# Resins from *endo*-Dicyclopentadiene Dioxide*

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Introduction

In curing conventional epoxy resins, considerable study has been devoted to the effect of structure of polycarboxylic acid anhydrides on reactivity and resin properties. The resistance of cured resins to stress at elevated temperatures, for example, increases as the functionality or the compactness of the anhydride increases.[1] Pyromelletic dianhydride,[2] chlorendic anhydride,[3] and methyl Nadic anhydride[4] have been developed as curing agents leading to high softening resins. More recently, attention has also been given to the synthesis of new types of epoxides as another method of modifying the resin forming properties. The approach was stimulated by the development of economical and efficient methods of epoxidation with the use of peracetic acid.[5] This paper is concerned with one of these epoxides, namely *endo*-dicyclopentadiene dioxide (Union Carbide Chemicals Co., Unox epoxide 207, m.p. 185°C.):
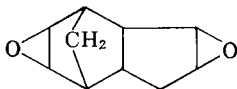
Unox 207

Anhydride Curing Agents

A variety of polycarboxylic acid anhydrides is available as curing agents for polyepoxides. The reactivities of anhydrides toward epoxides differ greatly and are related to the strength of the respective acids and to steric hindrance. Maleic anhydride, which is derived from a strong acid, reacts very rapidly, whereas alkenylsuccinic anhydride reacts slowly because of the bulky side chain. We have observed that maleic anhydride and Unox 207 have several unique and desirable properties in forming resins.

The thermal stability of resins from Unox 207, maleic anhydride, and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane) was examined as a criterion for optimum formulations. The polyol was added to initiate the reaction. The mixtures, which are homogeneous, mobile

liquids at 50°C., were gelled at 80°C., cured for 6 hr. at 120, 160, and 200°C., and aged for 25 hr. at 260°C. in a circu⁻ ‛ing-air oven.   Figure 1 shows that resins derived from 0.3–0.5 mole of a⌐ ydride for each epoxide equivalent were most stable.   Deflection temperatures were greater than 300°C., the temperature limit of the test instrument, and were therefore no assistance in defining optimum ratios.   When the hydroxyl:anhydride ratio was less than unity, it had little effect on the thermal stability.   The highest flexural strength was 14,200 psi at 0.6 mole of anhyaride (Fig. 1).
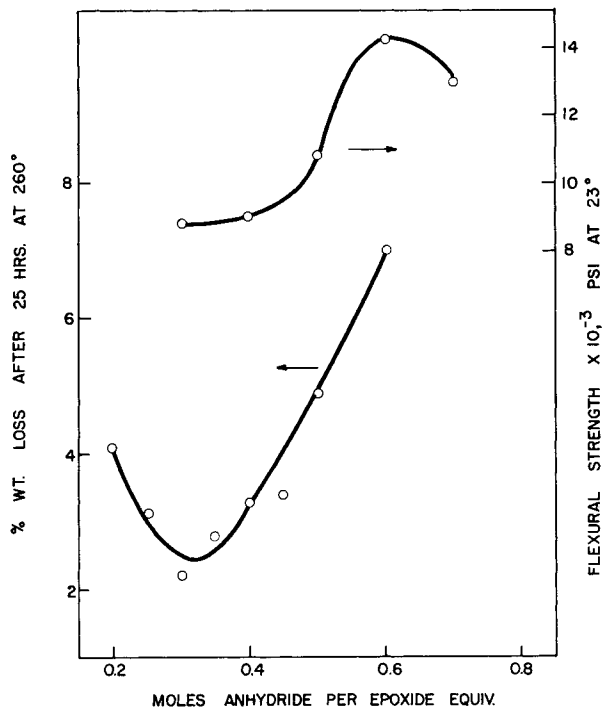

Fig. 1. Flexural strength (cure: 2 hr., 120°C.; 6 hr., 160°C.) and weight loss.   Hydroxyl content; 0.2 equiv. per epoxide equiv.

The formulation given in Table I was selected on the basis of thermal stability; for applications that require only modest thermal stability, higher proportions of anhydride may be more suitable.

The reactivities of mixtures of Unox 207 and maleic anhydride are illus-

TABLE I
Formulation 1

	Wt.-%
Unox 207 (1.0 epoxide equiv.)	63.2
Maleic anhydride (0.4 mole)	30.1
Trimethylolpropane (0.2 hydroxyl equiv.)	6.7

