

Epoxy Resins from Fats. I. Epoxidized Glycerides Cured with Phthalic Anhydride¹

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A LARGE potential market exists for fatty acid derivatives in the rapidly expanding epoxy resin industry. Predictions have been made that by 1960, 82 million pounds of epoxy resins will be produced annually (5). Thermosetting resins of this type are very hard and have good impact resistance, excellent chemical resistance, and excellent electrical properties. They are finding widespread use as casting and potting resins, for adhesives and laminates, and for use in protective coatings of all kinds.

Chemically epoxy resins are cross-linked polymers obtained by curing glycidyl ethers of polyfunctional phenols with a polyfunctional chemical, such as diethylenetriamine or phthalic anhydride. The most common glycidyl ethers used commercially are obtained from the reaction of bisphenol A and epichlorohydrin. The intermediate condensation product may be the simple structure A (Figure 1) or, more usually, it contains further condensation products B where n is a low integer. Curing results from the reaction of the epoxide group with the curing agent. When anhydrides are used as curing agents, the hydroxyl groups also may react. The nature of the reactive groups present in B suggests that epoxy resin intermediates may be modified by reaction with fatty acid derivatives.

To a degree such fatty derivatives have already been investigated, and some are in commercial use. For example: a) epoxidized soybean oil has been used to modify epoxy resins, to impart flexibility, and to prolong the working pot life (3, 4); b) polyamides (9, 10), which are condensation polymers of dimerized (or trimerized) unsaturated fatty acids and polyamines, have found similar uses; c) fatty diamines, such as Duomeen S,⁴ have been used as flexibilizers in epoxy systems to impart physical characteristics similar to those of a plasticized vinyl chloride resin (12); and d) tung oil and fatty acids have been used as epoxy modifiers and extenders for use in surface coatings (11). Epoxidized oils from unsaturated glycerides also have been used as a component in the manufacture of alkyd resins (6).

However, in practically all attempts at modification of epoxy resins with fatty derivatives, compounds of vegetable fat origin have been used. Aside from the work of Swern *et al.* (14) on the thermal polymerization of *cis*- and *trans*-9,10-epoxystearic acids, little work has been done on the utilization of fatty derivatives of animal origin in such modification; and little or no attempt has been made to synthesize epoxy resins directly from animal fat derivatives.

In the present work some fatty derivatives were synthesized as the primary intermediates in the prep-

aration of epoxy resins. Resins were made from these intermediates and phthalic anhydride, and their physical properties were evaluated. Other anhydrides are being investigated as curing agents for these intermediates and will be discussed in future papers. The requisite intermediates were made by epoxidizing lard oil, neatsfoot oil, soybean oil, perilla oil, triolein and trilinolein, compounds containing unsaturated natural fatty acids. These intermediates differ from the compounds of structure B (Figure 1) in having

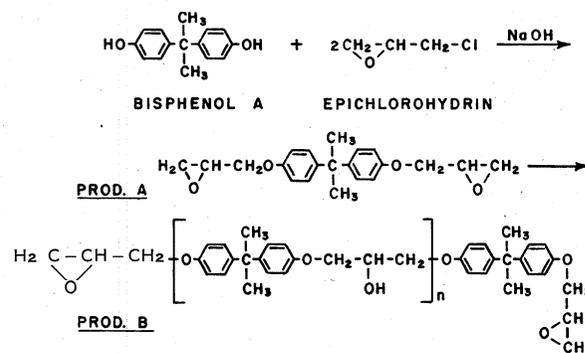


FIG. 1. Formation of commercial epoxide intermediates.

internal rather than terminal oxirane rings, in being composed of aliphatic chains instead of (chiefly) aromatic structures, and in lacking hydroxyl groups. Such structural differences may be expected to affect the rate of resin formation and the physical properties of these resins.

Discussion

In contrast to the rapidity of resin formation from commercial (glycidyl) epoxy intermediates and phthalic anhydride, no reaction was observed in the absence of an accelerator when fatty epoxy intermediates were substituted. The resin was made by heating to the gel point equivalent weights of fatty epoxide and phthalic anhydride at 150°C. in the presence of 2.5% benzyltrimethylamine, followed by curing for 10 hrs. at 150°C. Optimal molar ratio, reaction temperature, and cure time were obtained by correlation with heat-distortion temperature, modulus of elasticity, and tensile strength. Details for arriving at these optimum conditions are given in the experimental section.

