Epoxy Resins from Fats. III. Preparation and Properties of Resins from Blends of a Commercial Diglycidyl Ether and Epoxidized Glycerides Cured with Phthalic Anhydride[1]

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FATTY DERIVATIVES are playing an ever-increasing role in the modification of resins and plastics. Modifiers for epoxy resins have been sought for various specific purposes, such as to improve flexibility of the resin, to reduce the viscosity of the working mixture, to increase the pot life of the precured mixture, and to fill the resin and thereby simultaneously improve dimensional stability and lower the cost.

Modification of the typical diglycidyl ether monomer, as exemplified by Figure 1, can be achieved through the hydroxyl group by esterification or through the epoxide groups by reaction with fatty acids (8, 9), fatty diamines (10), fatty polyesters containing free hydroxyl and carboxyl groups (11), and fat-based polyamide resins containing active amino hydrogens (5, 6). Such fatty derivatives represent one broad category of reactive diluents for epoxy resins.

There is, in contrast to these materials which react with the epoxide intermediate, another broad class of diluents that react with the curing agent. In this class, for example, are certain monoglycidyl ethers based on glycerol (12), epoxidized terpenes (12), and epoxidized vegetable oils (2, 14). This class is generally characterized by the presence of epoxide groups in the molecule.

Epoxidized vegetable oils have been studied to a limited extent as reactive diluents for epoxy resins. Several investigations have been made in surface-coatings applications. For example, it has been shown that 25% of a diglycidyl ether polyester resin can be replaced by epoxidized soybean oil in both long and short oil media (1). The product was less expensive, had better gloss, and better resistance to gas checking. Chatfield (2) showed that alkyd resins could be made by reaction of epoxidized vegetable oils with small amounts of phthalic anhydride, either with or without such modifiers as rosin or its derivatives. Also a British patent (14) disclosed the successful use of epoxidized soybean, linseed, and cottonseed oils as substitutes for glycidyl ether compositions. As an example, compositions of up to 40% epoxidized oils were cured with polyamines or acid catalysts, such as citric acid, phosphoric acid, or boron trifluoride complex to give resins whose chemical and mechanical properties were much improved. Reference has even been made to resin systems based on diglycidyl ether-epoxidized soybean oil mixtures, cured with the aid of phthalic anhydride, but no details were given (1). The latter two references (1, 14) also made brief mention of a

rigid resin application. They describe the use of the epoxidized oil-modified glycidyl ether resins as encapsulating compounds but give no quantitative data on their physical properties. In view of the scantiness of the information concerning the preparation of resins from phthalic anhydride and mixtures of diglycidyl ethers with epoxidized, natural glycerides and concerning the properties of such modified resins, a systematic study of this kind was undertaken at this laboratory.

The scope of this paper is confined to the modification of a typical diglycidyl ether with epoxidized lard oil and epoxidized soybean oil, the curing of these blends with phthalic anhydride, and the correlation of such physical data as the heat distortion temperature (HDT), torsional modulus, tensile strength, modulus of elasticity, and elongation at break with epoxidized oil content. The purposes of the study were a) to determine whether the mixtures of uncured intermediates would be compatible in all proportions and whether they would remain compatible during the cure with equivalent weights of phthalic anhydride. b) to determine the extent to which epoxidized lard oil and epoxidized soybean oil are suitable as modifiers for diglycidyl ethers, and c) to observe what changes in the physical properties of the resins may result by varying the amounts of epoxidized oils in the pre-cured blends in the presence of a small amount of a tertiary amine.

Discussion

A comparison of the structure of epoxidized glycerides, as represented by Figure 2, with that of a diglycidyl ether (Figure 1) makes clear the difference
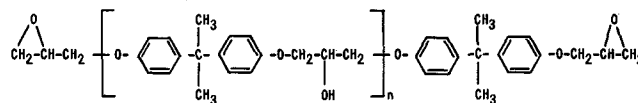

FIG. 1. A typical diglycidyl ether monomer for epoxy resins.

between terminal and nonterminal epoxide groups. Each of these epoxide types has a different order of reactivity toward other reagents, and therefore differences might be expected in the curing stage with phthalic anhydride. Moreover it will be noted that the number and arrangement of epoxide groups in the glyceride are quite different from those in the diglycidyl ether. The preponderance of one or the other type of epoxide molecule, then, would be expected to make noticeable differences in the properties of the cross-linked resins.

