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Filament-Winding Plastics

Part 5 - Epoxy-Amine Reactions and the Practical Use of High-Strength Plastics

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PREVIOUS REPORTS IN THIS SERIES

"Part I - Molecular Structure and Tensile Properties," J. R. Griffith and F. S. White, June, 1963, NRL Report 6047, Mar. 1964

"Part 2 - Role of the Resin in Glass Fiber Reinforced Structures Under Tensile Stress," F. S. White, Jr., NRL Report 6181, Dec. 1964

"Part 3 - Some Effects of Curing Agent Structure Upon Epoxy Resin Physical Properties," J. R. Griffith, NRL Report 6313, Sept. 1965

"Part 4 - Mechanical Properties and Cure of m-Aminobenzyl Amine (MABA)," J. R. Griffith, NRL Report 6433, Oct. 1966

The image shows a tilted rectangular stamp or form, likely a library or archival mark. It contains several lines of text and a grid structure at the bottom. The text is mostly illegible due to the high contrast and noise of the scan, but some words like 'LIBRARY' and 'SERIALS' are faintly visible. The grid at the bottom appears to be a table with several columns and rows.

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ABSTRACT

The plastics formed when epoxy resins react with polyfunctional amines have extremely complex molecular structures. Except for the basic reactions of simple epoxies, little is known regarding the molecular structures of such materials. Hence, probable structures for certain molecular regions of the cured plastics must be deduced from known structures of simple analogs.

In this work some relatively simple epoxy-amine systems were studied to obtain information regarding isomers, reaction sequences, and rates which are likely to prevail in complex polymerizations. The major reaction process of coreacting amines is an additive coupling. Gas chromatography and nuclear magnetic resonance were used to determine which of some possible isomers were formed in the reactions studied. Aromatic amines are not as reactive as aliphatic amines at moderate temperatures. Reaction rate and reaction temperature affect the properties of the resulting plastic. Proper conditions allow the production of a partially polymerized resin syrup of high-strength epoxies with reduced monomer content. When MABA is used as a curing agent, the reactions can be stopped when a suitable viscosity is reached for wet winding or preimpregnation of the reinforcement fibers.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

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FILAMENT-WINDING PLASTICS

PART 5 - EPOXY-AMINE REACTIONS AND THE PRACTICAL USE OF HIGH-STRENGTH PLASTICS

INTRODUCTION

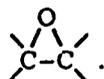
This report is a continuation of the series concerning the properties of epoxy-amine plastics suitable for use as filament-winding materials (1-4). The goal of this phase of the work has been twofold. First, the experiments were designed to learn more about the fundamental reaction processes which occur when liquid systems of epoxy resins and amines convert to solid plastics. Second, specific materials have been studied which have suitable characteristics for the production of impregnated glass fibers and rovings containing new, high-strength resin systems.

BASIC EPOXY-AMINE REACTIONS

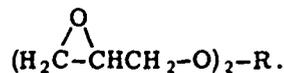
The cure of an epoxy-amine liquid resin into a solid plastic is an exceedingly complex process at the molecular level (5). During the process, relatively simple molecules convert to extensive networks of branched and crosslinked molecular chains of indefinite sizes. Although a total description of the molecular changes lies beyond present analytical abilities, many physical and mechanical properties of cured and uncured epoxy-amines can be reasonably attributed to known molecular characteristics of the components.

Possible Reactions

The basic epoxy structure is an oxirane ring,



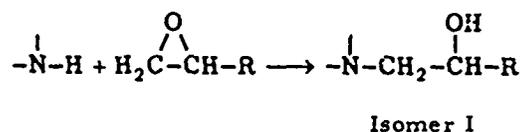
The reaction behavior of this strained, three-membered ring strongly depends on the total structure of the particular compound. Most of the practical epoxy resins contain the epoxy ring in a glycidyl ether structure,



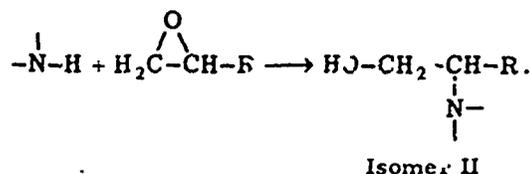
R is a hydrocarbon radical, usually aromatic, to which two or more glycidyl ether groups are attached.

There are two general classes of amines of value as curing agents - coreacting and catalytic. The coreacting amines are primary or secondary, that is, they carry one or two amino hydrogen atoms on each nitrogen atom. The catalytic amines are tertiary.

The major reaction process of coreacting amines is an additive coupling:

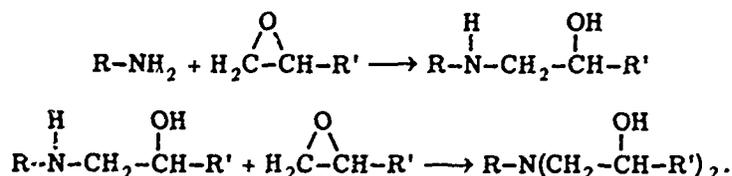


or



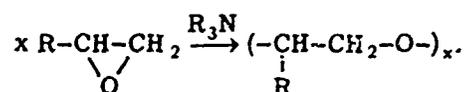
The first structural problem concerning the reaction is the direction of addition, i.e., is isomer I or II produced predominantly?

