Epoxy Resins from Bis-, Tris-, and Tetrakis-Glycidyl Ethers

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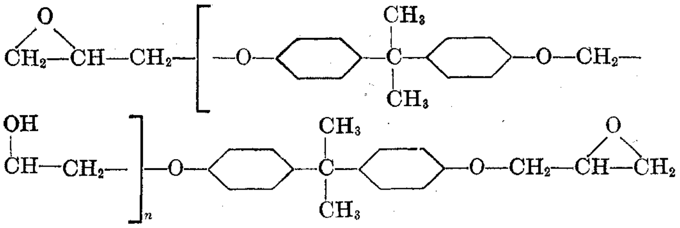
MOST of the commercial epoxy resins now available are mixtures of polyglycidyl ethers made by reacting epichlorohydrin with Bis Phenol-A, 2,2-bis(4′-hydroxyphenyl) propane, usually in the presence of alkali (*6*, *46*). The following basic structure (*44*) has been suggested for these resins:



They are liquid or solid depending on the degree of polymerization, indicated by *n*. Epoxy resins may be cured by condensation with anhydrides of polybasic acids, alkaline curing agents such as amines, or compounds containing reactive hydrogen atoms. Unlike the condensations leading to polyesters and polyamides, in which one water molecule is split out for each unit of the product, the epoxide condensation proceeds by opening cyclic structures which then combine to form chains. Since end groups are not lost, there is little volume change on condensation; furthermore, no water removal is involved. These two inherent properties are primarily responsible for the rapid growth in the use of these resins in recent years. Between 1946 and 1952, the demand for epoxy resins increased from less than 500,000 pounds per year to nearly 7,000,000 pounds. A fourfold expansion in production capacity is expected within a year (*42*).

The first reported attempt to prepare an aromatic polyglycidyl ether was in 1891; the synthesis was similar to the present commercial one, epichlorohydrin being condensed with 1,2-dihydroxybenzene instead of with Bis Phenol-A (*26*). The patent literature first described such ethers in 1933 (*3*); resins produced by curing them with polycarboxylic acid anhydrides were described in 1940 and 1943 (*7*, *10*, *12*), with alkaline curing agents in 1948 (*8*).

The over-all reaction by which polyglycidyl ethers are cured is complex, and its detailed mechanism is uncertain—at least two fundamental steps are involved. If any compounds containing active hydrogen are present, the analog of the ethylene oxide condensation will occur. Highly branched polymers can be obtained by this mechanism when bis- or higher glycidyl ethers are used. Second, condensation can occur between anhydride and epoxide rings to give cyclic diesters. Bisglycidyl ethers and monoanhydrides can give only linear molecular segments by this mechanism. If, however, polyanhydrides and glycidyl ethers higher than bis- are used, there clearly is opportunity for the production of many cross links. This should be accompanied by a significant increase in thermal yield temperature. Epoxy resins are extensively used for potting and casting; an obviously desirable property, therefore, is resistance to deformation under stress, especially at elevated temperatures.

The purpose of this paper is to present the results of an experimental study of resins made by curing aromatic polyglycidyl ethers of various structures with phthalic anhydride and by curing the polyglycidyl ether of Bis Phenol-A with anhydrides of various structures, both with and without amine accelerator.

Particular emphasis was placed on resins with cross-linking density potentially higher than that of resins made from phthalic anhydride and the polyglycidyl ether of Bis Phenol-A. In the preparation of ethers used in these resins, Bis Phenol was replaced by phenols either having a more compact structure or containing more glycidyl groups. Ethers were prepared from phenols of the following types: di-, tri-, and tetrahydric phenols based on benzene or naphthalene nuclei and on two, three, or four nonfused benzene rings attached to methane, butane, pentane, or hexane nuclei. The following acid anhydrides were evaluated as curing agents for the polyglycidyl ether of Bis Phenol-A: phthalic anhydride, dichlorophthalic anhydride maleic anhydride, 4-cyclohexene-1,2-dicarboxylic anhydride, adipic polyanhydride, and 1,5-dimethyl-2,3,4,6,7,8-hexahydronaphthalene-3,4,7,8-tetracarboxylic dianhydride. As amine accelerators, *N*,*N*-dimethylaniline, 4,4′-bis (diethylaminobenzophenone), 4,4′-methylenebis (*N*,*N*-dimethylaniline), 4,4′,4″-methylidynetris (*N*,*N*-dimethylaniline), and 4,4′-[4-hydroxybenzylidenebis (*N*,*N*-dimethylaniline)] were evaluated. The rate of deformation of sample bars of cured resin subjected to increasing temperature under fixed load was measured as a function of composition, in order to permit quantitative comparison of the mechanical properties of different formulations.

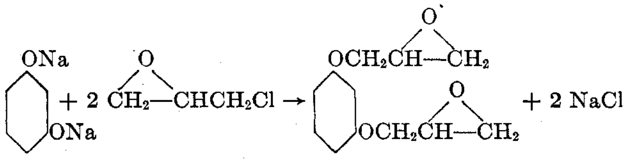
The results may be summarized as follows:

1. The reaction between polyglycidyl ethers and carboxylic acid anhydrides shows a stoichiometric relationship of one anhydride group to one epoxy-oxygen.
2. Resistance to deformation at elevated temperatures is increased by increasing the functionality of either the ether or the anhydride.
3. Resistance to deformation of samples cured for 20 hours at 120° C. is increased by the addition of amine accelerator, which catalyzes the polycondensation.

EXPERIMENTAL

MATERIALS. Syntheses of all materials not commercially available are given below. Epons 834 and 1001 are reported to be Bis Phenol-A polyglycidyl ethers (*6*) and are made by the Shell Chemical Corp.