Mixtures of Shell's Epon 828, a diglycidyl ether containing 9% oxirane (determined by the method of
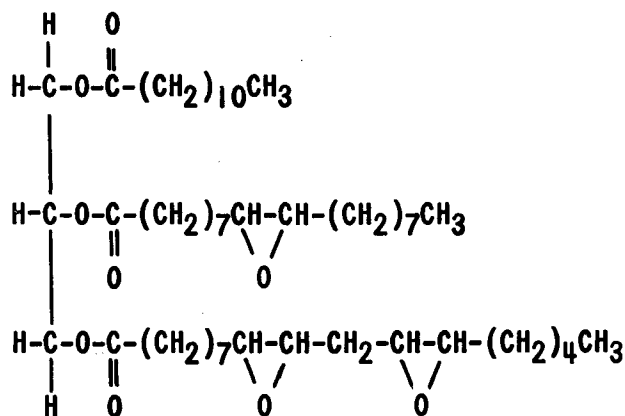
FIG. 2. A typical epoxidized natural glyceride.

Durbetaki [3]), and 0, 10, 20, 30, 40, 70, and 90%, respectively, of epoxidized lard oil (4.2% oxirane) were prepared in separate test tubes. In another series Epon 828 was mixed with 0, 5, 10, 25, 35, 50, 75, and 90%, respectively, of Paraplex G-62, epoxidized soybean oil (5.9% oxirane) from Rohm and Haas Company. In still a third series the same concentrations of epoxidized soybean oil in Epon 828 were prepared, but 0.5% by weight of a tertiary amine was added to each mixture. All the mixtures were cured with the appropriate amounts of phthalic anhydride (details given in the experimental section) at 150°C. for 18 hrs., giving hard, transparent, light amber resins. Physical measurements were then made on each resin.

The most significant physical criterion related to the composition of the resin is the heat-distortion temperature (HDT).[4] However the A.S.T.M. method was not used to determine the HDTs in this work because of the large sample required. Instead a procedure was used, involving a standard test for the stiffness properties of nonrigid plastics as a function

[4] Defined by the American Society for Testing Materials, Philadelphia, Pa., under designation D-648-56.
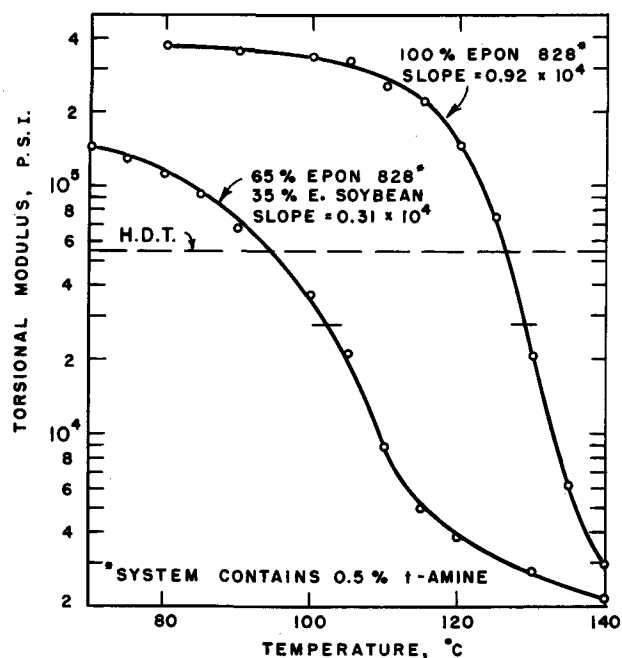
of temperature.[5] This procedure was shown to correlate very closely with the standard HDT. The temperature at which the specimen attained a torsional modulus of 5.5×10^4 p.s.i. (see dashed line in Figure 3), corresponded to the HDT of that resin. The correlation between torsional modulus and HDT was studied by two of the authors (15) and will be reported independently.

