Effect of Structure of Epoxidized Esters on the Physical Properties of Their Phthalic Anhydride Cured Resins

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IN THE development of epoxy resins, the major research effort has been centered on the curing of glycidyl ethers of bifunctional phenols, principally of 4,4′-isopropylidenediphenol (bisphenol A). Extensive studies have been made on the effects of various curing agents on the physical properties of resins derived from these glycidyl ethers and on the determination of optimum conditions for cure. On the other hand, except for the work of Dearborn (*1*) and Wynstra (*15*) on polygylcidyl ethers, comparatively little has been reported on the effect of varying the structure of the glycidyl ether on the physical properties of the final resins.

In contrast with the great effort with glycidyl resins, virtually no work has been reported in detail on the preparation of epoxy resins from nonterminal epoxides. This is surprising in view of the well known ease of preparation of nonterminal epoxides from nonterminal olefins and peracids (*7, 9-11*). In addition, many unsaturated acids, alcohols, and esters are readily available at low cost from agricultural sources. These chemicals may serve as starting materials in the preparation of multifunctional derivatives which, when epoxidized, can give polyepoxide monomers of widely varying structure. These polyepoxide structures differ in three ways from the polyglycidyl ether type: They have no terminal epoxide group, they have no activating influences like the ether group in a beta position to the terminal epoxides, and they do not contain hydroxyl groups or generate them during the cross-linking reaction with cyclic anhydrides. The architectural variety that is potentially available in these intermediates makes possible a broad range of physical and chemical properties in the final resins. Therefore, studies of the synthesis of resins from nonterminal epoxides and the effect of epoxide structure on the physical and chemical properties of the cured resin offer a fruitful field of investigation.

OBJECTIVES

The present work was initiated to determine whether useful epoxy resins could be made from fatty derivatives as principal components. An initial investigation showed that, in contrast to the glycidyl ethers (*1*), internal polyepoxides could not be cured with polycarboxylic cyclic anhydrides alone. Only soft, friable, opaque gels were obtained by cross linking internal epoxides of various structures with phthalic ahydride. However, in the presence of a tertiary amine, these same internal epoxides were cured with phthalic anhydride (or other cyclic anhydrides) to give transparent, hard, lustrous resins (*3*). Such cures were successfully accomplished on two types of polyepoxide structures: those whose fatty acid residues were converted to ester linkages and those whose long aliphatic chains were connected by amide linkages.

Reported here are the preparation and properties of a specific series of internal polyepoxide intermediates containing ester linkages, the preparation of resins from these polyepoxides and phthalic anhydride, and the characterization of these resins according to some physical properties —viz., heat distortion temperature, tensile strength, modulus of elasticity, and per cent elongation at break. Details of the series of epoxide intermediates and resins containing the amide linkages will be reported in another article.

It was of equal importance to determine whether any systematic correlation could be found between the structures of the polyepoxide intermediates and the magnitudes of the physical properties of the corresponding resins. To achieve this objective it was necessary to select with care the intermediate epoxides specifically for structural analogy. Among the possible variables for such structures were the number of acyl groups in the molecule, the number of epoxide groups in each fatty chain, and the number of atoms (distance) between any two epoxide groups.

For valid comparisons of intermediates differing only in the number of epoxide groups, the distance between epoxide groups had to be kept relatively constant. This condition was met by fully esterifying ethylene glycol, glycerol, pentaerythritol, and dipentaerythritol with oleic acid and epoxidizing the resulting di-, tri-, tetra-, and hexa-esters to the polyepoxides. (This group of polyepoxide intermediates is referred to here as the oleate series.) Thus were prepared intermediates whose maximum or fundamental distance between epoxide groups in each compound of this series is 22 or 23 atoms (23 or 25 in the case of dipentaerythritol, Figure 1). These particular epoxide groups will be known as reference epoxides because they produce with phthalic anhydride the cross links that characterize the network spacing. The position of each of these epoxide