GLYCIDYL ETHERS. The general method of preparation was based on methods described in the literature (*3*, *7*, *8*, *10–13*, *15–22*, *30–32*, *43*, *45*). The phenol was reacted with epichlorohydrin in the presence of sodium hydroxide, the reaction proceeding through the phenolate as shown for 1,3-dihydroxybenzene



The reactions were carried out in a three-necked flask equipped with reflux condenser, thermometer, dropping funnel, and high speed stirrer fitted with a sweeping Nichrome gauze paddle. The reactants were combined in the proportions shown in Table I, usually by adding the stoichiometric amount of sodium hydroxide dropwise as a 30% aqueous solution to the phenol dissolved in

TABLE I. SYNTHESIS OF GLYCIDYL ETHERS

Glycidyl ether of	Reactants, Moles			Reaction Temp., ° C.	Reaction Time, Hours
	Phenol	Epichlorohydrin	NaOH		
1,3-Dihydroxybenzene	1.0	4.0	2.0	55–70	1.3
1,4-Dihydroxybenzene	1.0	4.0	2.0	72–75	1.5
1,3,5-Trihydroxybenzene	1.0	6.0	3.0	65–80	2.3
1,5-Dihydroxynaphthalene (Na salt)	1.0	4.0	2.0	65–80	1.0
4,4′-Dihydroxydiphenylmethane	1.0	4.0	2.0	65–75	1.5
2,2-Bis(4′-hydroxyphenyl)-propane	1.0	4.0	2.0	55–65	3.5
Tris(4-hydroxyphenyl)-methane (Na salt)	1.0	15.0	3.0	70–92	1.0
2,2,3,3 - Tetrakis(4′ - hydroxyphenyl)-butane	1.0	16.0	(KOH) 6	68–72	1.5
2,2,4,4 - Tetrakis(4′ - hydroxyphenyl)-pentane	1.0	16.0	(KOH) 6	68–75	1.7
2,2,5,5 - Tetrakis(4′ - hydroxyphenyl)-hexane (Na salt)	1.0	12.0	4.0	76–78	2.0
2,2,5,5 - Tetrakis(4′ - hydroxyphenyl) hexane	1.0	16.0	(KOH) 6	68–72	1.5

twice the stoichiometric amount of epichlorohydrin. In the cases of the three phenols marked sodium salt, it was expected from experience with similar compounds that this method might produce a solid mass before the reaction was complete. Therefore, these phenols were first dissolved in 10% aqueous sodium hydroxide and added dropwise to between three and five times the stoichiometric amount of epichlorohydrin. In the syntheses of the glycidyl ethers of 2,2,3,3-tetrakis(4′-hydroxyphenyl) butane and 2,2,4,4-tetrakis (4′-hydroxyphenyl) pentane, and in one of two syntheses of the hexane analog, four times the stoichiometric amount of epichlorohydrin was used with one and a half times the stoichiometric amount of potassium hydroxide instead of the stoichiometric amount of sodium hydroxide.

The dropwise addition of hydroxide or sodium phenolate solution was begun at a flask temperature of 60° C. If an exothermic reaction started at this temperature, external heating was stopped and the temperature was allowed to reach the lower one specified in Table I. This was the lowest temperature at which the exothermic reaction continued, and it was maintained during the addition of the first third of the sodium hydroxide by adjusting the rate of addition and, in most cases, by the use of an ice bath. The remainder of the reaction, which is less exothermic than the first part, was run at the higher specified temperature which was maintained by use of an oil bath. Reaction times given in Table I include the time during which hydroxide was added plus a subsequent 1/2 hour at the higher specified temperature. High-speed stirring was used throughout the reaction. At the end of the reaction, the mixture was allowed to separate into an aqueous and an organic phase; the organic phase was washed in a Waring Blendor with successive portions of water until free of alkali. Crystalline products were dried in an oven, amorphous ones by vacuum distillation.

Data describing these ethers are given in Table II. The number of glycidyl groups present is expressed as epoxide equivalents, an epoxide equivalent of unity being equal to one glycidyl group. The epoxide equivalents per 100 grams of Epons 834 and 1001 are 0.36 and 0.20, respectively.

TABLE II. DATA ON GLYCIDYL ETHERS

Epoxide Equivalent			
Per ideal molecular weight	Per 100 grams	Physical Properties	Yield, %
1.40	0.63	Amber liquid	55
1.62	0.73	Tan crystalline solid, m.p. 108–111° C.	83
1.70	0.58	Amber amorphous solid, m.p. 88–94° C.	33
1.12	0.41	Brown crystalline solid, m.p. 105–110° C.	67
1.53	0.49	Yellow waxlike crystals, m.p. 81–85° C.	67
1.30	0.38	Amber liquid	66
1.49	0.32	Reddish amorphous solid, m.p. 72–98° C.	54
3.12	0.48	Amber liquid	71
3.42	0.52	Viscous brown liquid	78
1.97	0.29	Pale yellow amorphous solid, m.p. 83–104° C.	80
3.46	0.51	Light brown amorphous solid, m.p. 30–48° C.	67

These epoxide equivalents were determined as follows (*30*):

> A solution of pyridinium chloride in pyridine is made by adding 984 ml. of pyridine to 16 ml. of concentrated hydrochloric acid; this is standardized against 0.1*N* sodium hydroxide, using phenolphthalein as indicator. A 1-gram sample of the glycidyl ether in an excess of this pyridinium chloride solution is refluxed for 20 minutes during which pyridinium chloride hydrochlorinates epoxy (glycidyl) groups to chlorohydrin groups. After cooling to room temperature, unconsumed pyridinium chloride is back-titrated with 0.1*N* sodium hydroxide. The epoxide equivalent is calculated by considering 1 mole of hydrochloric acid to be equivalent to 1 epoxide group. The results are given in Table II in two forms. The second column gives the moles of epoxide oxygen reckoned on the ideal formula for the monomer, in which all phenolic hydrogens have been replaced by glycidyl groups. If this number is less than the integer—e.g., 4 for Compound No. 9—corresponding to the ideal formula, some condensation has occurred or else substitution was incomplete. The third column gives the practically useful figure, epoxide content on a weight basis.