When the HDTs were plotted against the percentage compositions of the epoxidized oils by the least squares method, a straight-line relationship was observed in each case (Figure 4). It is clear that
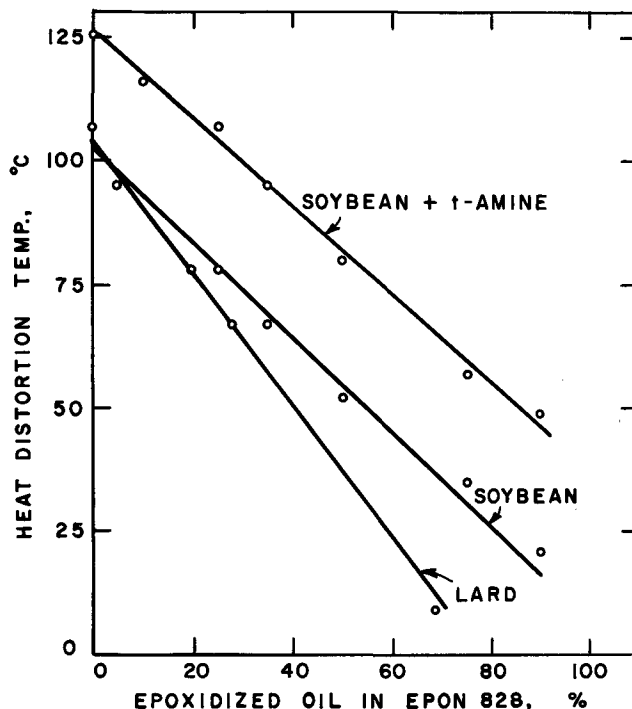

FIG. 4. Effect of epoxidized glyceride concentration on the heat-distortion temperature of diglycidyl ether resin cured with phthalic anhydride.

HDT decreases as the amount of fatty epoxide increases in the mixture. The HDT drops off at a rate faster in the case of epoxidized lard oil than in the case of epoxidized soybean oil. This may be explained on the basis of the relative number and position of epoxide groups in the two epoxidized oils; both factors are dependent upon the composition of the lard and soybean oil raw materials. Epoxidized soybean oil contains a high percentage of acyl chains bearing two epoxide groups very close together, a fair amount of chains with only one epoxide group, and very few chains which have no epoxide groups. On the other hand, epoxidized lard oil has a very high percentage of monoepoxide acyl chains and a moderate amount of chains which have no epoxide group. The lack of an epoxide group in a chain makes it impossible for that chain to produce a cross-link with the curing agent, and therefore segments of the molecule vibrate more freely under low thermal stress. This, of course, results in low HDT of the resin. When potential cross-links are plentiful and closely spaced, as in the case of epoxidized soybean oil, the cross-linked network is stiffened. Hence it resists thermal deforma-

FIG. 3. Effect of epoxidized soybean oil on the torsional modulus-temperature slope.

[5] Torsional Modulus Test defined by A.S.T.M., designation D-1043-51.

tion and exhibits a higher HDT. Inasmuch as epoxidized lard oil is the more deficient in potential cross-links, dilution of the Epon 828 with this oil would result in the lower HDTs of the two series. If, then, a modest HDT of about 80°C. is desired when using epoxidized lard as a diluent for a diglycidyl ether, no more than 20% should be used.

There is also shown in Figure 4 the effect on HDT of introducing 0.5% of a tertiary amine in the mixture of diglycidyl ether and epoxidized soybean oil. Although the slope of this line is about the same as that for the corresponding series without amine, the HDTs of the former are higher by a constant factor of 25 degrees. It is conceivable therefore that this principle may be extended to raise the HDTs of other systems, such as the epoxidized lard oil series.

Additional information not revealed in the HDT-% composition curves was obtained from the torsional modulus curves of Figure 3. A comparison of the two curves shows that the slope for the mixed system (65% Epon 828 and 35% epoxidized soybean oil), which is representative of a whole family of curves for resins based on different proportions of these ingredients, is one-third that for the 100% Epon 828. Curves for resins made without tertiary amine (not shown here) have slopes which fall in between the two shown. It is significant that a 50% drop in the torsional modulus from 5.5 x 10⁴ to 2.75 x 10⁴ p.s.i., takes place in a limited range (3 degrees) for the 100% Epon while a similar drop occurs in a broader range (9 degrees) for the mixed resin. This suggests that the HDT is not as critical for the diluted Epon as for the 100% Epon, and for many practical purposes this three-fold temperature latitude may be advantageous. For those compositions of Epon 828 and epoxidized oils which contained no tertiary amine, no significant difference was observed in the slopes.