trated in Figure 2.   A 35-g. mixture, containing 0.4 mole of anhydride for each epoxide equivalent, was placed in a 4-oz. bottle in a circulating-air oven maintained at 110°C.   The reaction was very slow, and gelation did not occur before 19 hrs.   Addition of trimethylolpropane (Formulation 1) increased the peak exotherm temperature, and gelation occurred in 5 hr. Small quantities of either benzyldimethylamine or stannic chloride further increased the reaction rate.   Apparently, an initiator is necessary to obtain a smooth, rapid reaction; the role of polyols in the curing mechanism is discussed in a subsequent section.
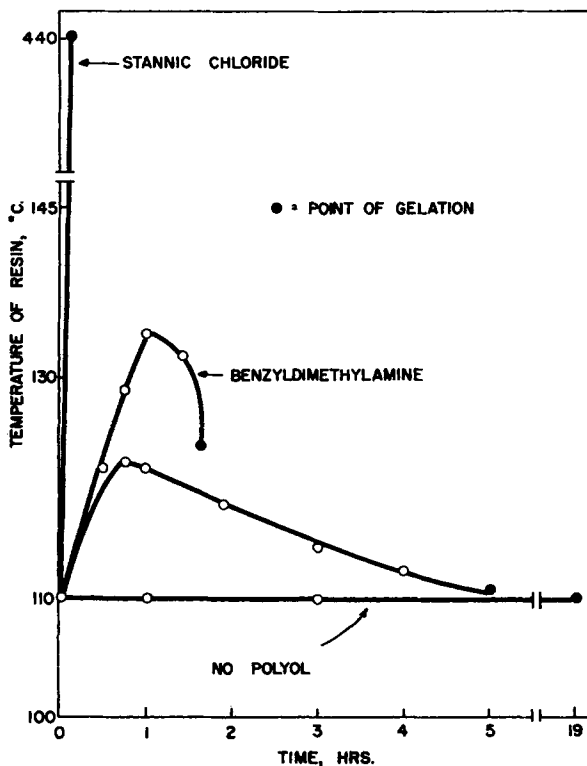

Fig. 2. Reactivity of formulations at an ambient temperature of 110°.   A 35-g. mixture of Formulation 1 was employed except as indicated.

The ambient temperature at which the three-component mixtures gelled had a marked effect on the reactivity.   Figure 3 gives the peak exotherm temperatures and gel periods at various temperatures for Formulation 1 and illustrates a marked reactivity dependence on temperature; consequently, the initial curing temperature is critical and depends on the resin mass, the presence of fillers, and the facilities for heat removal.

The large temperature dependence at 100–130°C. implies that curable mixtures would have a relatively long shelf life at low temperatures. Figure 4 shows the viscosity stability of Formulation 1 at 50°C. and indi-

cates that the formulation, which had a melt temperature of about 45°C., has a shelf life of about 4 days.   Mixtures containing larger proportions of anhydride had lower melt temperatures and could be stored as mobile liquids for one week or more at room temperature.

The functionality and molecular shape of the polyol initiator had a significant effect on deflection temperature of the resin cured at 160°C. Table II, for example, shows that glycerol, a compact, stable trihydric alcohol, led to a value of 202°C., whereas 1,5-pentanediol, a long-chain,
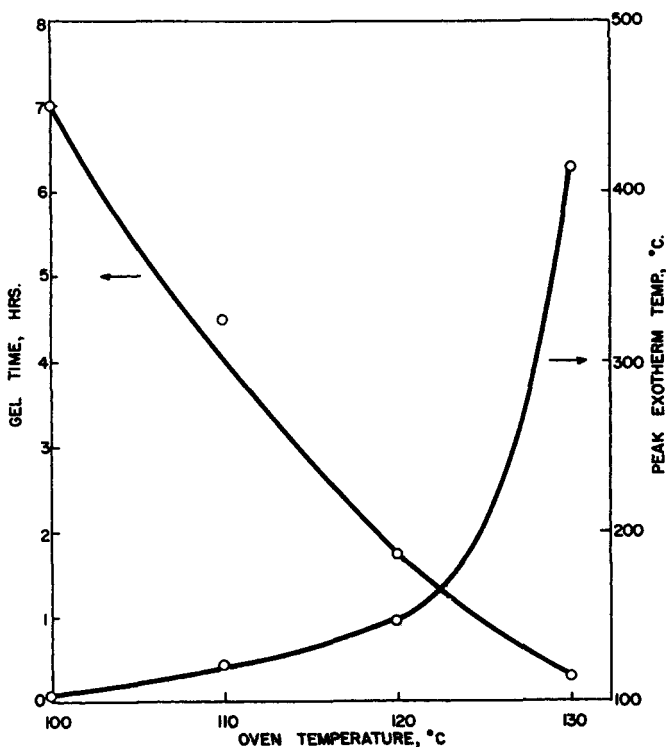

Fig. 3. Gelation time and peak exotherm temperature for Formulation 1 as a function of ambient temperature.

dihydric alcohol, led to a value of 134°C.   Decreasing the functionality and increasing the chain length of the polyol apparently yields resins having lower softening temperatures   Further curing at elevated temperatures produced a curious effect in the deflection temperatures of the resins: after a final cure of 6 hr. at 260°C., the resins had equivalent deflection temperatures of about 294°C.