If the amine is primary, a second coupling reaction of the same type is possible:



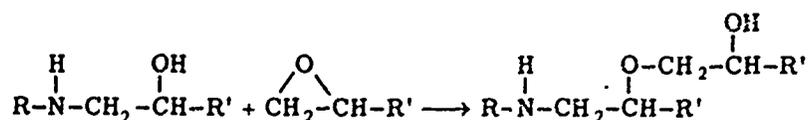
Thus, a primary amine couples once to produce a secondary amine, which may then couple with another epoxy molecule to produce a tertiary amine.

Low-molecular-weight, aliphatic tertiary amines cause the liquid-to-solid transition of epoxy resins by a different mechanism. Such an amine is a Lewis base and its effect upon the electronic patterns of an epoxy ring initiates epoxy-epoxy coupling:



Depending upon the particular materials, primary, secondary, and tertiary amines (produced in the coupling reaction) may promote this concurrent epoxy-epoxy reaction to a greater or lesser degree.

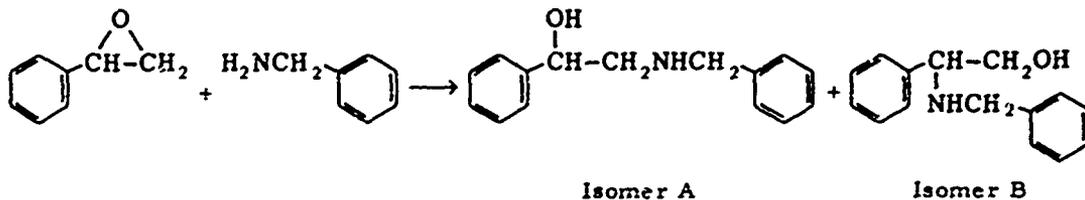
In some systems the hydroxyl group generated in the coupling reaction may also become involved:



The Isomer Question

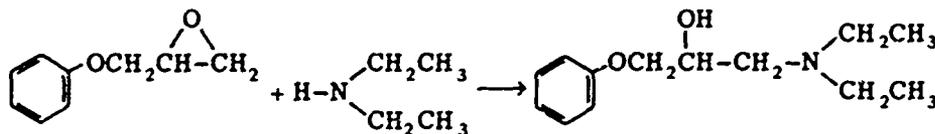
Most epoxies are physically and chemically unsymmetrical. A glycidyl ether, obviously, has less steric congestion around the exterior carbon atom than around the interior carbon of the oxirane ring. Also, the ether oxygen exerts an electronic influence upon the oxirane ring, which affects its reactivity.

Some analytical studies have been made of epoxy-amine reactions for the purpose of determining isomer ratios of the products. In the absence of auxiliary catalysts, it is usually found that terminal connection of nitrogen predominates. For example, Browne and Lutz (6) studied the following reaction:



According to their analysis, 16 parts of isomer A are produced for each part of isomer B. They also made an observation which may be of practical importance in epoxy resin applications. The hydrochloride of isomer B was hygroscopic and water-soluble, while that of A was not. There is a substantial difference in the water resistances of different epoxy-amine resins that may depend partially upon the relative amounts of the two isomers.

Shechter, Wynstra, and Kurkijy (7) showed that the reaction of phenyl glycidyl ether and diethylamine is a clean, rapid coupling at 50°C, with no significant side reactions. No attempt was reported to prove that in the reaction



the product was the isomer shown.

In the following experiments this reaction was restudied with the assistance of gas chromatographic and nuclear magnetic resonance measurements.

Experimental — Good commercial grades of diethylamine and phenyl glycidyl ether were examined on a gas chromatograph. The amine gave a single peak with a retention time of 16 sec. The phenyl glycidyl ether gave a large peak at 14 min and three small peaks which constituted less than 0.1% of the total area under all four peaks.

An equimolar solution of diethylamine and phenyl glycidyl ether was placed into a small test tube and heated to 30°C in an oil bath. Microliter samples were removed periodically during 4 hr of reaction and analyzed on the gas chromatograph by peak area measurements. A single product peak appeared at a retention time of 1.5 hr. As the reactant peaks decreased in area, the product peak increased proportionately. The bath temperature was raised to 52°C for 3 hr, and then to 100°C for 3 days. The reactant peaks disappeared completely, and only a single large product peak and the original impurity peaks remained.

The product was distilled in a stream of nitrogen and analyzed for carbon, hydrogen and nitrogen.