PHENOLS. The tetraphenylol compounds used in the above syntheses were prepared by diketone-phenol condensations in which the 2 carbonyl oxygens of the dione combine with the parahydrogens of 4 molecules of phenol so that 2 molecules of water are split off and a tetrahydroxyphenyl alkane is formed. Methods were based on ones described in the literature for condensations of phenol with mono- and with diketones (*24, 25, 27, 28, 33–40, 41*).

Tris(4-hydroxyphenyl)methane was prepared by the reduction of aurin by zinc dust and acetic acid (*9*).

2,2,3,3-Tetrakis(4′-hydroxyphenyl)butane was prepared as follows. Phenol (564 grams, 6 moles) and thioglycolic acid (18.4 grams, 0.2 mole per mole of ketone) in 37% hydrochloric acid 10 ml. were placed in a 1-liter, three-necked flask equipped with condenser, mercury seal stirrer, thermometer, dropping funnel for the introduction of ketone, and tube extending to the bottom of the flask for the introduction of hydrogen chloride gas. After heating the flask contents to 55° C. and saturating with hydrogen chloride (from concentrated sulfuric acid dropped onto dry sodium chloride), 2,3-butanedione (diacetyl) (86 grams, 1 mole) was added dropwise with continuous stirring during 1 hour at 59–61° C. The reaction was moderately exothermic. During the addition of the ketone, a continuous rapid stream of hydrogen chloride was passed through the solution. This was continued for an additional 20 minutes at 60° C. and also while the flask was cooled by an ice bath to 30° C. The flask was then sealed and allowed to stand at 30° C. for 20 days. The resulting viscous liquid was washed twice with cold water and 6 times with hot water, 10 times its volume of water was used for each washing. It was then dried during 30 minutes at 65° C. and 5-mm. pressure. The product was a brilliant dark blue viscous liquid; yield 241 grams, 56% of theoretical.

2,2,4,4-Tetrakis(4′-hydroxyphenyl) pentane was prepared by the method given for the butane analog using 2,4-pentanedione (acetylacetone) (100 grams, 1 mole) in place of the butanedione. In this case the contents of the sealed flask became a nearly solid mass of reddish crystals after 4 days. The product was then purified by washing 4 times with cold water, 3 times with 5% sodium carbonate solution, and 6 times with hot water. After drying at 85° C., it was a light pink, crystalline solid. The yield was 309 grams, 70% of theoretical. Another sample further purified by recrystallization from ethyl acetate by the addition of toluene melted at 248–249 °C. Analysis: carbon 78.0%, hydrogen 6.0% (theoretical, carbon 78.6%, hydrogen 6.4%). Elementary analyses were made by C. K. Fitz of Boston.

2,2,5,5-Tetrakis(4′-hydroxyphenyl)hexane was prepared by the method given for the butane analog using 2,5-hexanedione (acetonylacetone) (114 grams, 1 mole) in place of the butanedione. It was purified as follows: After the reactants had formed a nearly solid mass of crystals (7 days), all adhering liquid was removed by suction-filtration through glass wool. The crystals were then washed 3 times with cold 95% ethanol and dried in an 85 °C. oven. The product was a white crystalline solid which melted with partial decomposition at 292° to 295° C. (uncorrected). The yield was 189 grams, 42% of theoretical. A sample, further purified by 2 recrystallizations from 95% ethanol, gave the following analysis: carbon 79.3%, hydrogen 6.7% (theoretical, carbon 79.3%, hydrogen 6.6%).

Tris(4-hydroxyphenyl)methane was prepared as follows: Aurin (145 grams, 0.5 mole) in 500 ml. of 95% S. D. 30 ethanol was brought to the boiling point of ethanol in a 2-liter round-bottomed flask equipped with a high speed stirrer. Zinc dust (98 grams, 1.5 moles) was added. Then glacial acetic acid (180 grams, 3 moles) was added in portions during 20 minutes while the mixture was maintained at the boiling point by a water bath. After boiling for another 10 minutes, the hot solution was filtered to remove excess zinc, and the product was precipitated by adding 2 liters of water slowly with agitation. After 20 minutes the precipitate was filtered off, dissolved in 200 ml. of ethanol, reprecipitated by the slow addition of 800 ml. of water, and dried at 100° C.; it was a pink crystalline solid, suitable for use without further purification; yield 83 grams, 57% of theoretical. A sample further purified by 6 recrystallizations from ethanol by the addition of water was a nearly white crystalline solid that decomposed to a red liquid between 218° and 230° C. Analysis showed carbon 77.9% and hydrogen 5.6% (theoretical 78.0% and 5.5%).

CARBOXYLIC ACID ANHYDRIDES. 1,5-Dimethyl-2,3,4,6,7,8-hexahydronaphthalene-3,4,7,8-tetracarboxylic dianhydride, prepared by a Diels-Alder reaction between maleic anhydride and 2,5-dimethyl-1,5-hexadiene-3-yne (*1, 4, 5*), which was made by dehydrating 2,5-dimethyl-3-hexyne-2,5-diol with phosphoric acid (*29*).

2,5-Dimethyl-3-hexyne-2,5-diol (Air Reduction Chemical Co.) (300 grams, 2.1 mole) and 60% phosphoric acid 3 liters were placed in a 5-liter flask equipped with a spiral condenser, dropping funnel for the introduction of water, and tube extending to the bottom of the flask for the introduction of carbon dioxide. The mixture was distilled during 45 minutes at an oil bath temperature of 160° C. while a rapid stream of carbon dioxide was passed through the mixture and water was added at such a rate as to keep the concentration of the acid at 60%. After removing the water phase from the distillate, the product was dried over anhydrous magnesium sulfate, then distilled at 8-mm. pressure through a fractionating column. The product was a clear yellow liquid boiling at 30° to 37° C. at 8-mm. pressure, n_D^{20} 1.4839. The yield was 120 grams, 54% of theoretical.