The thermal stability was determined by exposing resin bars measuring $5 \times \frac{1}{2} \times \frac{1}{2}$ in. (25 g.) to 260 ± 2°C. in a circulating-air oven.   Table II indicates that little correlation between weight loss and polyol was observed. Apparently, the presence of β-hydrogen atoms in the polyol is relatively
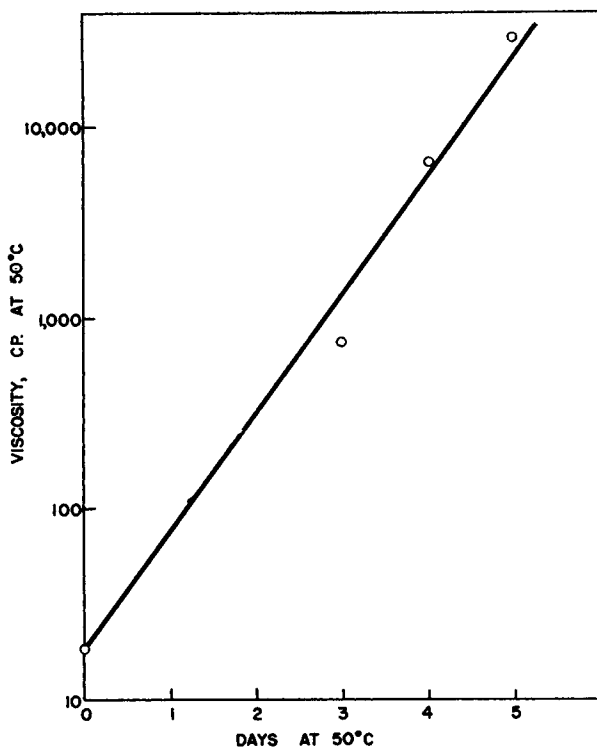
Fig. 4. Pot life of Formulation 1 at 50°C.

TABLE II
Effect of Polyols on Deflection Temperatures

	Deflection temperatures, °C.[a]			
Polyol[b]	Cured at 160°C.	Cured at 200°C.	Cured at 260°C.	Wt. loss, %[c]
Glycerol	202	257	294	21.3
Bisphenol A	187	234	277	18.2
Trimethylolpropane	183	240	294	19.6
1,2,6-Hexanetriol	173	239	292	22.0
Ethylene glycol	159	218	293	20.0
Neopentyl glycol	152	209	293	18.6
1,4-Butanediol	149	202	295	21.7
1,5-Pentanediol	134	184	294	21.8

[a] ASTM method D 648-56, 264 psi. Resins were gelled at 80°C. and cured for 2 hr. at 120°C. prior to consecutive cures of 6 hr. at temperatures indicated.

[b] Formulation: 0.4 mole of maleic anhydride and 0.2 hydroxyl equiv. for each epoxide equiv. Flexural strengths were 10,000 ± 1000 psi at 23°C. after the 160°C. cure.

[c] Loss after 1000 hr. at 260°C.; resins measured $5 \times 1/2 \times 1/2$ in. initially.

unimportant, and if ester cracking is involved in the degradation mechanism it must be related to the esters from the carboxyl–epoxide reaction.

The aged surface had several fissures and was affected more than the interior; furthermore, resins aged in the absence of air retained higher strengths. These data indicate that degradation occurs chiefly by oxidation. Certain aromatic structures are resistant to oxidation whereas others are antioxidants. Bisphenol A, for example, increased thermal stability (Table II) when employed as the polyol initiator; furthermore, mixtures of Unox 207 and glycidyl ethers of bisphenol A and hardeners derived from pyromellitic dianhydride gave resins having excellent resistance to aging at high temperatures.[6]

Anhydrides, such as phthalic, chlorendic, and pyromellitic, are effective curing agents for Unox 207. Formulations derived from phthalic anhydride and trimethylolpropane, however, are less reactive than those from maleic anhydride, and after a 200°C. cure, an ultimate deflection temperature of 230°C. was obtained for a resin based on 0.5 mole of anhydride and 0.2 hydroxyl equivalent for each epoxide group and 0.5 wt.-% of benzyldimethylamine. Chlorendic anhydride and pyromellitic dianhydride are high-melting, reactive curing agents and can best be incorporated in the resin by using a flux such as maleic anhydride or by precondensation with certain polyols.

Acid Curing Agents

In comparison with anhydrides, polycarboxylic acids have achieved less commercial success as curing agents for epoxy resins. The acids, in general, have higher melting points and are less soluble at low temperatures; furthermore, the functionality of epoxides toward carboxylic acids is lower, and consequently softer, less crosslinked resins are obtained. Acids, nevertheless, are more reactive and less volatile than corresponding anhydrides.