The physical properties of the resulting resins are given in Table I. The heat-distortion temperature (that temperature at which the resin first bends under a specified load) varied from -9.5 to 88°C. in the order of neatsfoot oil, <triolein, <lard oil, <soybean oil, <perilla oil, and <trilinolein. Tensile strengths varied from 70 to 6,510 pounds p.s.i., and the modulus of elasticity from 8.13×10^3 to 1.82×10^5 pounds

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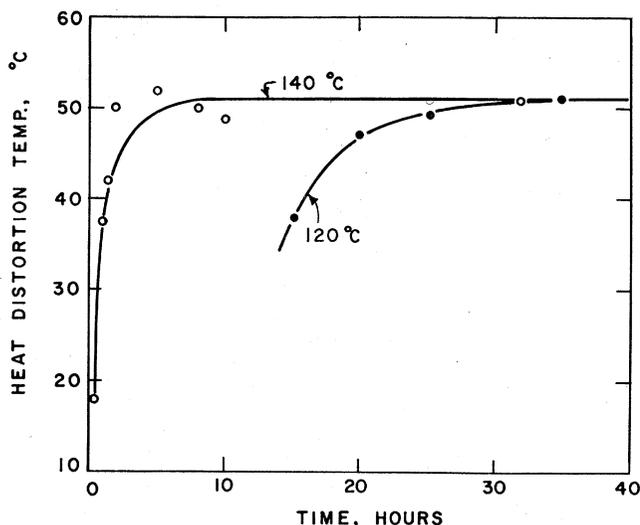


FIG. 2. Effect of cure time on heat-distortion temperature in the system: epoxidized soybean oil/phthalic anhydride (1:1) and 5% benzylidimethylamine. Cured at 120°C. and at 140°C.

p.s.i. in the same order. The percentage of elongation however was moderately high (11–20%) for the neatsfoot oil, lard oil, and triolein.

The potential value of epoxidized intermediates from unsaturated fatty acids cannot be estimated unambiguously from the natural glycerides but must be assessed from pure glycerides. It may be seen from the data in Table I that the tensile strength and modulus of elasticity of the resins derived from lard and neatsfoot oils were only slightly lower than those of the resin derived from the corresponding pure glyceride, triolein, and the heat-distortion temperatures were about the same. Thus, in spite of their high content of saturated (nonreactive) fatty acid residue (about 20%), both neatsfoot and lard oils may be substituted for the pure triolein.

TABLE I
Physical Properties of Resins Made from Epoxidized Fatty Glycerides

Epoxidized glycerides	Heat-distortion temp.	Modulus of elasticity lbs./sq. in. $\times 10^{-3}$	Elongation %	Tensile strength lbs./sq. in.
	°C.			
Neatsfoot.....	-9.5	8.65	17.2	100
Triolein.....	-9.5	9.55	20.0	150
Lard oil.....	-5.0	8.13	11.1	70
Soybean.....	49.0	165.00	2.0	2,685
Perilla oil.....	72.0	208.00	3.1	5,480
Trilinolein.....	88.0	182.00	5.3	6,510

On the other hand, when compared with the resin from the corresponding pure glyceride trilinolein, the resins derived from soybean and perilla oils are markedly affected by their content of saturated and mono-unsaturated fatty acid residues. Epoxidized soybean oil contains 13% nonparticipating saturated fatty acid residues, 25% mono-epoxidized acids, and 62% poly-epoxidized acids. Epoxidized perilla oil contains 7.5% saturated fatty acid residues, 8% mono-epoxidized acids, and 84.5% poly-epoxidized acids. This difference in composition is directly reflected in the resins, the magnitude of whose physical properties, except modulus of elasticity, increase in the order of soybean oil, perilla oil, and trilinolein (Table I).

A comparison of the epoxide values (Table II) with the heat-distortion temperatures of the different res-

ins (Table I) shows that the oxirane content of the oil, *per se*, is not the deciding factor for the magnitude of the heat-distortion temperature. For example, although epoxidized triolein had an oxirane content 14% higher than epoxidized lard oil, no appreciable difference was noted in the heat-distortion temperatures of the corresponding resins. On the other hand, with almost identical oxirane values, perilla oil and trilinolein give resins whose heat-distortion temperatures differ by 16 degrees. Thus it would appear that the distribution of the oxirane groups in the glyceride holds more significance than their number.