2,5-Dimethyl-1,5-hexadiene-3-yne (119 grams, 1.12 moles), maleic anhydride (294 grams, 3 moles), and dry xylene (280 ml.) were placed in a 1-liter flask equipped with a spiral condenser plugged at the top with a cork containing two tubes, one to serve as a vent and one for the introduction of carbon dioxide. The mixture was refluxed under a steady stream of carbon dioxide at a flask temperature of 140° to 144° C. for 2 hours, then chilled in an ice bath. The resulting mass of crystals was broken up, suction filtered, washed twice with hot xylene, then digested twice for 15-minute periods with hot ethyl acetate. After drying at 85° C. this dianhydride was a white crystalline solid melting with partial sublimation and partial decomposition at 255° to 258° C. (uncorrected). The yield was 54 grams, 16% of theoretical.

A sample, further purified by two 30-minute digestions with boiling xylene and two 15-minute ones with boiling ethyl acetate gave the following analysis: carbon 63.4%, hydrogen 4.8% (theoretical, carbon 63.6%, hydrogen 4.7%).

Adipic Polyanhydride (*23*). Adipic acid (146 grams, 1 mole) and acetic anhydride (487 grams, 4.8 moles) were placed in a 1-liter flask equipped with a reflux condenser fitted with a calcium chloride tube.

The solution was refluxed for 6 hours, after which volatile constituents were removed at 2-mm. pressure at 100° C. While the product was still molten, 150 ml. of dry benzene was added. On chilling, adipic polyanhydride separated slowly as a microcrystalline white powder which, after drying at 110° C. and 90 to 5 mm. pressure during 30 minutes, solidified to a near-white, waxy solid with melting point of 52° to 57° C. The yield was 30 grams, 23% of theoretical.

METHODS

CASTING AND CURING. Samples were prepared for casting by thoroughly mixing the molten carboxylic acid anhydride with the polyglycidyl ether that had been previously heated to 130° C.; when dichlorophthalic anhydride was used, the ether was heated to only 80° to 90° C., since higher temperatures caused almost immediate gelling. 1,5-Dimethyl-2,3,4,6,7,8-hexahydronaphthalene-3,4,7,8-tetracarboxylic dianhydride was added to the ether dissolved in molten phthalic anhydride; its very high melting point made direct addition impractical. Compatibility of this anhydride with phthalic anhydride was limited to 1 part in 5. When amine accelerators were used, anhydride and ether were mixed as above before addition of the amine. The mixtures were then poured into preheated molds and usually cured during 20 hours at 120° C. The molds consisted of two 5 × 5 × 0.25 inch steel plates (32 grind) separated by a squared, U-shaped Teflon spacer. After treating the plates with a silicone lubricant (Dow Corning high vacuum silicone grease), the mold assembly was clamped together by four C clamps and preheated for 30 minutes in a 120° C. oven.

THERMAL YIELD POINT. Resistance to deformation under stress at elevated temperatures was determined by the following test, which involves subjecting a simple beam of the test material to a stress of 1500 pounds per square inch, raising the temperature at a constant rate, and determining the temperature at which the material begins to deflect rapidly. This temperature is defined as the constant-stress yield point. The apparatus used is a modification of that used in the standard method for the heat distortion temperature of plastics (*2*). The test assembly is supported, as shown in Figure 1, by an aluminum plate resting on the edge of a 2-liter beaker. The sample is supported by cylindrical rods, $^5/_{32}$ inch in diameter spaced 2 inches apart on centers and held in place by an aluminum framework attached to this plate. Pressure is applied to the center of the sample by a cylindrical bearing $^5/_{32}$ inch in diameter and long enough to bear across the entire width of the sample. This bearing is set into a rod surmounted by a platform on which are placed pound lead disks and lead shot. A dial micrometer is arranged with a plunger resting against the platform so that, as the sample deflects, the load will press against the plunger, indicating the deflection on the micrometer.

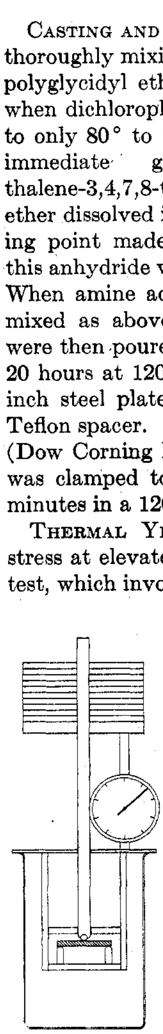


Figure 1. Schematic letter Diagram of Testing Apparatus

Enough light mineral oil (Kaydol) is placed in the beaker to fill it to a level 3 or 4 inches above the sample, and a thermometer is placed with its bulb close to the center of the specimen. The oil is heated by a resistance wire grid supported by a Bakelite ring,

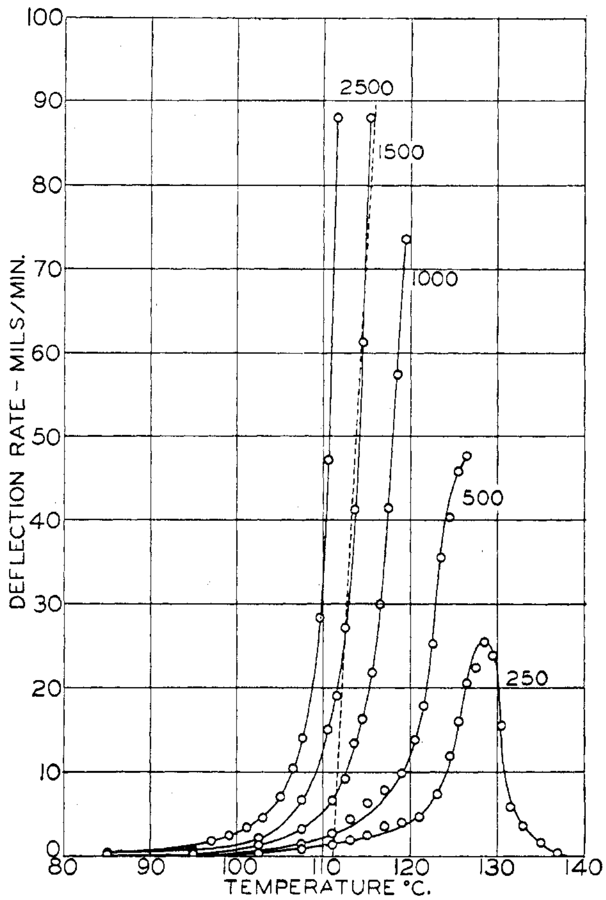


Figure 2. Yield Curves as Function of Test Load for Epon 834 with 30% Phthalic Anhydride