Useful curing agents can be prepared by condensing anhydrides and acids with polyhydric alcohols in proportions that give carboxyl endgroups. A viscous, liquid hardener having a carboxyl equivalent weight of 156 was prepared by condensing 2.7 moles of maleic anhydride and one mole of trimethylolpropane at 100°C. A resin derived from 0.4 carboxyl group for each epoxide group had deflection temperatures of 156, 193, and >300°C., after consecutive cures of 6 hr. at 160, 200, and 260°C., respectively. The handling characteristics and resin properties can be varied by using different anhydrides and polyols.

Modification with Vinyl Monomers

Vinyl monomers, such as styrene, vinyl acetate, and methyl methacrylate, have been used extensively in crosslinking polyesters derived from unsaturated dicarboxylic acids and dihydric alcohols. The technique, however, has not been applied commercially to polyesters prepared from polyepoxides and unsaturated carboxylic acids and anhydrides. We have

TABLE III
Formulation 2

	Wt.-%
Unox 207 (1.0 epoxide equiv.)	47.8
Maleic anhydride (0.4 mole)	22.8
Trimethylolpropane (0.2 hydroxyl equiv.)	5.0
Styrene (0.4 mole)	24.4

observed, for example, that mixtures of Unox 207, maleic anhydride, polyols, and styrene are mobile solutions that can be gelled readily at moderate temperatures. Resin formation takes place in one operation through reaction of the epoxide and carboxyl groups and copolymerization of the vinyl and maleate groups.

Formulation 2 (Table III) was prepared by dissolving the first three components at about 80°C., cooling to 35°C., and adding styrene.

Since uninhibited styrene was used, only a small quantity of benzoyl peroxide (0.05%) was added to promote polymerization through the un-
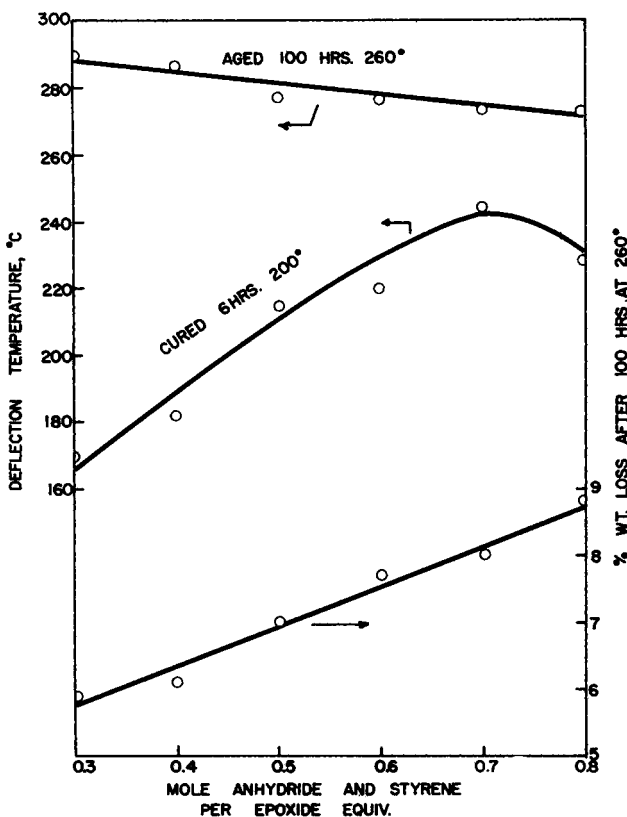

Fig. 5. Deflection temperature and thermal stability of resins derived from Unox 207, maleic anhydride, styrene, and trimethylolpropane (0.2 hydroxyl).

saturated groups. No catalyst for the epoxide-carboxyl reaction was employed. A 35-g. sample gelled after 40 min. and had a peak temperature of 140°C. in an oven at 50°C. A resin cured for 6 hr. at 120 and 200°C. had a deflection temperature of 182°C.

