						Avg.	Range	Avg.	Range
2,2'-Bis(4-hydroxy-3-methyl phenyl)-propane	CH ₃ R ₁ = CH ₃		14 days at 73°F.	260	410	1.8	1.6-1.9	1.5	1.2-1.8
1,3-dihydroxybenzene	—		14 days at 73°F.	2130	290	16.5	7.1-20.4	10.3	5.9-17.0
						8.0*	1.7-19.4	3.1*	1.0-6.6

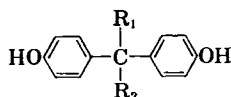
* Impact values obtained on a second batch of the 1,3-dihydroxybenzene resin.

Federal Test Method Standard No. 175, Method 1033.

The impact strength of the cured adhesive-bonded joints was tested on a standard pendulum-type im-

pect machine in accordance with Federal Test Method Standard No. 175, Method 1051. The load was applied so as to subject the adhesive joint to impact essentially in shear. Except where noted

TABLE IV
Derivatives of Bisphenol



Substituent R ₁	Substituent R ₂	Method of preparation	% yield of derivative	Melting point of pure compound, °C.		
				Observed	Literature	Reference No.
CH ₃	—CH ₃	A	86	152–153	155	14
CH ₃	—CH ₃	A	76	122–123.5	125	15
CH ₃	<i>i</i> -C ₃ H ₇	A	64	195–197	194	14
CH ₃	<i>i</i> -C ₄ H ₉	A	55	150–152	150	15
CH ₃	—(CH ₂) ₆ —CH ₃	A	75	55–56	Not previously reported in the literature	
CH ₃	—(CH ₂) ₈ —CH ₃	A	72	Liquid	Not previously reported in the literature	
—(CH ₂) ₂ —CH ₃	—(CH ₂) ₂ —CH ₃	A	57	158–159	154	14
—	$\begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CH}_2 \text{—} \text{CH}_2 \end{array}$	B	48	156–157	156	15

otherwise, the bonded area was approximately 0.5 in.² in each case.

Results and Discussion

All the bisphenols listed in Tables I–III were reacted with epichlorohydrin to produce a series of pale, amber-colored viscous liquids. When combined with stoichiometric amounts of DETA, these liquids polymerized to hard resins. The resins were evaluated as adhesives (1) by measuring the shear strength of bonded joints at normal and high temperature and (2) by measuring impact strength of bonded joints at normal and low temperature. The shear strength of this type of adhesive often falls at high temperature, while the impact strength decreases at low temperature due to increased brittleness. The resins were used unmodified to facilitate correlation of performance and composition.

Examination of the shear strength data in Tables I and II indicates that shear strength at 160°F. is a simple index for correlation of chemical composition with mechanical properties. As one of the methyl groups in the original bisphenol A is replaced by successively larger hydrocarbon side chains the shear strength falls off regularly, as shown in Figure 1. This behavior is in accordance with theory and expected behavior. When both methyl groups in the original bisphenol A are replaced with *n*-propyl groups a shear strength of 760 psi is obtained at 160°F. This shear strength is even higher than would be expected for the replacement of a

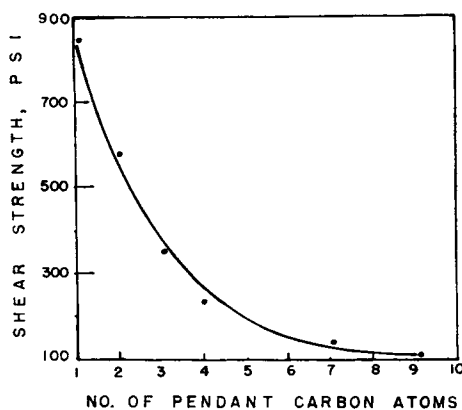


Fig. 1. Shear strength at 160°F. vs. number of pendant carbon atoms.

single methyl group with a propyl group. The data listed in Table I show that a decrease in shear strength is obtained at 160°F. with the other resins as a single methyl group is replaced by increasingly longer aliphatic chains. It is felt that this relatively high strength obtained with the 4,4'-bis(4-hydroxyphenyl)heptane is due to maintaining symmetry in the bisphenol portion of the polymer. This symmetry probably explains why shear strength at elevated temperature remained relatively high as compared with that at normal temperature. It is interesting to note that both bisphenol A and the latter polymer retain approximately 78% of their original shear strengths at 160°F.

Interpretation of shear strength behavior at 73.5°F. is more difficult. The shear strength of an adhesive-bonded joint is a complex phenomenon. It depends not only on the inherent strength of the adhesive but also on the modulus and elongation. An adhesive that will yield slightly under stress will usually give higher shear strengths than an inherently stronger but more brittle adhesive. At room or low temperatures premature failure is often due to localized stresses which may readily occur with a brittle resin. A rise in temperature will often increase mobility in the resin and minimize local stresses.

Examination of the shear strength data of Series 1A shows that at 73.5°F. a maximum is reached with resins based upon 2,2'-bis(4-hydroxyphenyl)isohehexane to 2,2'-bis(4-hydroxyphenyl)nonane. It is believed that the resins listed before these in Table I may be inherently stronger but more brittle at 73.5°F. while those which follow do not have the inherent strength.