TABLE II
Yield Data for Epoxidized Fatty Esters

Epoxidized ester	Yield	Oxirane content		Purity	Epoxide ^b equiv.	Iodine value
		Found ^a	Calc.			
	%	%	%	%		
Lard oil	96.0	4.15	4.63 ^c	89.7	386	2.36
Neatsfoot oil	97.3	4.06	4.35 ^d	93.2	394	2.11
Triolein	91.4	4.84	5.15	94.0	330	1.00
Trilinolein ^e	85.0	9.07	9.40 ^f	96.5	176
Soybean oil	5.91	270
Perilla oil	9.04	10.35 ^g	177

^a Method of Durbetaki (7).

^b Grams of epoxidized oil containing one gram equivalent of oxygen = 1,600/% oxirane found.

^c Calculated from iodine value of lard oil (77.1).

^d Calculated from iodine value of neatsfoot oil (72.2).

^e M.P. 35–37°C.

^f Calculated from iodine value of trilinolein used (164.8).

^g Calculated from iodine value of perilla oil (183.3).

It should be noted that the epoxide content of the particular sample of epoxidized soybean oil which was used is less than average. Had an epoxidized soybean oil of higher oxirane content been used, a higher heat-distortion temperature would probably have been obtained.

Experimental

Preparation of Acids. Oleic acid of low-saturates content was prepared by distilling commercial oleic acid (Groco 5L,⁵ iodine value 88). The fractions boiling in the range 173–190°C. at 0.06 mm., n_{D}^{30} 1.4565–70, iodine value 92 (calc. 89.9), were employed. Linoleic acid, obtained from safflower seed oil by the procedure of Swern and Parker (13, 15), had an iodine value of 178 (calc. 181).

Preparation of Glycerol Esters. Triolein was prepared by the Wheeler (16) procedure except that the molecular distillation was omitted. Yield 63.5%; saponification number found, 187.7; calc. for glycerol trioleate, 190; iodine value found, 86.3; calc., 86.2; hydroxyl value, 0.0. Trilinolein was prepared by a similar procedure. Yield, 33.5%; iodine value found, 162.5; calc. for glycerol trilinoleate, 173; hydroxyl value 0.0. Iodine value was raised to 164.8 by passing the oil, diluted with diethyl ether, through a bed of activated alumina and distilling out the solvent.

Epoxidation. The procedure of Findley *et al.* (8) for the epoxidation of unsaturated fatty materials was employed with commercially available peracetic acid to epoxidize lard oil, neatsfoot oil, perilla oil, triolein and trilinolein. The yields, oxirane values, purities, and other pertinent data are given in Table II. Crystals (m.p. 35–37°C.) were obtained by cooling epoxidized trilinolein in acetone (1 g. of epoxide to 5 ml. of acetone) at -20°C. The other epoxides were obtained as oils. However partial crystallization

⁵ A product of A. Gross and Company, Newark, N. J.

TABLE III
Effect of Variation of Phthalic Anhydride on the Heat-Distortion Temperature and Modulus of Elasticity of Resins Made from Epoxidized Soybean Oil

Phthalic anhydride	Heat-distortion temperature	Modulus of elasticity
mole %	°C.	lbs./sq. in. $\times 10^{-5}$
+20	49	1.8
+10	48.5	2.15
Equivalent	51	2.44
-10	48	1.49
-20	32	0.85

2.5% Benzyltrimethylamine, cured at 140°C. for 10 hrs.

was observed in epoxidized triolein and lard oil after several days.

Preparation of Specimens. Each resin specimen was made in a 7 \times 24 mm. Pyrex tube closed at one end. Methyl oleate was found satisfactory as a mold-release agent. The phthalic anhydride and epoxide ester were weighed into the tube, melted in an oil bath, and mixed thoroughly. The accelerator, benzyltrimethylamine, was then added and mixed thoroughly, and the gelation-time count was started. After gelation (the point at which viscous flow was no longer observed by tilting the tube), the sample was cured for 8-10 hrs. at the desired temperature in an oven. When cool, the glass was carefully cracked with a hammer and peeled from the specimen. A 4-in. rod was the minimum length prepared for physical measurements. From this rod, flat test-specimens of dimensions 0.098 \times 0.25 \times 2.5 in. were machined and used in physical measurements.