Figure 5 shows the effect of formulation change on deflection temperature and weight loss on exposure to 260°C.; one mole of styrene was used for each mole of maleic anhydride. The styrene-modified resins (13-g. bars) were more stable toward thermal degradation, as illustrated in Figure 6. Apparently, the reaction of styrene and maleic anhydride occurs
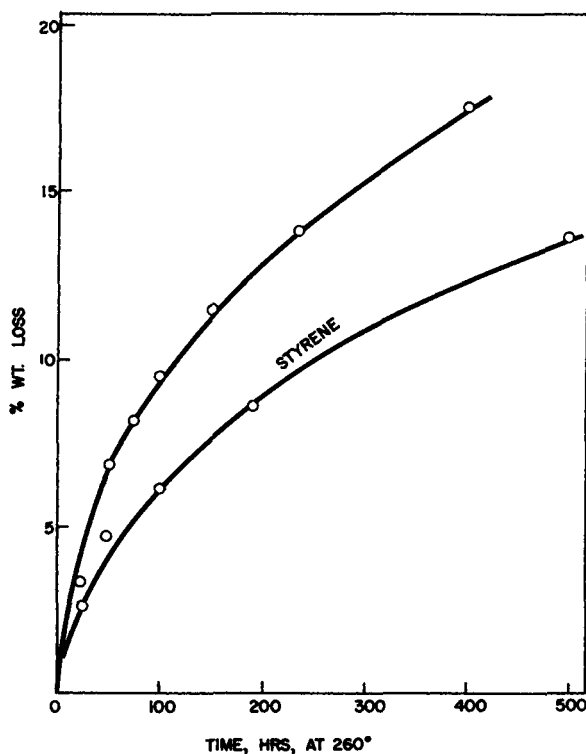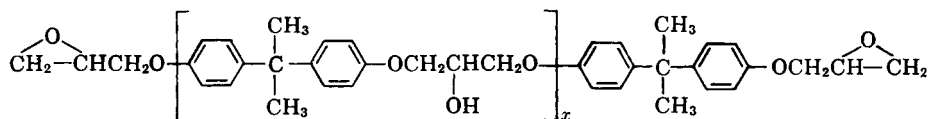

Fig. 6. Comparison of thermal stabilities of resins from Formulation 1 and Formulation 2 (styrene).

initially and is responsible for the high reactivity. Most of the epoxide–carboxyl reaction takes place after the vinyl polymerization. Some anhydride groups were present in the resin until the 260°C. cure was effected, in accord with the low reactivity of alkyl-succinic anhydride toward epoxides. The reaction sequence is consistent with the observed reactivities and the effect of curing cycle on deflection temperature. The sequence of reactions and the required cure should be dependent upon the reactivity of the unsaturated monomers, the reactivity of the epoxide toward carboxyl groups, and the selection of catalysts for each reaction.
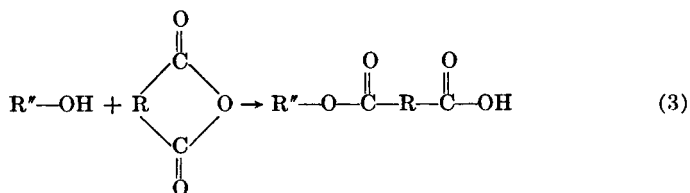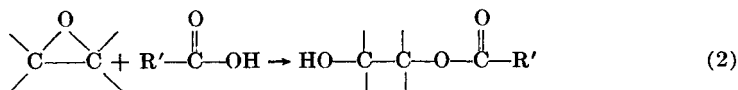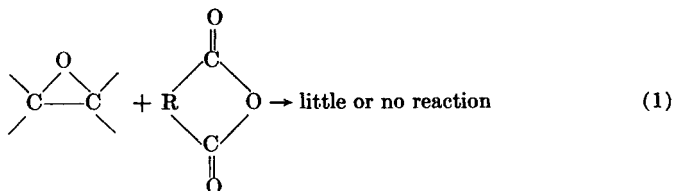
Unox epoxide 201, 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate, for example, is very reactive with carboxylic acids and can be employed advantageously in similar formulations.

Mechanism of Polymerization

Epoxides and carboxylic acid anhydrides react very slowly in the absence of initiators.[7-9] Polymeric glycidyl ethers of bisphenol A, for example,

$$
CH_2\!-\!CHCH_2O\!-\!\!\left[\!\!\begin{array}{c} CH_3 \\ | \\ C \\ | \\ CH_3 \end{array}\!\!-\!OCH_2CHCH_2O\!\!\right]_x\!\!\begin{array}{c} CH_3 \\ | \\ C \\ | \\ CH_3 \end{array}\!-\!OCH_2CH\!-\!CH_2
$$

(where $x > 0$) react faster than the monomer ($x = 0$) with pure anhydrides because of the hydroxyl groups in the polymer. Carboxylic acids are also effective in initiating the reaction sequence:

$$
\begin{array}{c} O \\ \diagdown\!\diagup \\ C\!-\!C \end{array} + \; R \begin{array}{c} O \\ \| \\ C \\ O \\ | \\ C \\ \| \\ O \end{array}\!\!O \rightarrow \text{little or no reaction} \qquad (1)
$$

$$
\begin{array}{c} O \\ \diagdown\!\diagup \\ C\!-\!C \end{array} + \; R'\!-\!\overset{O}{\overset{\|}{C}}\!-\!OH \rightarrow HO\!-\!\overset{}{\underset{|}{C}}\!-\!\overset{}{\underset{|}{C}}\!-\!O\!-\!\overset{O}{\overset{\|}{C}}\!-\!R' \qquad (2)
$$

$$
R''\!-\!OH + R\begin{array}{c} O \\ \| \\ C \\ O \\ | \\ C \\ \| \\ O \end{array}\!\!O \rightarrow R''\!-\!O\!-\!\overset{O}{\overset{\|}{C}}\!-\!R\!-\!\overset{O}{\overset{\|}{C}}\!-\!OH \qquad (3)
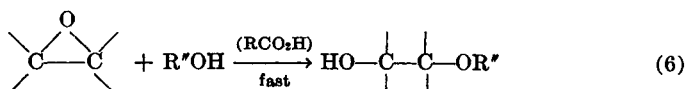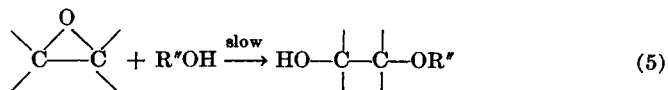$$