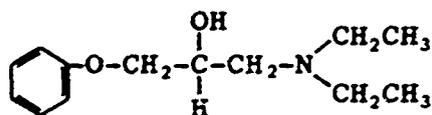
| | Theory | Found |
|----------|--------|--------|
| Carbon | 69.92% | 69.25% |
| Hydrogen | 9.48% | 9.59% |
| Nitrogen | 6.27% | 6.85% |

The distilled product was analyzed for relative amounts of hydrogen atoms on different positions by its nuclear magnetic resonance spectrum, with the results in Table 1.

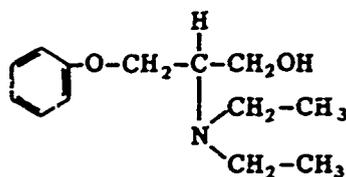
Table 1
Isomer Discrimination by NMR

| Acetone-d ₆ | | Benzene | | |
|------------------------|--------------------|---|----------------|--------------------|
| δppm | Relative Intensity | Assignment | δppm | Relative Intensity |
| 6.95 | 5 |  | Not determined | |
| 3.88 | 4 | $\left\{ \begin{array}{l} \text{O}-\text{CH}_2-\text{C} \\ \quad \quad \\ \quad \quad \text{H} \end{array} \right.$ | 3.86 | 3 |
| | | | 3.5 | 1 |
| 2.50 | 6 | $-\text{CH}_2-\text{N} <$ | 2.3 | 6 |
| 0.96 | 6 | $-\text{CH}_3$ | 0.82 | 6 |

The ratio of protons in the 3.5-ppm region to those in the 2.5-ppm region is observed to be 1 to 6, which corresponds to the assignments for isomer I; isomer II would have given a 6 to 4 ratio.



Isomer I



Isomer II

The single gas chromatographic peak for product and the nmr data indicate only one mode of addition by diethylamine to phenyl glycidyl ether in a solventless reaction between 30° and 100°C. It is reasonable to assume that the early reaction in an epoxy-amine polymerization involving structures similar to these is terminal carbon attachment by nitrogen. Whether or not the process remains so unique in the viscous pregel and solid-state, postgel periods, is undetermined at present.

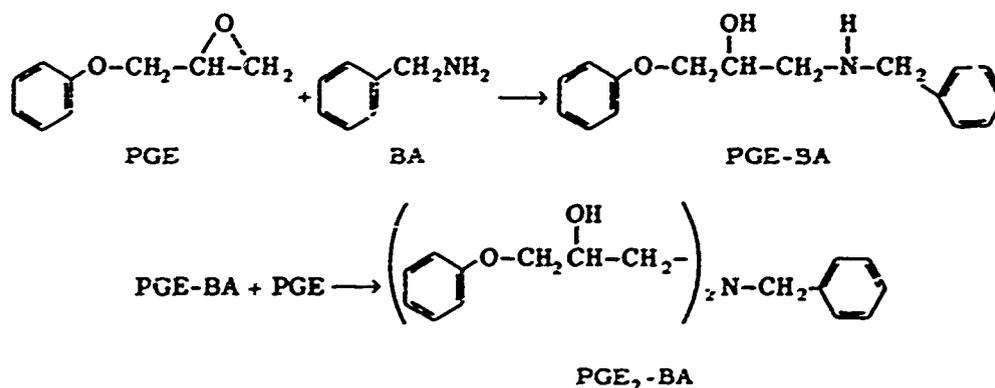
COMPETITIVE, CONSECUTIVE COUPLING REACTIONS

The secondary amine produced by the coupling reaction of a primary amine and an epoxy competes with the primary amine for the remaining epoxy. At least three factors determine the effectiveness of the competition—the inherent reactivities of the components, the steric freedom of the secondary amine intermediate, and the reaction temperature. Shechter et al. (7) showed that the reaction of phenyl glycidyl ether with *n*-butylamine had no stepwise character that could be clearly recognized at 50°C. Tertiary amine appeared early in the reaction process.

The Isolation of Secondary Amine Intermediates

By the selection of bulky and/or slow reactants it is sometimes possible to isolate secondary amine intermediates.

Experimental — An equimolar solution of benzylamine and phenyl glycidyl ether (1/80 of a mole of each) was placed into a small test tube and held in a constant-temperature bath at 50°C. During the reaction



microliter samples were withdrawn periodically and analyzed on a gas chromatograph. Infrared spectra were recorded also as the reaction progressed. A similar solution of aniline and phenyl glycidyl ether was treated identically.

After 190 min at 50°C, the reacting mass solidified. The secondary amine intermediate was then extracted and purified.

The mixture of reaction products and unreacted benzyl amine was dissolved in warm ethyl ether. A white crystalline solid precipitated when the solution was cooled in ice water. It was filtered and dried to yield 0.90 g (60% of the theoretical amount of PGE-BA based on the reaction curves). The melting point of this intermediate was 74°C and its nitrogen analysis was as follows:

Theory for PGE-BA: 5.44% N. Found: 5.45% N.

A viscous syrup, composed of PGE₂-BA, excess benzyl amine, and polyether, remained when the filtrate solvent was evaporated.