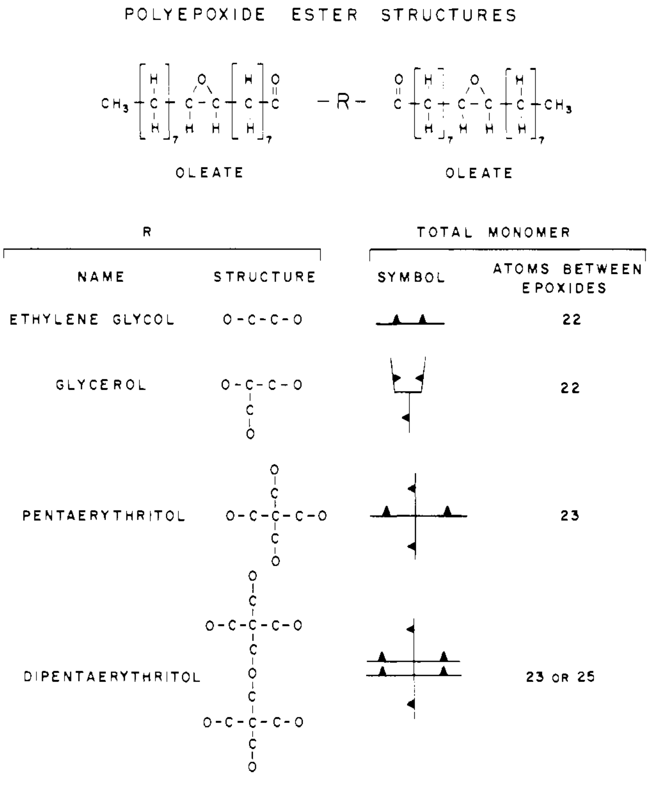

Figure 1. Structural relationships of polyepoxides
Each triangle represents an epoxide group

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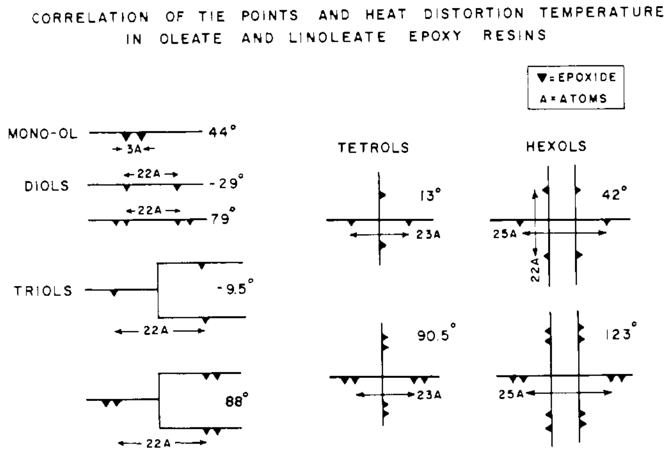


Figure 2. Correlation of tie points and heat distortion temperature of resins derived from epoxidized oleate and linoleate esters

Numbers at upper right of each diagram are heat distortion temperatures, ° C.

groups in the molecule will be called a cross-link site. The number of epoxide groups in each intermediate corresponds to the number of hydroxyl groups in the parent polyalcohol and to the number of acyl chains—viz, 2, 3, 4, and 6, respectively. A similar series of polyepoxide esters might have been synthesized from such polyhydric alcohols as erythritol, arabitol, and mannitol, but the presence of secondary hydroxyl groups would have made the reactions much more difficult and less complete.

For comparison, a second group of polyepoxide intermediates with the same spacing between reference expoxides as described for the oleates (Figure 2) was synthesized from linoleic acid and the same polyols. (This group will be called the linoleate series.) The number of epoxide groups in each intermediate of this series is double the number of acyl chains. Each member of this series differs structurally from the corresponding member of the oleate series only by the addition to each chain of an auxiliary epoxide group on the outer side of each reference epoxide. The over-all chemical effect of the extra epoxide group was to provide another potential cross link or tie point at the cross-link site.

To evaluate the effect of distance between a reference epoxide pair, a constant number of epoxide groups had to be maintained while varying the distance between them radically. This was accomplished by comparing the resins from the diepoxide of ethylene glycol dioleate, which contains a 22-atom spacing between epoxides, with that from the diepoxide of methyl linoleate, which contains a 3-atom spacing between epoxides (Figure 3).