Interpretation of impact strength appears to be very complex but the authors would like to point out two tentative points.

(a) Symmetry in the bisphenol as shown in



seems to be influential in minimizing changes in impact strength that may result when temperatures are reduced.

(b) Impact strength seems to be influenced by shear strength at room temperature and by "polarity." Of the two, "polarity" may be more important. If shear strength at 73.5°F. is relatively low and a large nonpolar segment is present, as in 2,2'-bis(4-hydroxyphenyl)undecane, impact strengths are low as shown in Table I. If shear strength is high as in 2,2'-bis(4-hydroxyphenyl)isohehexane and 2,2'-bis(4-hydroxyphenyl)nonane, moderate impact strengths are obtained. If polarity is high and shear strength fair, as in bisphenol A and 2,2'-bis(4-hydroxyphenyl)butane, reasonably good impact strengths result.

When the methyl groups in the original bisphenol A are replaced by an alicyclic group to give an asymmetric system, room temperature shear strength decreases as the number of carbon atoms in the alicyclic groups is increased (Table II). An in-

crease in shear strength obtained at 160°F. with 1,1'-bis(4-hydroxyphenyl)cyclohexane indicates that the adhesive does not completely cure at room temperature. Elevated temperature cure gives higher room temperature shear strength, while bond strength at 160°F. remains about the same as in the previous test. When a hydrogen is replaced by a methyl group on the alicyclic group of the 1,1'-bis(4-hydroxyphenyl)cyclohexane, a substantial loss in shear strength occurs at 160°F., as noted for the 1,1'-bis(4-hydroxyphenyl)-4-methyl cyclohexane and 1,1'-bis(4-hydroxyphenyl)-3-methyl cyclohexane. When substitution with the methyl group is such as to allow greater asymmetry of the molecule, as in the 1,1'-bis(4-hydroxyphenyl)-3-methyl cyclohexane, shear strength is seriously reduced at 160°F. Poor impact strengths are also obtained with this resin.

Methyl groups replaced adjacent to the reactive hydroxy groups in the original bisphenol A, as in 2,2'-bis(4-hydroxy-3-methylphenyl)propane, offer steric hindrance during the curing process, with resultant low-strength room temperature bonds (Table III). However, as the temperature is increased during the curing process these steric effects are diminished as shown by an increase in bond strength at 160°F.

Reaction of resorcinol with epichlorohydrin produces a resin with very superior impact properties (Table III). However, high-strength shear bonds obtained with this resin polymer at room temperature decrease by 84% at 160°F. It is likely that more heat resistant bonds would be obtained if hydroquinone were used in place of the resorcinol as the reactant with epichlorohydrin because of the greater symmetry of the hydroquinone.

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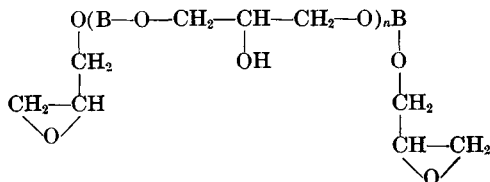
References

1. Werner, E. G., and E. Farenhorst, U. S. Pat. 2,467,171 (April 12, 1949).
2. Dannenberg, H., U. S. Pat. 2,631,138 (March 10, 1953).
3. Bradley, T. F., et al., U. S. Pat. 2,716,099 (August 23, 1955).
4. Shokal, E. C., et al., U. S. Pat. 2,643,239 (June 23, 1953).
5. Goppel, J. M., U. S. Pat. 2,801,227 (January 30, 1957).
6. Baeyer, A., *Ber.*, **5**, 280, 1096 (1872).
7. Lanjac, A., *Chem. Zentr.*, **1**, 1650 (1904); **2**, 550 (1908).

8. Zincke, T., *Ann.*, **302**, 237 (1898).
9. Stodel, G., *ibid.*, **194**, 329 (1878); **330**, 66 (1904).
10. Claus, A., and E. Trainer, *Ber.*, **19**, 3004 (1886).
11. Auwers, K., and E. Rietz, *Ann.*, **356**, 153 (1907).
12. Fabinyi, R., *Ber.*, **11**, 283 (1878).
13. Eberhardt, C., *ibid.*, **27**, 1804 (1924).
14. Reid, E. E., and E. Wilson, *J. Am. Chem. Soc.*, **66**, 967 (1944).
15. McGreal, M. E., V. Niederal, and J. B. Niederal, *J. Am. Chem. Soc.*, **61**, 345 (1939).