Pure epoxides and anhydrides containing no active hydrogen atoms require a suitable initiator for a smooth, rapid reaction. The foregoing reaction series indicates that in addition to acids, polyols should also be very effective. We have observed that polyols are generally more satisfactory because of the economics, the variety of selection, and the ease of dissolution. Carboxyl groups are generated in situ [reaction (3)] and react subsequently with epoxide [reaction (2)] to propagate the reaction chain.

The optimum curing ratio of anhydride and epoxide is considerably less than unity and indicates that etherification is important in the reaction mechanism. We have found also that equimolar quantities of cyclohexene oxide and acetic acid react in the following way:

$$\text{(4)}$$
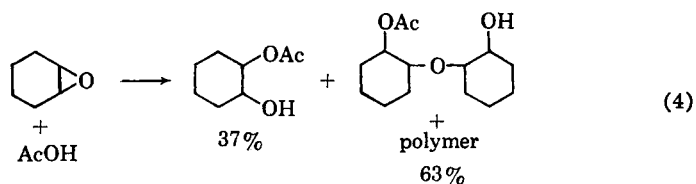
The epoxide–alcohol reaction, which is very slow in the absence of initiators, is apparently accelerated by carboxylic acids, as illustrated by reactions (5) and (6).

$$\underset{C}{\overset{O}{\triangle}}C + R''OH \xrightarrow{\text{slow}} HO-C-C-OR'' \qquad (5)$$

$$\underset{C}{\overset{O}{\triangle}}C + R''OH \xrightarrow[\text{fast}]{(RCO_2H)} HO-C-C-OR'' \qquad (6)$$

The curing mechanism is more complex with unsaturated anhydrides, such as maleic anhydride. Figure 7 shows that carboxylic acid is con-
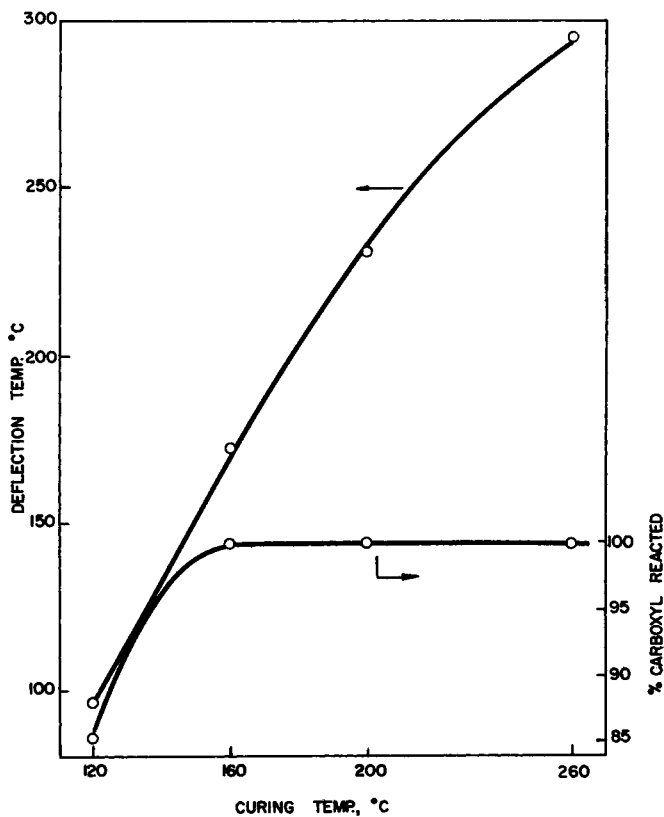
Fig. 7. Effect of curing temperature on deflection temperature and reaction of carboxyl groups (Formulation 1).

sumed completely after curing for 4 hr. at 160° and that the softening temperature continues to increase after additional curing at higher temperatures. The additional cure may be attributed in part to reaction of epoxide and hydroxyl groups [reaction (5)]; however, to examine the phenomenon more closely, we investigated the infrared spectra of the cured resins. Absorption bands at 6.1 and 12.0 μ, due to maleate linkages, decreased in intensity as the curing temperature and time were increased; furthermore, absorption at 12.9 μ appeared during the cure, indicating the presence of fumarate linkages. Nearly all of the unsaturation disappeared after 24 hr. at 260°C. Ultraviolet light and certain peroxides were mildly effective as curing accelerators. These data indicate that crosslinking occurs at the unsaturated sites. Maleic anhydride and maleates react with many materials by addition to the double bond; for example, they homopolymerize[10] and copolymerize with vinyl monomers and they add anionic reagents such as amines and certain organometallic materials.