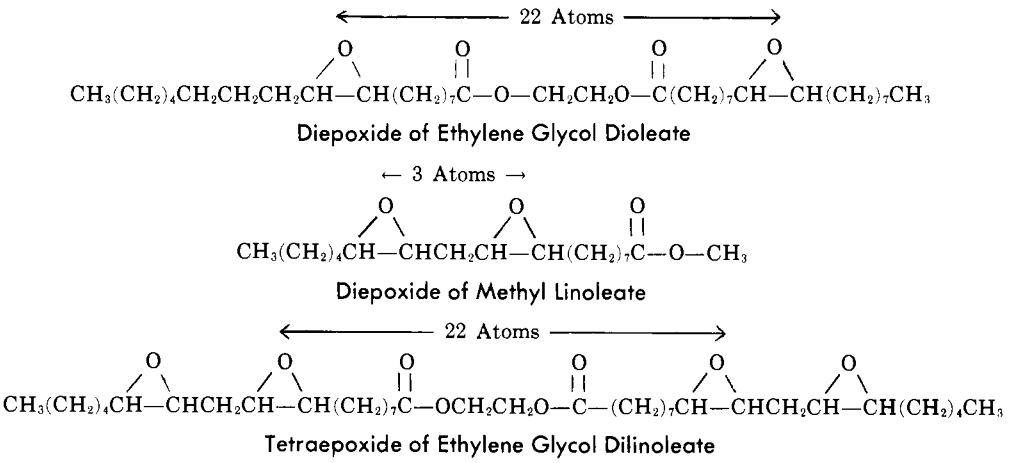
EXPERIMENTAL

Oleic acid and methyl oleate of low polyolefin and low saturates content were prepared from olive oil by the method of Knight and others (*4*). Linoleic acid and methyl linoleate of low saturates and monounsaturates content were prepared from safflower seed oil and purified by the urea crystallization technique of Swern and Parker (*6, 12*). The physical constants of these starting materials are listed in Table I.

Preparation of Polyesters. Polyesters of oleic and linoleic acids were made from primary polyols (ethylene glycol, glycerol, and commercial pentaerythriol) by the Wheeler procedure (*13*), except that the molecular distillation was omitted. Dipentaerythritol hexaoleate and hexalinoleate were made by the method of Lundberg and Chipault (*5*) from dipentaerythritol hexaacetate and the unsaturated methyl esters. A modification in the purification of dipentaerythritol hexaacetate, involving clarification with Nuchar and recrystallization from ether at −20° C., yielded high purity ester in a minimum of time. Saponification number calculated for $C_{22}H_{34}O_{13}$, 666; found, 655; melting point, 67–8° C. The yields, analytical data, and purities of the polyolefinic esters are summarized in Table II. Small amounts of polyunsaturates were carried into the oleate esters, and some monounsaturates were carried into the linoleate esters. These impurities had a limiting effect on the maximum purities possible for the polyepoxides.

Preparation of Polyepoxides. Each polyolefin was epoxidized in chloroform by the conventional method with commercial peracetic acid (*7, 9–11*). Crystallization techniques were used to remove incompletely epoxidized molecules and those containing unreactive hydroxy-acetoxy groups formed by ring opening (*7, 8*), a competing, consecutive reaction in the epoxidation step. The difficulties in achieving high purities were especially pronounced in the higher functionality intermediates. The presence of nonreactive impurities was found, in previous work with epoxidized glycerides (*3*), to have an adverse effect on the heat distortion temperature (HDT). Therefore, high purity of the polyepoxide intermediate is a prime requisite for high HDT. The final yields, analytical data, and purities for these polyepoxides are listed in Table III.

Preparation of Resins. Each resin was made in a corked glass tube, 9 inches by 9 mm., coated with a film of methyl oleate as a mold release agent. Equivalent weights of the polyepoxide and phthalic anhydride, with 2.5 weight % of benzyldimethylamine, were heated in a 150° C. oil bath.