Test load pounds per square inch

which is attached, 2 inches below the specimen, to the framework described. The oil is agitated by a 2-inch steel rod that rests on the bottom of the beaker and is driven by a magnetic stirrer. The heat supplied by the wire grid is regulated by means of a variable resistance box in series with the line voltage.

A sample bar of resin 2.25 × 0.5 × 0.25 inch is placed on the supports in the apparatus, and enough lead weights are added to the platform to give a total fiber stress of 1500 pounds per square inch. The necessary load P was calculated (*2*) by the formula

$$P = 2Sbd^2/3l$$

where
S is 1500 pounds per square inch
b is measured width of the test bar
d is its measured thickness, and
l is 2 inches, the distance between the cylindrical supports

The loads were approximately 15 pounds, varying as required by the actual dimensions of the individual samples. After adjusting the dial micrometer to read zero, the temperature of the oil is raised by the immersion heater, the rate being kept constant at exactly 1° per minute by continuous adjustment of the resistance. The total deflection registered by the micrometer is noted at 5-minute intervals at the start, then 2-minute, and finally when the sample begins to deflect rapidly, at 0.5-minute intervals.

The rate of deflection in mils per minute (mil = 0.001 inch) during each interval was calculated and plotted against the average temperature of that interval. Figure 2 shows typical results obtained by this test method for a sample consisting of 70% Epon 834 and 30% phthalic anhydride, which had been cured for 20 hours at 120° C. For a stress of 250 pounds per square inch, the bar remains rigid up to about 100° C., after which it begins to bend at a rate which increases to a maximum at 128° C. The rate of deflection then decelerates, and beyond about 136° C., the bent bar now supports the load without further distortion. At this temperature the polymer segments between cross links are presumably nearly all stretched to their limits and the resin can again resist a deforming force. Below and above the range of the maximum, the material acts as an elastic (Hookian) solid, with different moduli in the two ranges; through the range of the maximum, the resin behaves like a viscoelastic substance. As the stress is increased, the temperature at which deflection begins decreases, and the curve steadily gets steeper. A reproducible temperature can be defined by approximating the rising part of the curve as a straight line and extrapolating it to the temperature axis. A stress of 1500 pounds per square inch was chosen arbitrarily and the corresponding intersection temperature was defined as the thermal yield temperature; it correlates closely with brittle point or so-called second order transition temperature. As the temperature rises, any given stress will of course produce a more rapid deflection because increasing thermal agitation weakens the secondary bonding between polymer segments and allows them to approach the new equilibrium positions corresponding to the external force. Just as the peak in dielectric dispersion moves to lower temperatures with decreasing frequency —i.e., longer time of applied electrical force—the yield temperature decreases with increasing load. If the logarithm of the load —which is proportional to the rate of application of stress—is plotted against reciprocal absolute yield temperature, the points

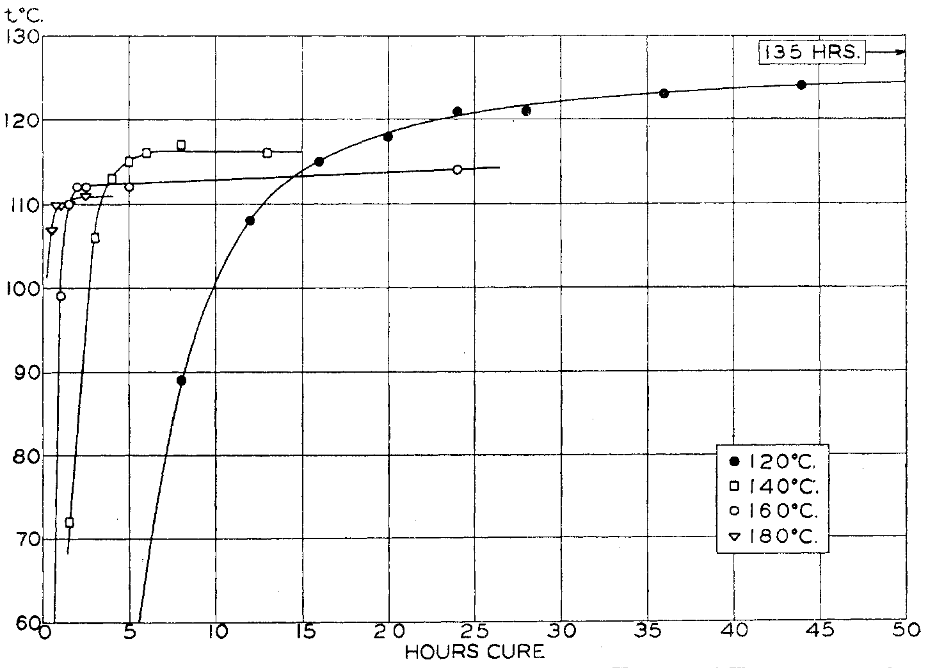


Figure 3. Yield Temperature as Function of Curing Time and Temperature for Epon 834 with 30% Phthalic Anhydride

may be approximated by a straight line. From the slope of the latter an activation energy of 47 kcal. was computed for the flow process in the sample shown in Figure 2. The value of 1500 pounds per square inch represents a convenient load for routine work, in that it gives deflections large enough to measure with reasonable precision without distorting the sample too drastically. Maximum deflections amounted to about 0.33 inch. On removal of the load, the samples always recovered their original shape; hence the deformations were elastic and not the consequence of irreversible flow.