Figure 1 shows measured decreases in the normalized amounts of phenyl glycidyl ether and benzylamine plus calculated amounts of the secondary amine intermediate, PGE-BA, and final product, PGE₂-BA. In the infrared spectra, a band developed during the reaction in the 9.0-μ wavelength region which has been attributed to the ether linkage resulting from epoxy-epoxy coupling (8). To the extent this reaction occurred, the calculations are in error.

When phenyl glycidyl ether was completely consumed, 1/3 of the original quantity of benzylamine was unreacted. The early divergence of the curves representing remaining amounts of phenyl glycidyl ether and benzylamine also indicates that the intermediate is an effective competitor of benzylamine for the available epoxy. The curve at the top of the figure shows that the aromatic amine, aniline, is much less reactive at 50°C than the aliphatic amine, benzylamine, or the secondary intermediate.

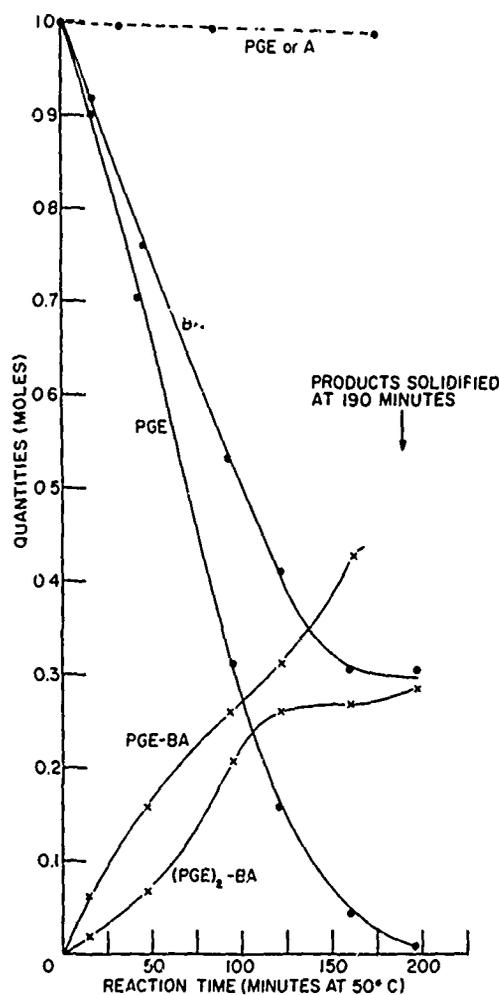
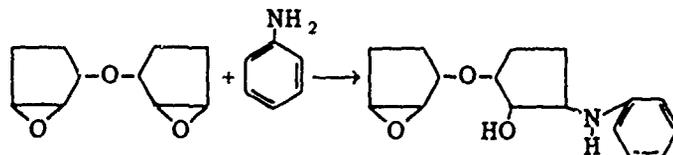


Fig. 1 - Reactions of phenyl glycidyl ether (PGE) with benzylamine (BA) and with aniline (A)

Several deductions regarding the course of glycidyl ether-amine polymerizations may be drawn from these results. First, the obvious fact is that aromatic amines are not as reactive as aliphatic amines at moderate temperatures. Second, there is a step-wise reaction of primary aliphatic amine to give secondary amine and then tertiary amine. The primary amine does not go directly to tertiary amine by simultaneous reactions of two epoxy groups with one primary amino group. However, the secondary aliphatic amine is an effective competitor for available epoxy. Third, when primary aliphatic amines are used as coreactants, epoxy-epoxy coupling to produce some polyether also occurs.

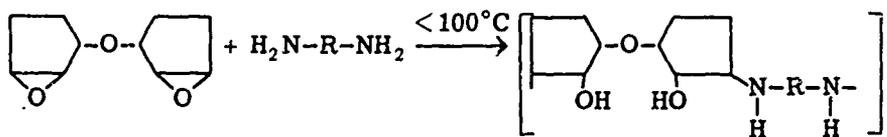
Another secondary amine intermediate was isolated from the reaction of a difunctional epoxy, bis(2,3-epoxy cyclopentyl)ether, and aniline. This material is not a typical glycidyl ether although it formally contains the basic structure:



Experimental – Equimolar quantities of aniline and the trans isomer of bis(2,3-epoxy cyclopentyl)ether (0.025 mole of each) were mutually soluble. The solution was placed into a small test tube and maintained at 72-76°C for 72 hr. After this reaction period, an equal weight of benzene was added to dissolve the products and unreacted starting materials. This solution was cooled, and white crystals slowly precipitated. The solid was filtered, washed with ethyl ether, and recrystallized from petroleum ether. It melted at 122-124°C. The following analysis was obtained:

| | Theory (mono-coupling product) | Found |
|----------|--------------------------------------|--------|
| Carbon | 69.79% | 69.65% |
| Hydrogen | 7.69% | 7.96% |
| Nitrogen | 5.09% | 5.39% |