Diepoxide of Ethylene Glycol Dioleate

Diepoxide of Methyl Linoleate

Tetraepoxide of Ethylene Glycol Dilinoleate

Figure 3. Relative distances between epoxide groups in oleate and linoleate polyepoxides

Table I. Physical Constants of Starting Reagents

Compound	Iodine Value		Acid Number		Sapon. No.		n_D^{30}	B.P., ° C./Mm. Hg.
	Calcd.	Found	Calcd.	Found	Calcd.	Found		
Oleic acid[a]	89.9	89.5	198.9	198.0			1.4563	
Linoleic acid	181.4	181.6	200.3	197.3			1.4658	171-5 /0.45
Methyl oleate	85.6	86.1			189.2	190.0	1.4481	170-72/1.8
Methyl linoleate	172.8	169.2			190.5	191.0	1.4588	178-80/3.5

[a] Made by saponification of methyl oleate.

(One epoxide equivalent of intermediate requires one mole of phthalic anhydride.) Other tertiary amines found equally effective were trimethylamine, triethylamine, triamylamine, and β-dimethylaminopropionitrile. The ingredients were mixed by inverting the tube several times before gelation. In certain cases (high functionality epoxides) homogeneity could not be obtained at 150° C. because gelation was too rapid. In such cases, the temperature was lowered to 135° C. The specimens were not removed from the bath for at least 6 hours in order to minimize stresses which produce cracks in the resin. Cures were then completed in the oil bath or an air oven. The curing schedules used are given in Table IV. Lower temperature-longer time curves were beneficial for the intermediates of higher functionality, giving higher HDT's. However, no systematic attempt was made to determine the best temperature and time combination.

Adoption of the use of equivalent weights of polyepoxide and phthalic anhydride, and of the 2.5% level of tertiary amine, was based on previous studies with glycerides (*3*).

In a typical example of resin synthesis, 3.1 grams (0.021 mole) of phthalic anhydride were melted in the glass mold at 150° C. From a small test tube, a melt of 3.9 grams (0.021 equivalent) of tetra(*cis,cis*-9,12-diepoxystearoyl) pentaerythritol, epoxide equivalent 185, was poured into the anhydride. Care was taken to ensure complete transfer. The tube was corked, mixed by inverting several times, and heated again. Benzyldimethylamine (0.2 ml.) was pipetted in and mixed well by the inversion method. Timing was started. This mixture was gelled in 4 minutes and was kept in the oil bath for 8 hours. After cooling, the resin was removed by carefully shattering the glass. The specimen was machined to a special size, and torsional modulus measurements were taken at different temperatures. The temperature on this curve corresponding to a modulus of 5.5×10^4 p.s.i. was taken as the HDT (*14*). It was unexpectedly low (53° C.), an indication of incomplete curing. When further cured at 120° C. for 65 hours, the HDT was 90° C.

RESULTS AND DISCUSSION

Physical measurements (Table V) were made on the resins made from the multifunctional epoxide intermediates of the oleate and linoleate series. These data may be treated and interpreted in two different ways: plotting HDT as a function of the number of epoxide groups, and plotting HDT as afunction of the number of acyl groups (or hydroxyl groups in the parent polyalcohol). In the first treatment straight lines are obtained by the method of least squares for the oleates and linoleates (Figure 4). Thus, in the range studied, the HDT is raised 17.5° for each epoxide group added in the oleate series and 6.2° per epoxide in the linoleate series. Although Dearborn (*1*) obtained a general correlation between epoxide functionality and resistance to deformation at elevated temperatures for polyglycidyl ether resins, there was no specific mathematical relation. Wynstra's data (*15*) concerning the effect of amine functionality in the curing agent on HDT, however, reveals a quasilinear relationship at low functionalities with a leveling-off effect at high functionalities. A similar effect would probably be observed in the present oleate and linoleate series at epoxide functionalities higher than 12. This idea is supported by the observation that a HDT of only 44° C. was obtained from a resin of phthalic anhydride and poly(vinyl epoxystearate) whose epoxide functionality was 80.

