

Amine-Cured Epoxy Resins: Adhesion Loss Due to Reaction with Air

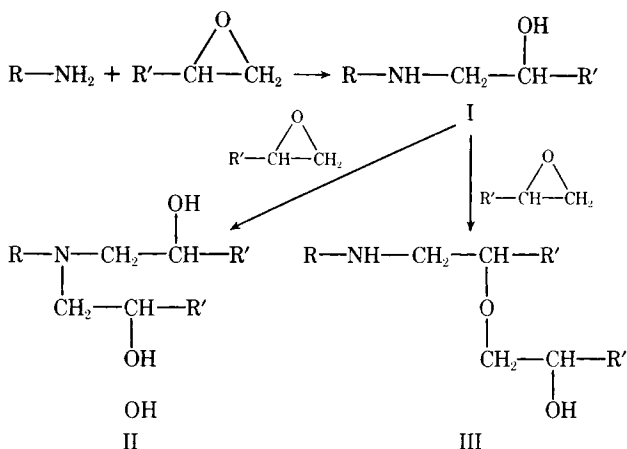
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Synopsis

The variability in adhesive bond strength and extent of cure of room-temperature, amine-cured epoxy resins has limited their applications. This paper reports the observation of microscopic crystal formation at the interface of the resin with air, resulting in a variably lower resin curing rate, extent of cure, and up to ten times lower adhesive bond strength. These crystals were identified as an amine bicarbonate salt, resulting from the reaction of the amine at the surface of the curing mixture with air. The bicarbonate formation seems to be general for the types of hardeners used in room-temperature curing. The amine-bicarbonate compound can be decomposed back to the amine by heating above 80°C. Otherwise, exposure of room-temperature systems to air before bonding is undesirable.

INTRODUCTION

A significant amount of work has been reported in the literature with regard to the amine curing of epoxy resins. Schecter, Wynstra, and Kurkijy¹ used model compounds to investigate the chemistry of the reaction of glycidyl ethers with amines. They postulated that three reactions could take place:



In their proposal,¹ the primary amine reacts with an epoxide group to yield a molecule containing a secondary amine and a hydroxyl group. This molecule

can then react with another epoxide ring to yield a tertiary amine (II) or an ether (III). They found that the amount of reaction III could hardly be distinguished from the experimental error and that the overall reaction was therefore due to the reaction of the primary and secondary amines.¹ These results are consistent with work reported by O'Neill and Cole² and Dannenberg.³

Anderson⁴ found that specific amines could induce reaction III when used in ratios significantly below stoichiometric. His work showed that when 25% of the stoichiometric amount of diethylaminopropylamine, DEAPA, was used, about 95% of the epoxide groups disappeared. A similar observation was reported by Kwei,⁵ who found that etherification played an important part in the network formation in the case of a 50% stoichiometric amount of 1,6-hexanediamine. Other research using 50% stoichiometric amount of diethylenetriamine resulted in no significant ether formation.⁶

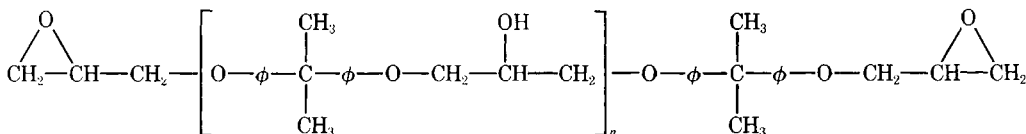
Although such side reactions of the epoxide ring have been extensively studied, very little has been reported about other reactions of the amines. In their standard procedure for the analysis of amines, Critchfield and Johnson⁷ suggested the use of a brine cooling bath; the carbon dioxide from an acetone-Dry Ice bath interfered with the analysis. Kucharsky and Safarik⁸ suggested that precautions be taken in the analysis of amines since many compounds, such as ethylenediamine, absorb carbon dioxide. This carbon dioxide is subsequently titrated as acid, causing the analytical result to be erroneous.

During the investigation in our laboratories of the room-temperature curing of the diglycidyl ether of bisphenol A (Epon 828, manufactured by Shell Chemical Co.) by diethylenetriamine (DTA), significant variations were found in the rate and extent of reaction.⁶ These variations seemed to be a function of the sample thickness, but insertion of a tiny thermistor into the reaction mixtures during cure showed a heat rise of less than 2°C, which did not account for the variability of the results. Further investigation of the surfaces of the samples under a microscope revealed small crystals, and we decided to investigate the nature and the source of the crystal formation and its effect upon the kinetics, extent of reaction, and the adhesive strength of the cured resin. We have found no reference in the literature to such crystal formation in epoxy resins.