B-Stage Resins

B-stage resins, which are partially cured, fusible resins, are useful in many applications. Laminates prepared by dry lay-up techniques, for example, can be made from thermosetting resin solutions. Solid, grindable B-stage resins are utilized in fluid-bed coatings and as compressive-molding compounds. The resins are often stored for long periods before fabrication and it is desirable to have compositions which remain fusible indefinitely at moderate temperatures.

The temperature dependence of the reactivity of Unox 207–maleic anhydride mixtures suggests that partially cured resins should be resistant to further reaction at low temperatures and, consequently, should be ideally suitable as B-stage resins. To test this postulate, Formulation 1 was stored at 25°C. and was checked periodically for carboxyl content and fusibility. Figure 8 shows that 35–40% of the available carboxyl groups remained unchanged at 1–2 months and that 23% remained at 14 months; the resin was soluble and fusible after this period. We believe that one of the epoxide groups in Unox 207 is much less reactive than the other toward acids and is responsible, in part, for the decrease in the reaction rate.

Unox 207, maleic anhydride, and polyol react very exothermally and, therefore, were converted to a B-stage resin in an inert solvent. A refluxing toluene medium was very effective in removing energy, and large batches (100 gal.) could be prepared in a reactor with adequate agitation and cooling facilities. The following materials were charged to a kettle at 25°C.: Unox 207, 100 parts (by weight); maleic anhydride, 48.2 parts; trimethylolpropane, 10.9 parts; toluene, 78.5 parts. The solution was stirred and heated rapidly to the refluxing temperature of toluene and to a kettle temperature of 125–130°C. The reaction mixture was cooled to 50°C. after 5 hr., and 27.8 parts of acetone was added to ensure homogeneity. The B-stage resin solution contained 35% of its initial acidity,

was 60% solids, had a viscosity of about 150 cpoise, was stable for periods of at least 6 months, and was substantially free of maleic anhydride.

Solid B-stage resin was prepared both by solvent removal and by partially reacting the components in the absence of solvent. The latter technique required effective temperature regulation of large batches to avoid an uncontrollable reaction. The solid B-stage resin was brittle and grindable and had a sintering point of 50–90° after 30–70% of the carboxyl groups had reacted. Similar resins prepared from Niax triol LHT-240 (0.2 hydroxyl equiv.) in place of trimethylolpropane were very viscous
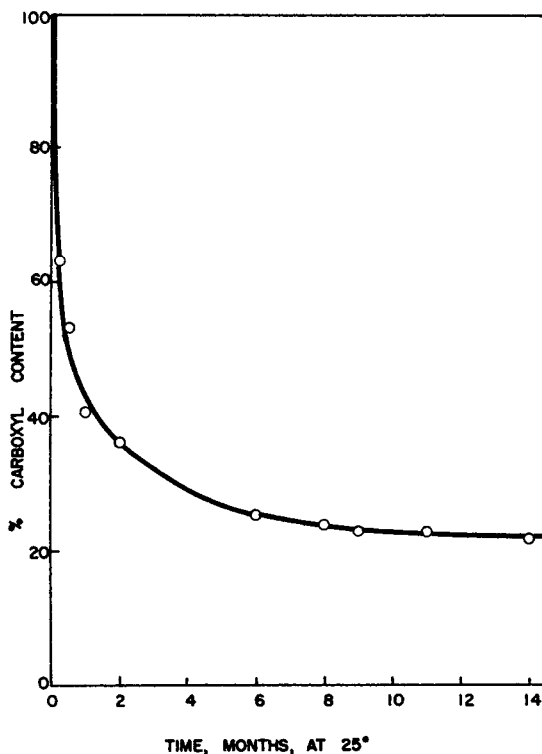

Fig. 8. Reaction of carboxyl groups at 25°C. (Formulation 1).

liquids soluble in toluene and styrene, illustrating that physical characteristics can be modified by using various polyols. Small quantities of long-chain polyols and unsaturated monomers, such as diallyl phthalate, can be incorporated in the B-stage resin solution to increase the flow during cure.

Laminated Resins

The B-stage resin solution was employed as a laminating varnish for 181 glass cloth with a Volan A finish. The cloth was impregnated with solution and dried at 120°C. for 2–5 min. to remove solvent. The prepreg can

be flexibilized to obtain more drape by adding small quantities of unsaturated monomers, such as diallyl phthalate, and polyols, such as Niax triol LHT-240.