If the number of epoxide groups were the sole factor in determining HDT, then intermediates of equal functionality, such as tetra(*cis*-9,10-epoxystearoyl) pentaerythritol and di(*cis,cis*-9,12-diepoxystearoyl) 1,2-ethanediol, should have the same HDT, and only one line should have been obtained. The formation of two lines indicates that other factors are involved, the most predominant of which is the epoxide distribution.

A relatively constant spacing of 22 or 23 atoms between epoxide groups (up to 25 for the dipentaerythritol ester) is noted in the oleates from Figure 1. However, Figure 3 shows that the linoleates contain mixtures of this long spacing and short spacings of 3 atoms. Comparing the HDT's of the resins from glycol dioleate and methyl linoleate (Figure 2) gives some idea of the magnitude of the short spacing contribution. The fundamental distance between epoxides is 22 atoms in the former and 3 atoms in the latter. The 73° increase in HDT for the linoleate resin must be attributed, esentially, to the proximity of its epoxide groups. This proximity factor seems to become less important with an increase in epoxide functionality, as shown by the drop in HDT differential in Figure 4, but the

Table II. Yield and Analytical Data for Polyolefin Esters

Ester	Funct.[a]	Yields	Iodine No.		Sapon. No.		Purity[b], %
		Yield, %	Calcd.	Found	Calcd.	Found	
Glycol dioleate	2	71.2	86.3	87.0	189.9	188.9	99.2
Glycerol trioleate	3	63.4	86.3	86.2	190.0	187.7	100.0
Pentaerythritol tetraoleate	4	79.0	84.7	85.1	187.2	184.8	99.6
Dipentaerythritol hexaoleate	6	90.7	83.1	82.8	183.0	184.0	99.7
Methyl linoleate	2	87.3	172.0	166.4	190.0	191.0	95.3
Glycol dilinoleate	4	88.4	173.0	167.3	192.0	192.0	93.5
Glycerol trilinoleate	6	29.0	173.5	164.8	192.3	196.0	90.2
Pentaerythritol tetralinoleate	8	90.0	171.5	167.8	189.0	191.8	95.7
Dipentaerythritol hexalinoleate	12	94.0	167.0	163.0	184.5	186.4	95.1

[a] Number of double bonds.
[b] Based on iodine values.

Table III. Yield and Analytical Data for Epoxidized Fatty Esters

Polyepoxide of	Yield, %	% Oxirane Calcd.	% Oxirane Found[a]	Purity, %	No. of[b] Oxiranes
Glycol dioleate	26.6	5.15	4.64	90.0	1.80
Glycerol trioleate	91.4	5.15	4.84	94.0	2.82
Pentaerythritol tetraoleate	94.0	5.10	4.98	97.7	3.91
Pentaerythritol hexaoleate	91.6	4.96	4.72	95.2	5.71
Methyl linoleate	46.0	9.82	9.30	94.8	1.90
Glycol dilinoleate	54.3	9.85	9.00	91.5	3.66
Glycerol trilinoleate	75.0	9.86	9.07	92.0	5.52
Pentaerythritol tetralinoleate	81.2	9.70	8.66	89.4	7.15
Dipentaerythritol hexalinoleate	82.0	9.51	8.53	89.7	10.76

[a] Method of Durbetaki, (2).
[b] Theoretical number of epoxide groups x % purity.

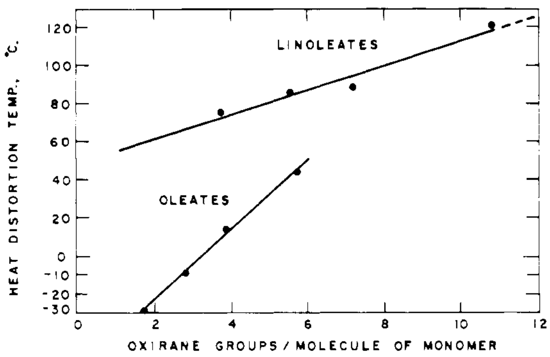


Figure 4. Heat distortion temperature of resins derived from epoxidized oleate and linoleate esters as a function of the number of oxirane groups.

drop may be due to the impurity of the intermediates. Nevertheless, the specific distribtuion of the epoxide group, in combination with the degree of epoxide functionality, is responsible for the higher HDT's of the linoleate resins.