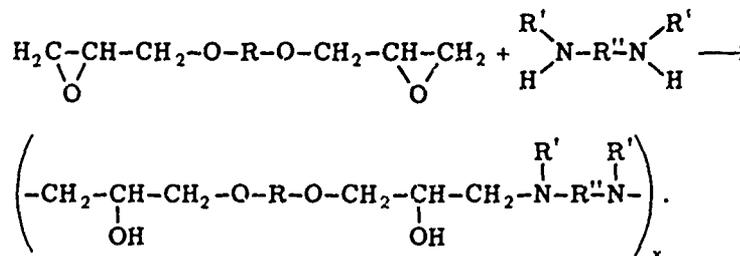
This diepoxide has been used to produce exceptionally strong plastics (3,9). It reacts slowly with amines relative to the normal glycidyl ether resins. The isolation of a stable secondary amine product from its reaction with aniline indicates the probability that its reaction course with aromatic diamines is different from that of normal diglycidyl ethers. For example, it may form relatively long, linear chains in the low temperature range and crosslink heavily only at higher temperatures:



As shown in the preceding section, a normal glycidyl ether begins to react in branching modes shortly after the first coupling reaction.

"Linear" Epoxy-Amine Polymers

The relative simplicity of the phenyl glycidyl ether-diethyl amine reaction suggested the possibility that linear epoxy-amine polymers could be produced from secondary diamines and diglycidyl ethers:



Such polymers would be expected to be thermoplastic, tough, and flexible. Their inclusion into standard epoxy-amine filament-winding systems should impart intrinsic toughness to these rigid, thermosetting plastics.

Experimental – Purified diglycidyl ether of bisphenol-A (equivalent weight, 173; theoretical, 170) was reacted with stoichiometric quantities of secondary diamines in which R' and R'' were both aliphatic, both aromatic, or mixed. Among the diamines were N,N'-diphenyl-p-phenylenediamine; N,N'-diphenylethylenediamine;

N,N'-diethyl-*p*-phenylenediamine; *N,N'*-dimethylhexamethylenediamine, and *N,N'*-dimethylethylenediamine. The polymers produced from amines in which *R'* or *R''* was aromatic appeared to be low-molecular-weight tars, gums, and soft plastics. One exception, *N,N'*-diphenylethylenediamine, produced a tough thermoplastic during 48 hours at 140°C. The aliphatic diamines were the most promising, particularly *N,N'*-dimethylethylenediamine.

Stoichiometric diglycidyl ether of bisphenol-A and *N,N'*-dimethylethylenediamine were blended, vacuum outgassed, and cast in open-face, steel molds for tensile specimens. The resin was allowed to solidify at room temperature. It was then cured at 150°C. The product was a hard plastic at room temperature with some thermoplastic character. It was soft at 150°C, but would not dissolve in organic solvents. Its ultimate tensile strength was 8200 psi. At 3% elongation, a slip zone, with a "necking" yield, developed in the tensile samples (Fig. 2). The elongation in the slip zone was estimated to be at least 50%. Over the 1-in. span of the extensometer, it constituted 0.8% elongation.

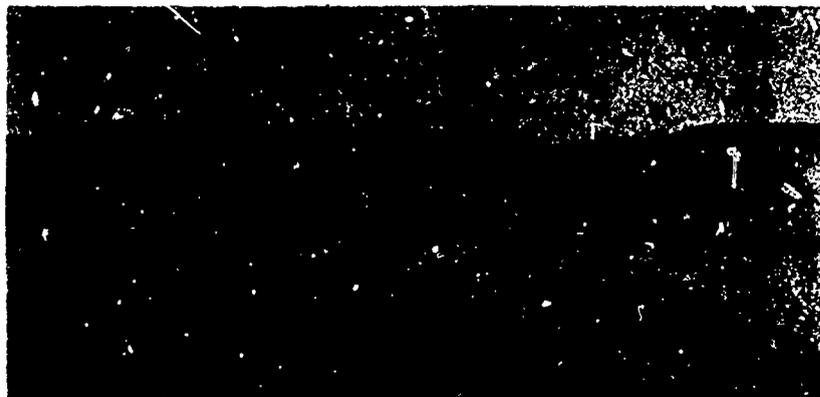


Fig. 2 - Tensile slip zone in plastic produced from *N,N'*-dimethylethylenediamine and bisphenol-A diglycidyl ether

This plastic was apparently composed of high-molecular-weight polymers with a moderate number of crosslinks between long chain segments. It could not be clearly classified as thermosetting or as thermoplastic since it displayed characteristics of both types.

Another pure, aromatic diglycidyl ether (resorcinol diglycidyl ether) produced an interesting system with *N,N'*-dimethylethylenediamine.

Experimental - A stoichiometric solution of resorcinol diglycidyl ether (equivalent weight, 114; theoretical, 111) and *N,N'*-dimethylethylenediamine was prepared at room temperature. Ten minutes after the components were blended, a sudden exothermic reaction occurred. The product was a viscous oil, which was converted into a hard rubber during 22 hr at 110°C.