For each polyglycidyl ether–anhydride system, yield points were determined at a series of ratios of ether to anhydride; curves showing yield point as a function of this ratio exhibit a maximum that defines a critical ratio of reactants.

Heat stability was further tested by making triplicate determinations of per cent weight lost by sample bars of resin 1 × 0.5 × 0.25 inch during 20 hours at 200° C. Heat loss was at a minimum near the composition corresponding to maximum yield temperature.

RESULTS AND DISCUSSIONS

The yield temperature naturally depends on the structure and amount of the components of the resins and on curing conditions. Therefore, it is necessary to consider these experimental variables before turning to the more fundamental parameters. The initial rate of cure as measured by the yield temperature is rapid and increases with increasing cure temperature (Figure 3). As reactive groups are consumed, the rate of condensation decreases and eventually becomes zero. The approach to the horizontal asymptote is more rapid the higher the temperature. But the height of the asymptotic yield temperature decreases with increasing cure temperature; this observation suggests that several competing reactions with different rate constants are involved in the over-all cure; this problem may be investigated further. In order to simplify the present experimental program of comparing different compositions, an arbitrary set of cure conditions, 20 hours at 120° C. was selected; this gives a yield point about 14° C. lower than the asymptotic limit for the composition 70% Epon 834–30% phthalic anhydride.

The dependence of yield temperature on composition is illustrated in Figure 4, for the system glycidyl ether of 2,2,4,4-tetrakis(4′-hydroxyphenyl)pentane–phthalic anhydride. The glycidyl ether cures to a soft tacky resin; as the amount of phthalic anhydride increases, hard resins appear. The yield point shows a sharp maximum at 40% anhydride. The existence of the maximum gives some information regarding the probable nature of the curing reactions. Self condensation of glycidyl ethers gives linear structures that would have low yield temperatures. These are presumably long chains containing secondary alcohols, which have their origin in the epoxide-oxygen atoms. As the anhydride content increases, cross links are formed between the linear segments and the yield point is increased. But if an excess of anhydride is used, it might be expected that monophthalates will form, because there will now not be enough secondary alcohol groups to combine with all the anhydride—i.e., the anhydride acts as a chain-stopper rather than as a cross-linking agent. Therefore, a correlation may exist between the amount of anhydride and the epoxide content of the ether. For the example shown in Figure 4, the maximum yield temperature appears at a ratio of 0.87 mole of phthalic anhydride to 1 mole of epoxide oxygen, the latter figure being based on the analysis of the ether given in Table II. The other ethers all gave curves qualitatively like Figure 4; Table III summarizes the significant numerical results. The ratio of moles of anhydride to moles of epoxide oxygen approximates unity for the different ethers; the unweighted average is 0.90. From this result may be drawn the important practical conclusion that the optimum composition—from the point of view of maximum thermal stability of mechanical properties—for epoxide resins is stoichiometric equivalence of anhydride and epoxide oxygen. The fact that the observed ratio is somewhat less than unity will be discussed after the effect of amines has been presented.

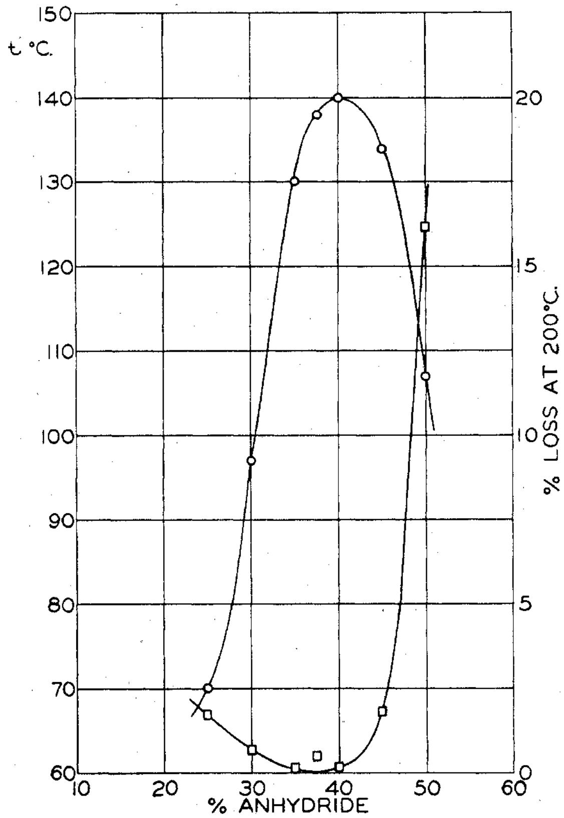


Figure 4. Yield Temperature as Function of Composition for Polyglycidyl Ether of 2,2,4,4-Tetrakis(4′-hydroxyphenyl)pentane and Phthalic Anhydride (Ordinates Left) and Heat Loss (Ordinates Right)

Table III. Maximum Yield Points of Glycidyl Ether–Phthalic Anhydride Compositions

(Cured 20 Hours at 120° C.)