In the second treatment of the data (Table V), the functionality is expressed as the number of acyl groups (Figure 5). The contributions of the many factors to HDT, such as the distance between epoxides, the number of epoxide groups, type of linkage, and special arrangement of chains are constants in the oleate series which define the position of the intercept of the oleate line on the ordinate axis. The slope of the line, calculated by the method of least squares, is a measure of the rate of HDT rise per unit of functionality. In Figure 4, the functionality unit is the epoxide group; in Figure 5, the unit is the acyl chain. Inasmuch as the acyl functionality is kept constant in both series, the lines in Figure 5 should be parallel. The fact that the slope of the linoleate line is smaller than that of the oleate line may be attributed to impurities in the polyolefin and polyepoxide intermediates. These impurities are nonreactive, have no sites for cross linking, and can produce "holes" in the main network of cross links (2) with corresponding decrease in HDT. In an attempt to approximate a correction for the impurities, the HDT's for the even whole number values of epoxide functionality were obtained from the linoleate line of Figure 4. The HDT values, which represent the minimum increase that may be expected for higher epoxide functionality, were then plotted against the number of acyl groups in each intermediate, resulting in the dotted linoleate line in Figure 5. The dotted line has a steeper slope than the original linoleate line in Figure 5 and shows a tendency to approach parallelism to the oleate line. This indicates that any further actual improvement in the purities of the intermediates would tend to raise the slope of the linoleate line even more. If absolutely pure intermediates were available, it is reasonable to believe that the lines of Figure 5 would be parallel and that the linoleate line would intercept the ordinate 108 units above the oleate intercept. The parallelism signifies that a constant structural factor is responsible for the constant increase in HDT of 108°. This structural factor is probably the additional epoxide group in the linoleate chain, placed in a very specific location with respect to the reference epoxide group of the oleate chain. This auxiliary cross link or tie point in each acyl chain of the linoleate intermediate increases the rigidity of the cross-linked network and raises the HDT Thus, this theory permits an evaluation to be made of the contribution to HDT of a specific structural factor, the extra tie point. If it were possible to add a third tie point at each cross-link site, the HDT might increase proportionately.

The anomalous position of the resin from methyl linoleate, because it does not fall on or near the linoleate line in Figure 5, indicates that it is not a true member of the linoleate series. Because methyl linoleate is a monoester, it ought to be the first member of the series. However, it lacks the main factor common to all the other linoleate intermediates: the long spacing between reference epoxide groups.

Examination of the other physical properties (Table V) shows a trend of increasing modulus of elasticity and tensile strength with an increase in epoxide functionality for both series. The decreases in tensile strength in the highest members of the linoleate series are unexpected and not understood. One opinion is that "in many known thermosetting polymer systems, an optimum degree of cross linking

Table IV. Curing Conditions for Resins from Polyepoxide Fatty Esters and Phthalic Anhydride

Polyepoxide of	Gelation Temp., ° C.	Gelation Time, min.	Oil Bath Temp., ° C.	Oil Bath Time, hr.	Oven Temp., ° C.	Oven Time, hr.
Glycol dioleate	150	72	150	8		
Glycerol trioleate	150	27	150	9		
Pentaerythritol tetraoleate	150	24	150	8		
Dipentaerythritol hexaoleate	135	15	135	8	100	82
Methyl linoleate	150	22	150	5	150	3
Glycol dilinoleate	150	8	150	6	150	2
Glycerol trilinoleate	150	7	150	6	150	2
Pentaerythritol tetralinoleate	150	4	150	8	120	65
Dipentaerythritol hexalinoleate	135	13	135	24		

[a] Theoretical no. of epoxide groups per molecule of monomer x % purity.
[b] Heat distortion temperature.
[c] At 23° C. and 50% relative humidity.