Another sample of the same composition was immediately cooled, after the components were blended, and placed into a refrigerator at -10°C for 22 hr. The product was a soft solid at room temperature, which became a rigid plastic at elevated temperatures.

A third sample was poured into a heavy steel mold with a cavity 1/2-in. square in cross section and 5 in. deep. In the presence of this heat sink, the exothermic reaction was moderated. After 24 hr at room temperature, the mold was placed into an oven at 110°C until the reactions were completed. The product was a tough elastomer which has retained its flexibility during 18 months at ambient temperatures. Its glass transition temperature is between 0° and 25°C. At 30°C the material has a remarkable mechanical "memory" (Fig. 3). It may be easily deformed into a strained state from which it will gradually recover when released. If a bar of the material is given a clockwise twist of several turns, then twisted rapidly in the counterclockwise direction and released, it will relax first by turning clockwise. After a momentary rest, it will then relax slowly in the counterclockwise direction. It is soluble in hot dimethyl sulfoxide except for a small amount of netlike residue.

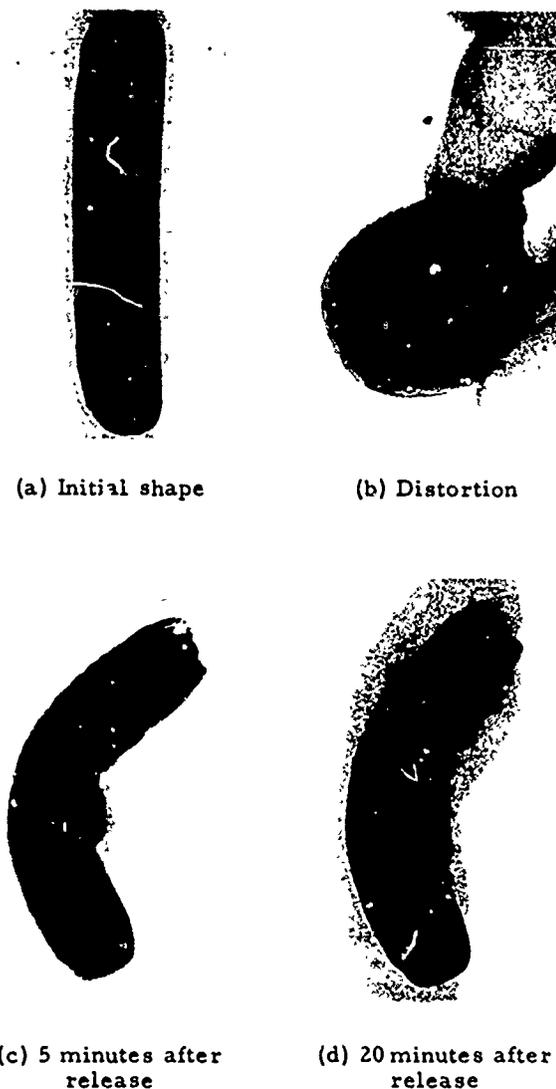


Fig. 3 - Gradual shape recovery of a distorted sample of plastic produced from N,N'-dimethylethylenediamine and resorcinol diglycidyl ether (30°C)

The production of a variety of materials from the same starting components in a fixed ratio indicates at least two reactions in the N,N'-dimethylethylenediamine-resorcinol diglycidyl ether system. A "runaway" reaction apparently produces low polymers and, possibly, small cyclic structures. A slow reaction at temperatures below ambient produces hard, insoluble plastics, which indicates crosslinking. Partial control of the reaction temperature produces tough elastomers which appear to be linear polymers within a skeletal network of crosslinked material.

Network Polymers

The molecular complexity of reacting epoxy-amine systems is profound when one of the components has a functionality of at least two and that of the other is three or greater. The classical "infinite network" problem is encountered with such systems (5). Superimposed upon the isomer problem and the competing consecutive reactions are a variety of complexities which defy detailed analysis. The same molecular circumstances which make these highly branched, crosslinked materials difficult to study also give them practical value, since they become strong, insoluble, infusible plastics.

However, there are techniques by which some degree of control can be exerted over the course of reaction. One method of controlling the reaction of multifunctional components is to include a functional group with dual reactivity. For example, a diamine curing agent with two primary amino groups may carry one that is aromatic while the other is aliphatic in its reaction behavior. Or, the epoxy molecule may be difunctional, one of the epoxy groups being a reactive glycidyl ether and the other a relatively unreactive oxirane ring. In this manner the coupling reactions can be biased in the pregel stages of polymerization at low temperatures, and the less-reactive groups can be forced to couple in the latter stages of cure at higher temperatures. Practical advantage can be gained from the use of such dual components, as shown in the following section.