Physical Measurements. The standard method of test (1) for stiffness properties of nonrigid plastics as a function of temperature (torsional modulus test) was used except that the temperature was raised at a rate of 2° per minute. A correlation was found⁶ to exist between the temperature at which the sample attained a torsional modulus of 5.5×10^4 pounds p.s.i. and the A.S.T.M. heat-distortion temperature, using a load of 264 pounds p.s.i. (2). The heat-distortion temperatures listed in this paper were determined by the torsional modulus method.

The tensile strength and modulus of elasticity were measured on an Instron Tensile Tester, using the specimen described above with a jaw separation of 1 in. and a rate of straining of 0.05 in. per minute. Only one specimen was available for each physical evaluation.

Finding Optimum Conditions for Resin Preparation. The heat-distortion temperature was considered to be the orienting physical criterion for determining the best conditions. Other physical properties were obtained to support this criterion. Commercially epoxidized soybean oil (Paraplex G-62)⁷ was used exclusively as the epoxide in a study to determine the proper amounts of phthalic anhydride and accelerator and the proper cure-temperature and time.

A series of resins was made to determine the optimum-mole-ratio conditions. With the parameters, temperature, cure time, and accelerator concentration held constant at 140°C., 10 hrs., and 2.5% by weight, respectively; the phthalic anhydride content was varied from a 20% molar excess to a 20% molar deficiency. The maximum heat-distortion temperature was found at the equivalence point, *i.e.*, one mole of anhydride to one epoxide equivalent. The heat-dis-

ortion temperatures and moduli of elasticity are given in Table III.

The proper amount of accelerator was determined by fixing the following parameters: a) ratio of reactants at the equivalence point, b) temperature of cure at 160°C., and c) time of cure at 10 hrs., while varying the amount of benzyltrimethylamine from 0.1 to 10% (based on the weight of all reactants). Maximum heat-distortion temperature was observed at the 2.5% level of accelerator. Other properties of these resins are given in Table IV.

TABLE IV
Effect of Varying Accelerator Concentration on the Properties of Epoxidized Soybean Oil/Phthalic Anhydride Resin

Accelerator ^a concentration	Heat-distortion temperature	Tensile strength	Elongation	Modulus of elasticity
weight %	°C.	lbs./sq. in.	%	lbs./sq. in. $\times 10^{-5}$
0.1	23	3,570	10.6	1.18
0.5	51	2,210	3.0	1.03
1.0	49	3,500	4.5	1.14
1.5	50.5	5,060	12.6	1.46
2.0	52	4,740	5.1	1.50
2.5	62	4,700	4.7	1.57
3.0	54	5,030	6.5	1.54
5.0	44	1,470	1.6	1.21
7.5	33	550	0.8	0.968
10.0	31	330	1.0	0.482

^a Benzyltrimethylamine, cured at 160°C. for 10 hrs.

In another series the cure times were varied while the anhydride, epoxide, and accelerator concentrations as well as the temperature were held constant. In this case equivalent weights of anhydride and epoxide, 5% benzyltrimethylamine, and 140°C. were arbitrarily chosen as the constants while the cure times were varied from 0.5 to 32 hrs. The heat-distortion temperature levelled off to 51°C. after four hours (Figure 2). For comparison, a similar series was made at 120°C. with cure times varying from 10 to 45 hrs. Again the heat-distortion temperature reached a maximum at 51°C., but 30 hrs. were required (Figure 2).

The final conditions established were: a) equivalent weights of epoxide and phthalic anhydride, b) 2.5% benzyltrimethylamine, c) temperature of 150°C., and d) a cure time of 8 hrs. The temperature was chosen midway between 140° and 160° to insure a reasonable gel and cure time. Under these conditions the epoxidized soybean oil resin had a heat-distortion temperature of 49°C. All other resins except that from perilla oil were made by this procedure. The perilla oil resin was cured for 24 hrs. at 135°C.

Summary and Conclusion

Epoxy resins were made from phthalic anhydride and the following epoxidized fatty glycerides: neat-foot oil, lard oil, triolein, soybean oil, perilla oil, and trilinolein. Some physical properties of these resins were measured and tabulated.

It has been shown that heat-distortion temperature, tensile strength, and modulus of elasticity increase with the unsaturation of the glyceride precursor of the epoxy intermediate.

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⁶ Details of this procedure to be reported in J. Poly. Sci. by Witnauer and Palm.

⁷ A product of Rohm and Haas Company, Philadelphia, Pa.

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