Table V. Physical Properties of Resins Made from Epoxidized Fatty Esters

Polyepoxide of	No. of[a] Oxiranes	HDT,[b] ° C.	Tensile Strength,[c] P.S.I.	Elongation at Break, %	Modulus of Elasticity, P.S.I. x 10^{-3}
Glycol dioleate	1.80	−29.0	30	9	5
Glycerol trioleate	2.82	−9.5	150	20	10
Pentaerythritol tetraoleate	3.91	13	1600	23	50
Dipentaerythritol hexaoleate	5.71	42	3500	4	130
Methyl linoleate	1.90	44	3700	7	130
Glycol dilinoleate	3.66	79	6200	7	170
Glycerol trilinoleate	5.52	88	6500	5	180
Pentaerythritol tetralinoleate	7.15	91	4400	2	210
Dipentaerythritol hexalinoleate	10.76	123	3500	2	260

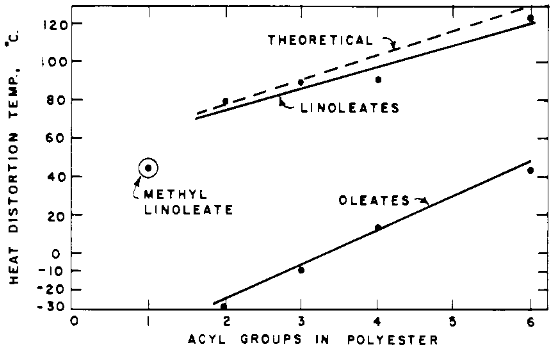


Figure 5. Heat distortion temperature of resins derived from epoxidized oleate and linoleate esters as a function of the number of acyl groups

exists beyond which tensile strength begins to fall off; modulus and elongation, however, do tend to increase and decrease, respectively, in a regular manner. That this effect was not seen in the oleate series may be an indication that the optimum functionality had not been reached in it" (*16*). The rate of increases in both tensile strength and modulus of elasticity for the oleate series is much greater than that for the linoleates. This is consistent with the behavior of the HDT's. The percentage elongations appear to be of a constant magnitude, except for the glycerol trioleate and pentaerythritol tetraoleate resins. No explanation is available for those high values at this time.

The data of Figure 2 shows marked differences in the magnitude of certain physical properties between the oleate and linoleate series. Another striking difference in the resin can be seen from torsional modulus-temperature curves. Examples of such curves are given in Figure 6 for two typical commercial (terminal type) epoxy resins and two nonterminal epoxy resins, one representative of the oleate series and the other of the linoleate series. The curves for the commercial (*A* and *C*) and the oleate (*D*) resin show a relatively rapid deformation of the resin network within a narrow temperature range. In contrast to this, the linoleate curve (*B*) drops slowly in torsional modulus over a much wider temperature range. This signifies a broader working temperature range for the linoleate resins than is indicated by the HDT alone.

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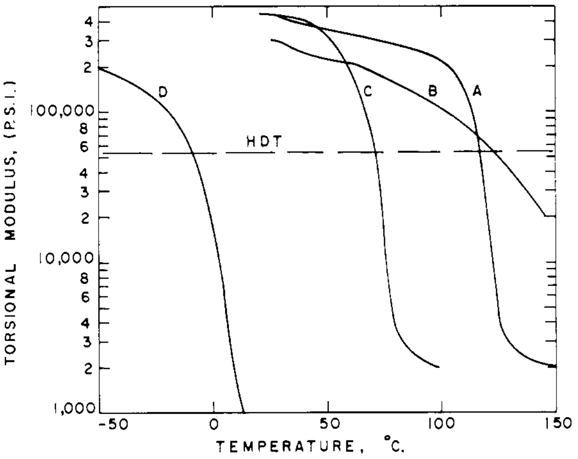

Figure 6. Torsional modulus of epoxy resins as a function of temperature

A. Epon 828 + diethylenetriamine
B. Polyepoxide of dipentaerythritol hexalinoleate + phthalic anhydride
C. Epon 562 + hexahydrophthalic anhydride
D. Polyepoxide of glycerol trioleate + phthalic anhydride

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