Synopsis

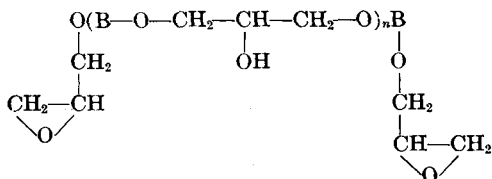
The effect of varying the molecular structure of epoxy resins on their mechanical properties when used as adhesives was studied. The work was directed toward preparation of bisphenols of the general formula $\text{HO}-\phi-\text{CR}(\text{R}')-\phi-\text{OH}$ where R and R' are either alkyl or alicyclic substituents, in which case the benzhydryl carbon is incorporated in a cyclopentane or cyclohexane ring for use in the preparation of glycidyl polyethers having the formula:



where B is the divalent hydrocarbon radical of the bisphenol and n is an integer of the series 0, 1, 2, 3, . . . Preparation of 13 epoxy resins which are liquids at room temperature is described. The effect of varying the structure of the dihydric phenol in the epoxy resin on the strength of adhesive-bonded joints was determined. The results indicate that relative bonding strengths of epoxy resins synthesized from various bisphenols can probably be attributed to the symmetry and chain length of the substituents attached to the carbon atom connecting the two aromatic nuclei. There is a high correlation between adhesive properties and steric influence of a substituted methyl group. Although the qualitative features of substitution on the central carbon atom are shown to be fairly well understood, there are a number of points that still require clarification. For instance, a more conclusive picture of the effect of branching is desirable. Also, there are uncertainties about the magnitude of the temperature effect and the influence of the substituent on the impact values.

Résumé

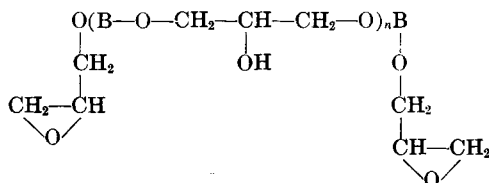
On étudie l'effet de la variation de la structure moléculaire des résines époxy sur les propriétés adhésives. On a orienté le travail vers la préparation de bisphénols de formule générale $\text{HO}-\phi-\text{CR}(\text{R}')-\phi-\text{OH}$ où R et R' sont, soit des substituants alcoyles ou alicycliques; dans le cas de ces derniers le carbone du groupement benzhydryle est incorporé à un cycle du cyclopentane ou du cyclohexane en vue de préparer des polyéthers glycidyles de formule:



où B est le radical bivalent hydrocarboné du bisphénol et où n peut prendre les valeurs 0, 1, 2, 3, . . . On décrit la préparation de 13 résines époxy, liquide à température de chambre. On a déterminé l'effet produit en variant la structure du phénol dihydrique de la résine époxy, sur la force adhésive de joints. Les résultats indiquent que l'on peut probablement attribuer la force de liaison des résines époxy synthétisées à partir de bisphénols variés à la symétrie et à la longueur de chaîne des substituants attachés sur l'atome de carbone diant les deux noyau aromatiques. Il y a une corrélation étroite entre les propriétés adhésives et l'influence stérique d'un groupement méthyle substitué. Quoique les traits caractéristiques de la substitution sur l'atome de carbone central soient passablement connus de manière qualitative, il persiste encore un certain nombre de points qui réclameront une élucidation. Par exemple, il serait nécessaire de trouver une description plus concluante de l'effet des ramifications. Il subsiste également certains incertitudes sur la grandeur de l'effet de la température et l'influence du substituant sur les valeurs d'impact.

Zusammenfassung

Es wurde der Einfluss der Molekülstruktur von Epoxyharzen auf ihre mechanischen Eigenschaften bei der Verwendung als Klebstoffe untersucht. Die Arbeit hatte die Darstellung von Bisphenolen der allgemeinen Formel $\text{HO}-\phi-\text{CR}(\text{R}')-\phi-\text{OH}$, wo R und R' entweder Alkylgruppen sind oder alicyclische Substituenten, bei denen der Benzhydrylkohlenstoff in einen Cyclopentan- oder Cyclohexanring eingebaut ist, als Ausgangsmaterial für die Darstellung von Glycidylpolyäthern mit der Formel



zum Ziel, wo B das zweiwertige Kohlenwasserstoffradikal des Bisphenols und n eine ganze Zahl in der Reihe, 0, 1, 2, 3, . . . ist. Die Darstellung von 13 Epoxyharzen, die bei Raumtemperatur Flüssigkeiten sind, wird beschrieben. Der Einfluss der Variierung der Struktur des Bisphenols im Epoxyharz auf die Festigkeit der mit dem Klebstoff hergestellten Verbindungsstellen wurde bestimmt. Die Ergebnisse sprechen dafür, dass die relative Klebefestigkeit von Epoxyharzen, die aus verschiedenen Bisphenolen synthetisiert wurden, wahrscheinlich auf die Symmetrie und Kettenlänge der Substituenten am Kohlenstoffatom, das die beiden aromatischen Ringe verbindet, zurückgeführt werden kann. Es besteht eine starke Korrelation zwischen den Klebeeigenschaften und dem sterischen Einfluss einer substituierten Methylgruppe. Obwohl, wie gezeigt wird, ein ausreichendes Verständnis der qualitativen Einflüsse einer Substitution am zentralen Kohlenstoffatom erreicht wurde, bleiben doch noch eine Reihe von Punkten zu klären. So ist ein schlüssigeres Bild des Einflusses einer Verzweigung wünschenswert. Auch über die Größe des Temperatureinflusses und über den Einfluss des Substituenten auf die Stossfestigkeit besteht noch Unklarheit.

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