When the tensile strengths of the resins were plotted against the percentage composition of epoxidized oils (Figure 5), the relationship was not linear. Here the 20% level appears to be significant since the tensile strengths of all the specimens are about the same (between 10,000 and 11,500 p.s.i.) at that concentration of diluent. However as the epoxidized oil content increases, the tensile strength decreases at different rates for each series. The tensile strength of the epoxidized lard oil series drops more rapidly than that of the epoxidized soybean oil. The tertiary amine appears to have a slight elevating influence on the tensile strengths.

The elongations at the breaking point of all the resins were of the same order of magnitude, in the range of 3 to 18%. Thus there is no significant difference in this property between the modified and unmodified Epon 828. Also the modulus of elasticity was not significantly different between the 100% Epon 828 and the modified resin up to a 50% concentration of epoxidized oils, ranging from 2.1 to 3.4 x 10⁵ p.s.i. Above 50% the modulus of elasticity dropped markedly in both epoxidized oil systems containing no amine and only slightly in the epoxidized soybean oil system with amine.

Combined assessment of all the data indicates (1) that both HDT and the tensile strength of a resin from diglycidyl ether cured with phthalic anhydride are markedly decreased by the addition of either epoxidized soybean oil or epoxidized lard oil, (2) that, regardless of which epoxidized oil is used to replace
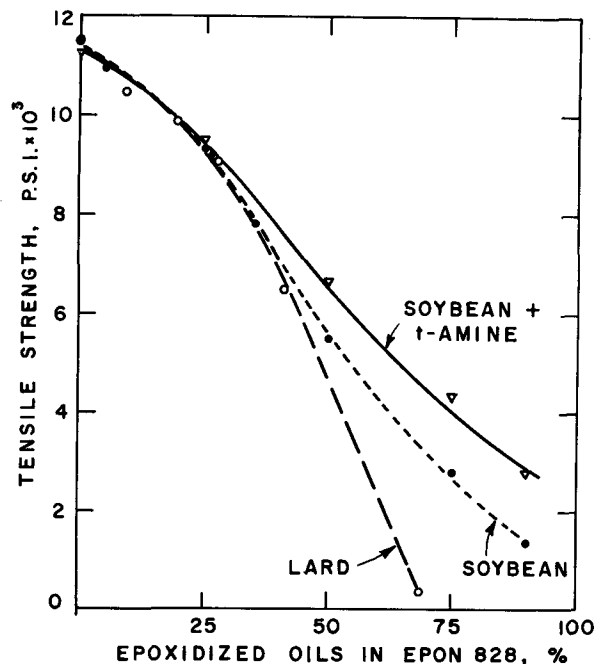

FIG. 5. Effect of epoxidized glyceride concentration on the tensile strength of diglycidyl ether resins cured with phthalic anhydride.

up to 20% of the diglycidyl ether, the differences in these properties between the two series are small, and (3) that either epoxidized oil may be used to replace up to 50% of the diglycidyl ether without affecting the modulus of elasticity or elongation properties of the resins.

Experimental

Lard oil (I.V. 77) was epoxidized by the method of Findley et al. (4) to an oxirane value of 4.2%, determined by the method of Durbetaki (3). Epoxidized soybean oil of 5.9% oxirane content was available commercially (Paraplex G-62). Epon 828, a diglycidyl ether containing 9% oxirane, was selected as representative of commercially used epoxy resins. The tertiary amine employed in this study was benzyldimethylamine.

Different amounts of Epon 828 were weighed into a series of test tubes, and epoxidized lard oil was added to each to make the concentrations approximately 10, 20, 30, 40, 70, and 90% of epoxidized lard oil, respectively. In another series of tubes were placed mixtures of Epon 828 and epoxidized soybean oil calculated to give concentrations of 5, 10, 25, 35, 50, 75, and 90% of epoxidized oil. These same mixtures were duplicated in a third series of tubes. Appropriate amounts of phthalic anhydride were added to each tube, and the tubes were corked and heated in a 150°C. oil bath. The amount of phthalic anhydride used for the epoxidized glycerides in each case was based upon equivalent weights [6] because previous work indicated this ratio to give optimum physical properties in the resin (7). The amount of phthalic anhydride used for the polyglycidyl ether however was only three-fourths of the equivalent weight because this ratio was reported to give optimum physical properties in resins made from low molecular weight diglycidyl ethers (13). Table I shows the

[6] One mole of phthalic anhydride to one epoxide equivalent, where epoxide equivalent = 1600/% oxirane.