EXPERIMENTAL

Materials

All materials in this investigation were used as obtained without further purification. The diglycidyl ether of bisphenol A, used in this study, has the following molecular structure:



where ϕ is a *para*-disubstituted benzene ring and $n \simeq 0.2$. Analysis by the modified⁹ method of Knoll et al.¹⁰ gave 5.22 meg of epoxide groups per gram resin, which result was used to calculate the quantity of amine required for a stoichiometric mixture.

Diethylenetriamine (technical grade, J. T. Baker Chemical Co.) (DTA) was chosen as the curing agent for the resin. The amine has the structure



and a molecular weight of 103. The DTA was analyzed by the method of Critchfield and Johnson⁷ and found to be 94.3% pure. The purity and an equivalence of 5 were used to calculate the weight of amine required for a given weight of resin.

Infrared Spectra Measurements

The extent of reaction was determined from the decrease in the absorbance of the 910 cm^{-1} epoxide band, employing the 1610 cm^{-1} band as an internal standard.^{11,12} Samples were postcured somewhat above the glass transition temperature, at 80°C for 48 hr, to obtain the absorbance at infinite time. Films were cast on KBr plates to allow surface exposure to air during cure and, conversely, were pressed between KBr plates¹³ to minimize air contact.

Thermogravimetric Analysis

The change in the weight of samples was monitored as a function of time with a thermogravimetric analyzer. The epoxy resin-amine mixtures and individual components were allowed to attain equilibrium in a stream of air before heating; if any weight gain was noted during the air flow period, a programmed heating cycle was started and weight change measured as a function of time and temperature.

Adhesive Strength Measurements

The adhesive strength of the Epon 828-DTA resin to aluminum (Aluminum Company of America, Grade 6061-T651) was measured by a previously reported torsional test method.^{14,15,16} A modified tubular butt assembly subjects the epoxy-aluminum bond to almost pure shear stress. The greater sensitivity of this method has been shown to allow the sampling of small populations and to show statistically significant differences.^{15,16,17} After application of the resin to the substrate, the samples were joined either immediately or after 45 min of air exposure. All bonds were allowed to harden for 15 days before bond strength measurements were made.

RESULTS AND DISCUSSION

Rate of Reaction

The fraction of epoxide groups converted versus time, given in Figure 1, shows that at the outset of the reaction the conversion of epoxide groups is rapid. As the reaction proceeds, the polymer glass transition temperature T_g rises and at some time becomes equal to or slightly above the reaction temperature. At this time, an apparent steady-state concentration of epoxide groups exists, because the reaction rate is too small to be detected in the time scale of the plot. The figure shows a definitely higher rate of conversion of epoxide groups in the case

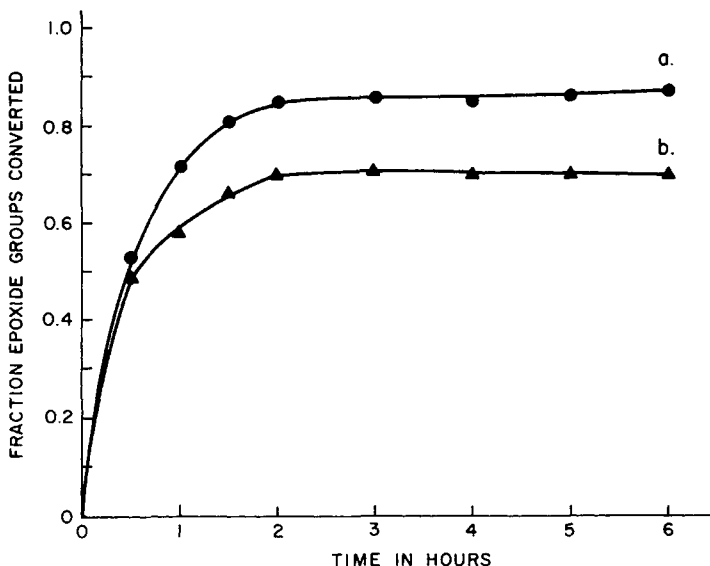


Fig. 1. Fraction epoxide groups converted vs. time for Epon 828-DTA.

● Cured between KBr plates Δ exposed to air.

of the sample which was cured between KBr plates and not exposed to air. This led us to suspect that air was being absorbed by the resin and possibly interfered in the reaction.

The gain in weight during air flow before heating in a thermogravimetric analyzer can be seen in Table I. Samples of Epon 828 and DTA were analyzed individually. The results show clearly that the weight gain of the sample was associated with the amine.

During the course of the experimental work, significant crystal formation was noticed on the mouth of the amine bottle. Some crystals from the amine bottle were removed from the glass surface and dried in air. Infrared analysis in chloroform¹⁸ of the amine crystals showed a significant carboxylate absorbance, which led us to suspect carbonate formation. A mass spectrograph of the crystals revealed significant peaks for water and carbon dioxide, which reinforced the IR results. The crystals were next analyzed qualitatively by a standard chemical reagent test procedure¹⁹ to differentiate between carbonate and bicarbonate anions, and were found to contain only the bicarbonate.