HIGH-STRENGTH EPOXY-AMINE PLASTICS

There is an inverse relationship between the sizes of epoxy resin molecules and the mechanical strengths of the plastics they yield (9). The smaller molecules produce stronger plastics. As the molecular weights of diepoxides decrease, their vapor pressures increase, and the loss of materials during long cure cycles at high temperatures poses a serious problem. This difficulty can be circumvented by increasing the molecular weights, but this should be done in such a manner that the strength advantages are not lost. A preferred means of accomplishing the desired result involves the use of curing agents which will couple with epoxy in a controlled manner. A proper temperature-reaction rate relationship allows the production of a partially polymerized resin syrup with reduced epoxy monomer content. The reactions can be stopped when a suitable viscosity is reached for wet winding or preimpregnation of the reinforcement fibers. The use of such prepolymers simplifies filament-winding manufacturing processes of high-strength resins.

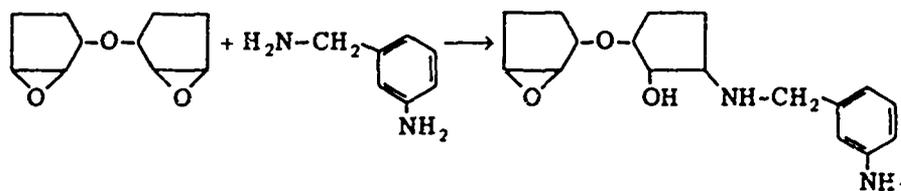
In a previous report (4) of this series, methods for the production of meta-amino-benzylamine (MABA) have been described. This curing agent is almost ideal for bodying high-strength epoxies, particularly the *trans* diepoxide of cyclopentyl ether. Because of the dual nature of MABA reaction behavior, the resin can be thickened until the average molecular weight of the syrup is appropriate, and the reactions can be stopped by cooling the syrup to practical temperatures. Thus, at 0°C a syrup of MABA and ERLA 0400* can be stored indefinitely. A freshly blended sample will remain liquid for about six weeks

*Trade designation of the Union Carbide Corp.

at room temperature. For comparison, a blend of ERLA 0400 and metaphenylenediamine will solidify in about two weeks at room temperature. At elevated temperatures the MABA-ERLA 0400 syrup can be cured to an exceedingly strong plastic with nominal losses due to volatilization of the components.

Viscosity-Volatility Relationships in MABA-ERLA 0400 Reactions

An excess of MABA above the stoichiometric quantity for ERLA 0400 is desirable for the production of a bodied syrup since the amount of epoxy monomer in the syrup should be minimized. Gas chromatographic studies of the model compounds benzylamine and aniline have shown that an aliphatic amino group reacts with ERLA 0400 more rapidly than an aromatic amino group. If MABA reacts in analogous fashion, the major component in a syrup should be formed from the benzyl amino group:



This reaction effectively suppresses the volatility of the syrup since much of the monomeric diepoxide is removed. The remaining aromatic amino group is apparently less reactive on MABA than is a corresponding group on meta-phenylenediamine. Perhaps two amino groups on the ring have an activating influence upon one another which is removed when one amino group is isolated.

Experimental — A solution of MABA in ERLA 0400 was prepared which contained 1.1 equivalents of the amine for each equivalent of epoxy. The ERLA 0400 epoxy equivalent weight was measured to be 95.6, and this value was used rather than the theoretical. The solution, total weight 129.1 g, was placed into a 150 ml beaker which was immersed in a silicone oil bath at 50°C. The reaction progressed continuously for 80 hr, during which the solution viscosity was measured periodically with a rotary viscometer and microliter samples were analyzed on a gas chromatograph. The data are shown in Fig. 4.

During the first 50 hr of reaction, the viscosity of the MABA-ERLA 0400 syrup increased only slightly, while the combined total amounts of volatile monomers decreased by more than 40%. Between 50 and 80 hr, the viscosity of the syrup increased rapidly, while the total volatile content decreased by only 10% additional. The results indicate that the first coupling products do not affect the viscosity of the solution markedly, since polymerization does not progress far. After 50 hr the polymerization of intermediates rapidly increases the solution viscosity, while remaining monomer continues to be consumed at a decreasing rate. Thus, a suppression of the total volatile content below 50% of the original amount does not appear to be practical. If the intermediate syrup is to be used for wet winding, the bodying reaction can be stopped after 55 hr at 50°C. A winding viscosity of about 5000 cps will be obtained. For the production of preimpregnated rovings, it is preferable to continue the reaction until a viscosity of about 30,000 cps is obtained. This material can be used to make resin-treated fibers that retain good tack without being too wet. The tack and flexibility of preimpregnated rovings is retained for several months during storage at -20°C.