TABLE I

Weight Ratios of Reactants in the Epon 828/G-62/Phthalic Anhydride Series

Wt. % G-62	Pts. Epon 828 [a]	Pts. G-62 [b]	Pts. PA [c] for Epon 828	Pts. PA [d] for G-62
5	168.15	13.5	105.45	7.4
10	159.30	27.0	99.90	14.8
25	132.75	67.5	83.25	37.0
35	115.05	94.5	72.15	51.8
50	88.50	135.0	55.50	74.0
75	44.25	202.5	27.75	111.0
90	17.70	243.0	11.10	133.2

[a] Epoxide equivalent = 177.
[b] Epoxide equivalent = 270.
[c] Three-fourths equivalent = 111.
[d] One equivalent = 148.

proportions in parts by weight of the reactants for the epoxidized soybean oil series. When the phthalic anhydride was melted, the tubes were removed from the bath and inverted several times to insure good mixing. To each tube of the third series was added 0.5% of benzyldimethylamine, based on the total weight of the epoxides and curing agent, and mixing was again accomplished by inverting the tubes. All were returned to the oil bath and observed periodically for gelation.

When cured with phthalic anhydride, the 100% Epon 828 gelled in slightly more than two hours. The mixtures containing the amine gelled within four minutes. This rapid cross-linking caused severe internal stresses which resulted in fissures in the specimens. The epoxidized lard oil series required about three hours for gelation while the epoxidized soybean oil mixtures (without amine) gelled in varying times, which decreased as the concentration of diluent increased. At the 75% level the gel time had dropped to about one hour. All the specimens were kept in the oil bath for three hours to minimize cracking and then were transferred to a 150°C. air oven for a total cure of 20 hrs. When cool, the glass tubes were carefully shattered from the hard, transparent resins, and the latter were prepared for the physical measurements (7).

Summary and Conclusion

Three series of resins were made by curing mixtures of a diglycidyl ether and epoxidized, natural glyc-

erides (lard oil and soybean oil) with phthalic anhydride. One property of the uncured system that was affected was the gelation time, a measure of the working pot life. All members of the epoxidized lard oil series took three hours to gel. The time of gelation of the epoxidized soybean oil series varied inversely with the concentration of diulent, and all members of the epoxidized soybean oil series containing tertiary amine gelled in four minutes.

Some physical properties of the resins were measured. The heat distortion temperature was a linear function of the percentage of epoxidized oil in each series. Up to 20% level both epoxidized glycerides had the same HDTs, but at higher concentrations the HDTs for the epoxidized lard oil resins decreased more rapidly. The blends containing a tertiary amine had HDTs constantly higher by 25 degrees than corresponding blends without amine.

The tensile strengths of the resins from each series decreased nonlinearly at the same rate up to a concentration of 20% of epoxidized glycerides. At higher concentrations the tensile strengths of the epoxidized lard oil series dropped the most and the amine-containing systems the least. Epoxidized lard and soybean oils appear promising as modifiers for diglycidyl ether resins up to a 20% level.

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UNDER DISCUSSION are investigations concerning a possible method of determining residual hexane present in solvent-extracted meal, using a modified Pensky-Martens closed-cup flash-point testing apparatus.

The standard apparatus and stirring motor were used. The major modification was to add two four-bladed propellers to the stirring shaft instead of the conventional single two-bladed propeller. One propeller was mounted on the bottom of the shaft and one about midway up. The blades of each propeller were turned so that they did not coincide or turn in the same plane vertically with each other. This imparted a twisting motion in the middle and upper

portions of the sample as well as a complete movement on the bottom. The bottom propeller was adjusted so as to scrape the flat, round bottom of the sample cup and to come as close to the sides as movement would permit without binding. The upper propeller is of the same pitch and diameter as the bottom one, or one and three-fourths inches.

One other modification became necessary because of the change in propeller arrangement. The standard A.S.T.M. flash-point thermometers with 57 mm. or 2¼-in. immersion and with brass ferrules could not be used because of the interference from the upper propeller. A standard laboratory thermometer reading from 30° to 300°F. was used by equipping it with