The reaction mixture shown in Figure 1, curve b, was examined under a microscope in polarized light and was found to contain an abundance of the same type of small crystals found for the amine alone. These can be seen in Figure

TABLE I
TGA Data for Amine and Epoxy Samples

Sample	Weight gain, %
Epon 828-DETA	11.8
DETA	17.0
Epon 828	0

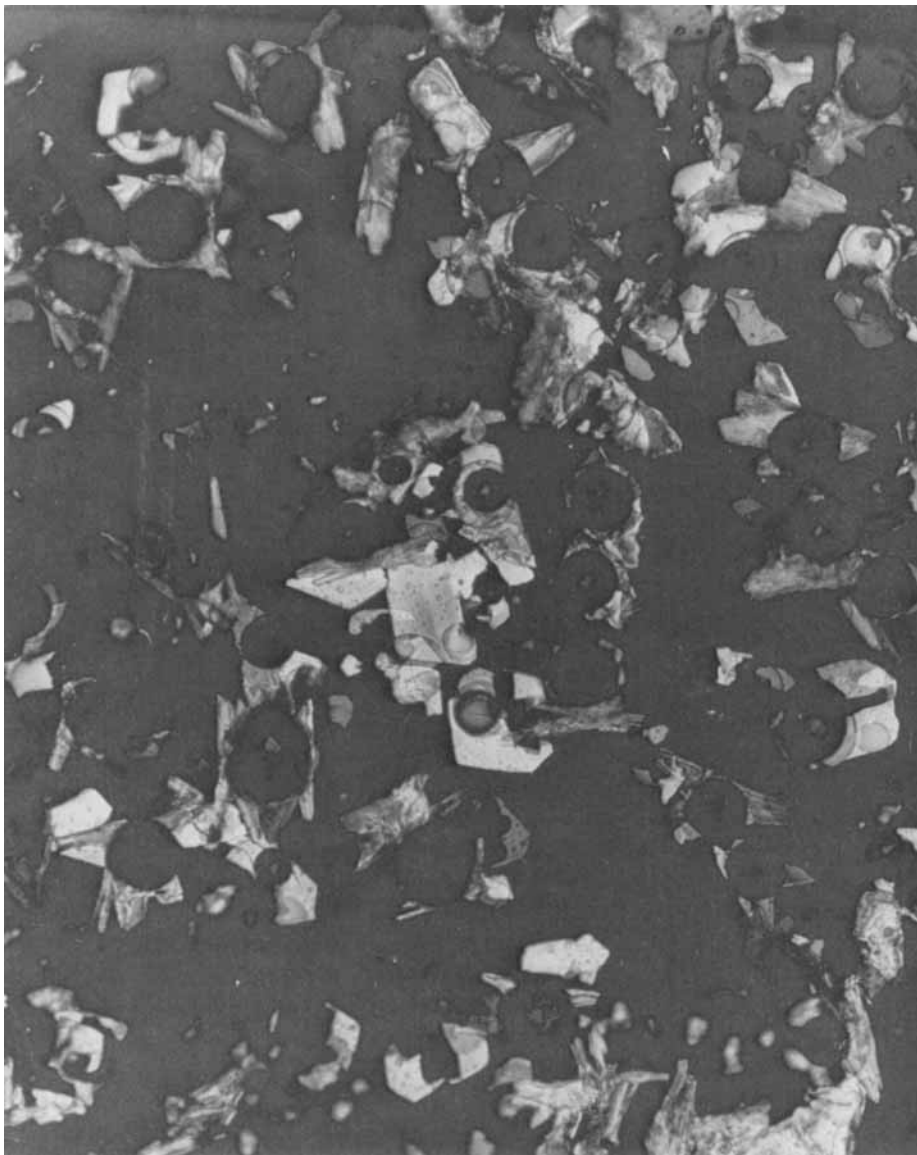
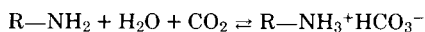


Fig. 2. Bicarbonate crystal formation observed in resin mixture (crossed polars, 100X).