Glycidyl ether of	Maximum Yield Point, ° C.	Phthalic Anhydride, %	Moles of Phthalic Anhydride per Epoxide Group at Maximum Yield Point
1,3,5-Trihydroxybenzene	154	40	0.77
2,2,5,5 - Tetrakis(4′ - hydroxyphenyl)hexane No. 11	149	40	0.88
2,2,4,4 - Tetrakis(4′ - hydroxyphenyl)pentane	140	40	0.87
2,2,5,5 - Tetrakis(4′ - hydroxyphenyl)hexane No. 10	137	30	1.00
Tris(4-hydroxyphenyl)-methane	134	30	0.89
1,5-Dihydroxynaphthalene	124	35	0.89
1,3-Dihydroxybenzene	115	50	1.07
1,4-Dihydroxybenzene	114	45	0.75
2,2 - Bis(4′ - hydroxyphenyl)propane (Epon 834)	114	30	0.81
2,2,3,3 - Tetrakis(4′ - hydroxyphenyl)butane	113	38	0.86
2,2 - Bis(4′ - hydroxyphenyl)-propane (Epon 1001)	110	23	1.01

The loss of material on heating for 20 hours at 200° C. also supports the mechanism proposed. Beyond the composition corresponding to maximum yield temperature, heat losses increase rapidly, indicating the presence of uncombined anhydride. The

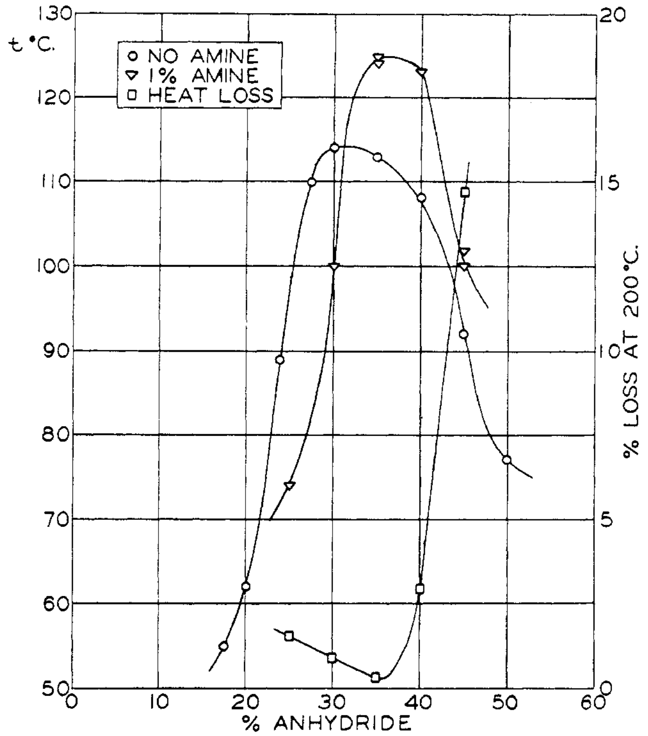


Figure 5. Yield Temperature as Function of Composition for Epon 834 and Phthalic Anhydride, with and without 4,4′-Methylenebis (*N,N*-dimethylaniline) (Ordinates Left); Heat Loss (Ordinates Right)

losses at the critical composition are negligible, as they should be if all the anhydride is combined. Unaccounted for is the small amount of volatile material present at compositions below the critical.

TABLE IV. MAXIMUM YIELD POINTS OF EPON 834 AND VARIOUS ANHYDRIDES

(Cured 20 Hours at 120° C.)

Anhydride	Maximum Yield Point, ° C.	Anhydride, %	Anhydride Groups per Epoxide Group at Maximum Yield Point
Maleic	119	23	0.85
4 - Cyclohexene - 1,2 - dicarboxylic anhydride	86	30	0.78
Adipic polyanhydride	43	30	0.93
Dichlorophthalic anhydride	133	30	0.55
Phthalic anhydride 27.1% 1,5 - Dimethyl - 2,3,4,6,7,8-hexahydronaphthalene - 3,-4,7,8-tetracarboxylic dianhydride 5.4%	125	32.5	0.88
Phthalic anhydride 33.4% 1,5 - Dimethyl - 2,3,4,6,-7,8 - hexahydronaphthalene-3,4,7,8-tetracarboxylic dianhydride 6.6% + 1% 4,4′ - bis(diethylamino)-benzophenone	136	40	1.25

Table IV summarizes the results for the systems in which Epon 834 was combined with various anhydrides. Curves similar to Figure 4 were obtained. Again, for all except the dichlorophthalic anhydride, the critical composition for maximum yield temperature appears at approximately a one-to-one ratio of anhydride to epoxide oxygen, and minimum loss on heating also occurs at this composition.

The dependence of thermal stability on the structure of the components may also be deduced from Tables III and IV, if Epon 834 and phthalic anhydride are used as reference materials. For anhydride fixed, the yield point is increased as the functionality of the ether is increased, as a consequence of a greater multiplicity and density of cross links. For example, the tris- and tetrakis- compounds give yield points 20° to 40° C. higher than the bis- derivatives. Furthermore, within a group of given multiplicity, the yield point increases with increasing compactness of the central nucleus to which the glycidyl ether residues are attached. This effect is nicely illustrated by comparing 1,3,5-trihydroxybenzene with tris(4-hydroxyphenyl)methane. The bis- ethers with a benzene nucleus gave about the same yield point as the standard Epon; the naphthalene derivative showed an increase of 10° C., which may possibly be ascribed to the increased difficulty of rotation of the polymer segments due to the bulk of the naphthalene group. Similar conclusions may be reached for the effect of anhydride structure. If, for example, phthalic anhydride is replaced by the long chain adipic polyanhydride, the yield point drops to 43° C. from 114° C., while the very compact dianhydrides raise the yield point by 10° to 20° C. The increase in the case of dichlorophthalic anhydride illustrates another method of raising the yield point. Dipole-dipole forces between the carbon-chlorine dipoles increase the energy density of van der Waal's binding forces and therefore require a higher temperature for yielding to a given test stress.