Weight Losses Due to Volatility

Although a bodied syrup of MABA-ERLA 0400 contains about 50% unreacted monomer, the actual weight loss during cure at elevated temperatures depends upon several

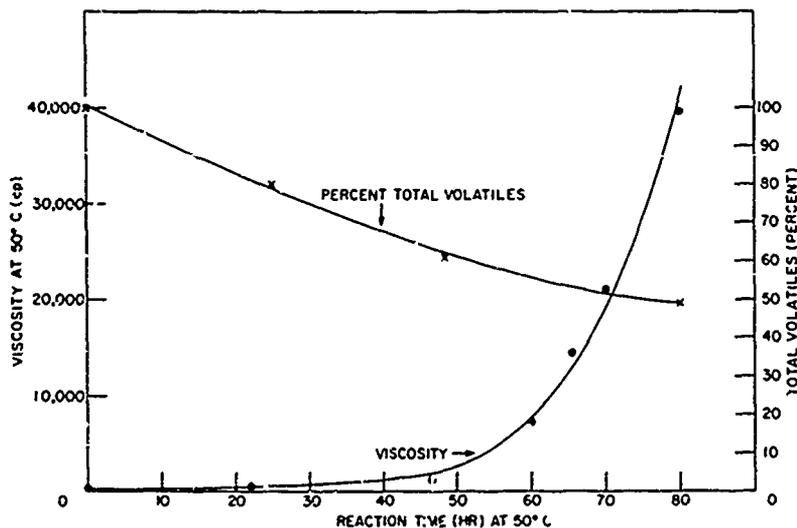


Fig. 4 - Viscosity-total volatiles relationships for MABA-ERLA 0400, 1:1 equivalents ratio, 50°C reaction temperature

variables, such as the viscosity of the syrup, the cure temperature, and, particularly, the surface-to-volume ratio of the sample. In order to obtain data concerning the maximum actual weight loss due to volatility, small samples were removed periodically during the bodying reaction, spread in a shallow container, to give a large surface-to-volume ratio, and cured at a high initial temperature.

Experimental — 1.00-g samples were removed during the course of the MABA-ERLA 0400 bodying reaction at 50°C, placed in the center of 2-in.-diameter, aluminum weighing dishes, and cured in an oven at 145°C for 2 hr. The weight loss of unbodyed samples was 11.0% (Fig. 5). Samples bodyed for 50 hr lost 5.8%, and those bodyed for the full 80 hr lost 4.9%.

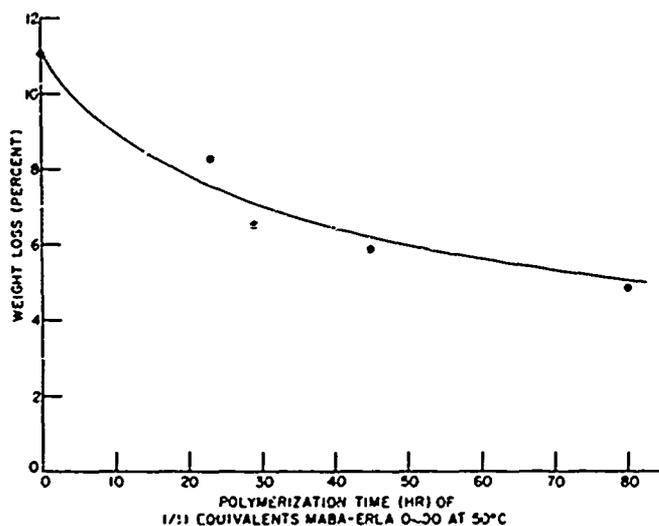


Fig. 5 - Weight loss of 1.0-g samples of MABA-ERLA 0400 during cure for 2 hr at 145°C

The practical weight loss parallels the amount of monomer retained in a bodied syrup, but most of the monomer reacts into the system before it can escape from the surface. A filament-wound article of appreciable wall thickness, such as an NOL ring, loses very little bodied resin. In order to evaluate the maximum weight loss from pre-impregnated roving, a sample of treated glass fibers was cured in a thin layer.

Experimental - A 3.891 g sample of single-end glass fiber, containing 25.5% MABA-ERLA 0400 of 37,000 cps viscosity, was loosely wound upon a glass mandrel of 1.25-in. diameter. The resin was cured at 140°C for 16 hr. The weight loss was 1.9% of the total weight of glass and resin.

Under these conditions, a large area of resin was exposed. From any actual structure, such as a cylinder with walls 1-in. thick, the loss of volatiles would be expected to be of small consequence.

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| 13 ABSTRACT The plastics formed when epoxy resins react with polyfunctional amines have extremely complex molecular structures. Except for the basic reactions of simple epoxies, little is known regarding the molecular structures of such materials. Hence, probable structures for certain molecular regions of the cured plastics must be deduced from known structures of simple analogs. In this work some relatively simple epoxy-amine systems were studied to obtain information regarding isomers, reaction sequences, and rates which are likely to prevail in complex polymerizations. The major reaction process of coreacting amines is an additive coupling. Gas chromatography and nuclear magnetic resonance were used to determine which of some possible isomers were formed in the reactions studied. Aromatic amines are not as reactive as aliphatic amines at moderate temperatures. Reaction rate and reaction temperature affect the properties of the resulting plastic. Proper conditions allow the production of a partially polymerized resin syrup of high-strength epoxies with reduced monomer content. When MABA is used as a curing agent, the reactions can be stopped when a suitable viscosity is reached for wet winding or preimpregnation of the reinforcement fibers. | | |

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