A laminate was prepared by pressing 12 plies of the prepreg at 160°C. for 3 min. at 17.5 psi, 3 min. at 70 psi, and 54 min. at 198 psi; the specimen was post-cured in an oven at 160° for 6 hr.   Properties of the laminate are given in Table IV.   The laminate had excellent strength, both initially and

TABLE IV
Properties of Unox 207 Laminate

Property[a]	
Ultimate tensile strength, psi	53,600
Ultimate compressive strength, edgewise, psi	53,000
Flexural strength, psi	
At 23°C.	90,000
At 260°C. after 6 hr. at 200°C. and 6 hr. at 260°C.	37,500
At 23°C. after 192 hr. at 260°C.[b]	37,700
At 23°C. after 192 hr. at 260°C.[c]	60,000
At 260°C. after 192 hr. at 260°C.[b]	25,000
Flexural modulus at 23°C., psi $\times 10^{-6}$	4.1
Deflection temperature (264 psi), °C.	>300
Burning rate[d]	Self-extinguishing

[a] Specimens: 12-ply, $1/8$ in. thick, 181 cloth, Volan A finish, 25% resin. ASTM methods were employed.
[b] Aged in circulating-air oven.
[c] Aged in sealed vacuum tube.
[d] ASTM method D-635.

after aging at 260°C.   A sample aged in the absence of air had even better retention of strength properties, indicating that degradation occurs primarily by oxidation and suggesting that antioxidants may improve further the aging characteristics.

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Synopsis

endo-Dicyclopentadiene dioxide, a diepoxide melting at 185°C., reacts with polycarboxylic acid anhydrides, such as maleic anhydride, to give high softening, crosslinked resins. Polyhydric alcohols and phenols can be added to initiate the reaction and to modify the resin properties. The monomeric mixtures are mobile liquids at 35–50°C. for about 1 week. Partially cured resins, or B-stage resins, are fusible and soluble for at least a year and are suitable for impregnating glass fibers in laminate applications. Crosslinking occurs at elevated temperatures by reaction of epoxide with carboxyl and hydroxyl groups and by reaction of maleate double bonds. In the optimum range of 0.3–0.5 mole of maleic anhydride for each epoxide equivalent, resins having an ultimate deflection temperature in excess of 300°C. and having excellent thermal stability are obtained. Vinyl monomers, such as styrene, can be used in the formulation to modify the reactivity and resin properties.

Résumé

Le dioxyde d'*endo*-dicyclopentadiène, diépoxyde fondant à 185°C, réagit avec des anhydrides d'acide polycarboxylique, comme l'anhydride maléique, pour donner des résines pontées hautement malléables. Des polyalcools et des phénols peuvent être ajoutés pour initier la réaction et pour modifier les propriétés des résines. Les mélanges monomériques sont des liquides à des témpeartures de 35 à 50°C et le restent durant une semaine environ. Des résines partiellement vulcanisées, ou des résines du type B sont fusibles et solubles au moins pendant un an et tout indiquées pour imprégner des fibres de verre dans des applications de laminage. Des pontages se produisent à température élevée par réaction de l'époxyde avec les groupes carboxyles et hydroxyles et par réaction des doubles liaisons du maléate. Dans le domaine de concentration optimum allant de 0.3 à 0.5 môle d'anhydride maléique pour chaque équivalent d'époxyde, on obtient des résines possédant une température de déformation définitive en excès de 300°C et caractérisées par une excellente stabilité thermique. Des monomères vinyliques, comme le styrène, peuvent être employés dans le processus pour modifier la réactivité et les propriétés des résines.

Zusammenfassung

endo-Dicyclopentadiendioxyd, ein bei 185°C schmelzendes Diepoxyd, reagiert mit Polycarbonsäureanhydriden, wie Maleinsäureanhydrid, unter Bildung von vernetzten Harzen mit hohem Erweichungspunkt. Mehrwertige Alkohole und Phenole können als Reaktionsstarter und zur Modifizierung der Harzeigenschaften zugesetzt werden. Die Monomermischungen bilden bei 35–50°C für etwa eine Woche bewegliche Flüssigkeiten. Teilweise gehärtete Harze, oder B-Stufen-Harze, sind während mindestens eines Jahres schmelzbar und löslich und zur Imprägnierung von Glasfasern bei Anwendung als Platten verwendbar. Vernetzung erfolgt bei erhöhter Temperatur durch Reaktion des Epoxyds mit Carboxyl- und Hydroxylgruppen und durch Reaktion der Maleinsäuredoppelbindungen. Im optimalen Bereich von 0,3 bis 0,5 Mol Maleinsäureanhydrid pro Epoxydäquivalent werden Harze mit einer Beanspruchungstemperaturgrenze von 300°C und ausgezeichneter thermischer Stabilität erhalten. Vinylverbindungen, wie Styrol, können im Ansatz zur Modifizierung der Reaktivität und Harzeigenschaften verwendet werden.