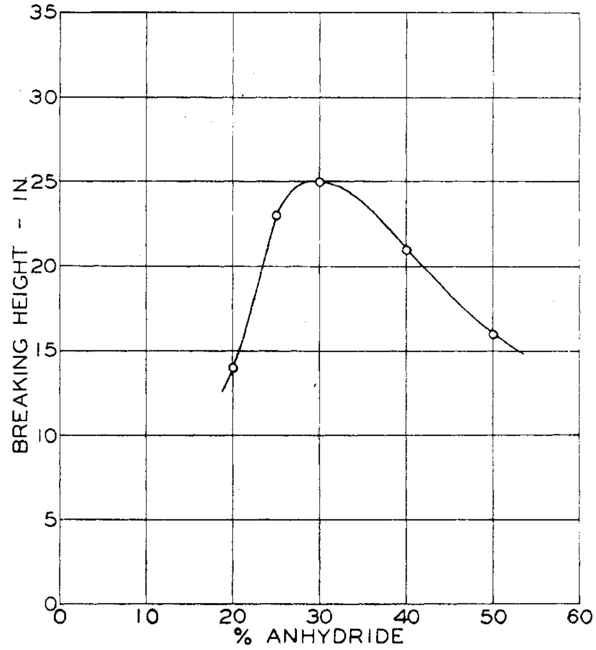


Figure 6. Impact Strength as Function of Composition for Epon 834 and Dichlorophthalic Anhydride

One interesting exception to the rule of increasing yield temperature with increasing functionality appears. Reference to Table III shows that the resin from the tetrafunctional glycidyl ether of 2,2,3,3-tetrakis(4′-hydroxyphenyl)butane has a maximum yield temperature of only 113° C., as compared to 149° C. for the hexane and 140° C. for the pentane resins. This difference is almost certainly the consequence of a difference in structure of the butane derivative as contrasted with the pentane and hexane derivatives. That such a difference exists, and has its origin in the parent substance, is clearly shown by the marked difference in color of the butane derivative compared to the two other members of the series. The tetrakis-phenol from diacetyl was a brilliant blue compound, while that from acetylacetone was pink, and that from acetonylacetone was white. It is planned to study this contrast further.

A chance observation led to the discovery that amines are potent accelerators for the epoxide resins. Nigrosine was added to a batch in order to obtain a black product; the mixture solidified with startling rapidity. A variety of amines were therefore investigated. The time required for a 70 to 30 Epon 834–phthalic anhydride mixture to gel at 135° C. was about 70 minutes. The addition of 1% 4,4′-methylenebis(*N*,*N*-dimethylaniline) reduced this time to 1.3 minutes. Figure 5 shows a typical cure-composition curve for a resin with and without amine. Two significant differences appear, the yield temperature is increased, and more anhydride is required to produce the optimum composition. Curves similar to Figure 2 showed that the yield temperature as a function of cure time reached its asymptote in less than 1 hour at 120° C.; the increase in yield temperature over the control in Figure 5 is therefore due to the fact that the control had not yet reached complete cure. In other words, the amine accelerates the reaction between epoxide and anhydride without changing its essential nature. The hypothesis that the amine functions as an accelerator rather than as a reagent is also substantiated by the fact that only stoichiometrically small amounts suffice to complete the cure.

The data of Tables III and IV gave averages somewhat less than unity for the critical anhydride-epoxide ratio. These data all correspond to 20 hours' cure at 120° C. Figure 2 and the results with the amines show that the reaction was not yet complete at 20 hours. But if the reaction goes to completion, the ratio reaches the exact value of unity within the experimental error of locating the maximum in the yield point–composition curves. An abstract of the results for a series of amines is given in Table V.

TABLE V. MAXIMUM YIELD POINTS OF EPON 834–PHTHALIC ANHYDRIDE–AMINE ACCELERATOR COMPOSITIONS

(Cured 20 Hours at 120° C.)

Amine Accelerator	Maximum Yield Point, ° C.	Phthalic Anhydride, %	Anhydride Groups per Epoxide Group at Maximum Yield Point
1% 4,4′,4″-Methylidynetris-(*N*,*N*-dimethylaniline)	129	35	1.01
1% 4,4′-Bis(diethylamino)-benzophenone	127	35	1.01
1% 4,4′-[4-Hydroxybenzylidenebis(*N*,*N*-dimethylaniline)]	126	35	1.01
3% 4,4′-Methylenebis(*N*,*N*-dimethylaniline)	126	35	1.01
1% 4,4′-Methylenebis(*N*,*N*-dimethylaniline)	125	35	1.01
1% *N*,*N*-Dimethylaniline	124	35	1.01

Finally, a close correlation between the arbitrarily defined yield temperature and a familiar mechanical property should be mentioned. Figure 6 shows that impact strength—measured by the minimum height of free fall of a 1-inch steel ball required to shatter a test sample of resin 0.125 inch thick, at room temperature—reaches its maximum at the same composition as that for which the yield point has its maximum value. The example shown is Epon 834 cured with dichlorophthalic anhydride; similar results were obtained for other systems.

SUMMARY

The reaction between polyglycidyl ethers and carboxylic acid anhydrides was studied, using the thermal yield point as the significant experimentally observed variable. The yield point increases with increasing anhydride content of the molding compound to a maximum which corresponds to a ratio of one mole of anhydride to one mole of epoxy-oxygen. Maximum impact strength and minimum heat loss likewise appear at this stoichiometrically critical composition. Amines were found to accelerate the reaction markedly; for example, 1% 4,4′-methylenebis (*N*,*N*-dimethylaniline) gave a complete cure in 1 hour at 120°C. as contrasted to nearly 50 hours without amine. The following compositions are described, together with the synthesis of new intermediates: phthalic anhydride with the glycidyl ethers of 1,3,5-trihydroxybenzene, 2,2,5,5-tetrakis(4′-hydroxyphenyl) hexane, 2,2,4,4-tetrakis(4′-hydroxyphenyl)pentane, 2,2,3,3-tetrakis(4′-hydroxyphenyl)butane, 2,2-bis(4′-hydroxyphenyl) propane, tris(4-hydroxyphenyl)methane, 1,5-dihydroxynaphthalene, 1,3-dihydroxybenzene, and 1,4-dihydroxybenzene; Epon 834 (Shell Chemical Corp.) with phthalic, maleic, 4-cyclohexene-1,2-dicarboxylic, adipic poly-, dichlorophthalic and 1,5-dimethyl-2,3,4,6,7,8-hexahydronaphthalene-3,4,7,8-tetracarboxylic anhydrides. Increasing the functionality of the glycidyl ether and/or that of the anhydride increases the thermal yield point.

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