2. The crystals were found to have an identical melting point²⁰ and extinctions²¹ to those taken from the amine bottle. We therefore concluded that the bicarbonate crystal formation (in the resin mixture) as well as that for the amine alone, occurs at the interface. The reaction with air can be expressed as



Since some of the amine is tied up in the bicarbonate, the reaction rate with the remainder with epoxy groups is slower, and the epoxy conversion at any time is lower. Similar reactions with air were also found with diethylaminopropylamine, triethylenetetramine, N-aminoethylpiperazine, and curing agents U

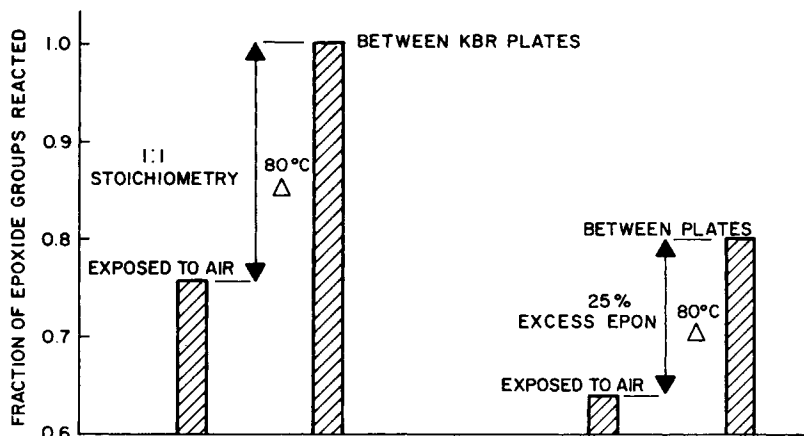


Fig. 3. Residual cure in samples due to reaction with air.

(Shell Chemical Company) and U-25 (Shell Chemical Company); U-25 is a polyamide. The phenomena, therefore, seem to be general for the types of hardeners used in room-temperature curing.

Extent of Reaction

Infrared examination of the resin reacted between KBr plates after 15 days showed total conversion of the epoxide groups, while the sample exposed to air had a fractional conversion of 0.755. These data can be seen in Figure 3. Heating the sample at a temperature of 80°C, somewhat above its T_g , for 48 hr produced total conversion of the epoxide groups. The inference is that the amine bicarbonate can be decomposed back to the amine by heating.

Another set of samples was prepared with 25% excess Epon 828. The fractional conversion of epoxide groups can be seen in Figure 3. Heating the sample exposed to air produced the theoretically expected fractional conversion of epoxide groups found in the sample cured between KBr plates. At this temperature, we concluded that the decrease in the conversion of the epoxide groups was due to the liberation of amine and not to the ether formation found by Anderson⁴ or Kwei.⁵ The residual cure in the samples exposed to air was calculated as the

TABLE II
Effect of Air Upon Epon 828—DTA Adhesive Bonding to Aluminum

Maximum shear stress, psi	
Series 1, 45-min air exposure	Series 2, minimal air exposure
153	1992
122	1587
118	1905
131	2165
Ave. 131	1912

final fractional heating minus the fractional conversion of the sample that was exposed to air only, divided by the final conversion. For 1:1 stoichiometry, 0.245 was calculated versus 0.202 for the 25% stoichiometric excess Epon 828 sample. The values show, for samples of similar thickness, that the bicarbonate formation is proportional to the amount of amine present and that the magnitude of the side reaction is quite significant; it represents 20–25% of the possible stoichiometric conversion.

Samples of Epon 828-DTA were cast as films in differing thicknesses and exposed to air. Upon completion of the reaction, they were analyzed for residual cure by differential scanning calorimetry DSC.²² The agreement between residual cure as measured by IR and that measured by DSC was quite good. In general, the residual cure found seemed to be inversely proportional to the thickness. Problems encountered in casting the films precluded evaluating the effect of thickness on a quantitative basis.

Decrease in Adhesive Bond Strength

The results of the adhesive bond strength measurements can be seen in Table II. The effect of air exposure upon the bond is a reduction in strength by more than an order of magnitude, in comparison to the strength obtained with minimal air contact. These results reinforce the microscopical observations that the side reaction occurs mostly at the surface of the resin.

The individual test results of each series were compared with each other by the Wilcoxon–Mann–Whitney test²³ at a significance of 0.057 to determine if the two series came from the same population (two-sided test) and if the two series are equal (one-sided test). In both cases, the null hypothesis was rejected; the two series are neither from the same population nor equal.

CONCLUSIONS

The variability and reduction in the rate of conversion of epoxide groups in the room-temperature curing of Epon 828 with DTA was found to be due to a side reaction of the amine, resulting in bicarbonate formation. This phenomenon appears to be reversible at higher curing temperatures, which may solve the problem in some instances. The bicarbonate formation seemed to be general for the types of hardeners used in room-temperature curing.

Since the reduction in the fractional conversion was roughly proportional to the thickness of the sample, and was as large as 0.25, the side reaction is very likely to cause problems in thin applications of the resin, particularly if mechanical or adhesive properties are important.

The crystal formation was found to occur primarily at the interface of the resin with air. The adhesive strength of the resin decreased drastically if the adhesive interface was exposed to air for a significant period of time. One concludes that when room-temperature curing systems are to be used as adhesives, the assemblies should be joined quickly to preclude air exposure and subsequent bicarbonate formation.

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