

## Imidazole Catalysis in the Curing of Epoxy Resins

ADALBERT FARKAS and PAUL F. STROHM,  
*Houdry Laboratories, Air Products and Chemicals, Inc.,  
Marcus Hook, Pennsylvania 19061*

### Synopsis

The high catalytic activity of imidazoles and particularly of 2-ethyl-4-methylimidazole (EMI) for the curing of epoxy resins and the properties of the resulting resins prompted this study concerned with the nature of the curing reaction. Epon 828 epoxy resin and the model compound phenyl glycidyl ether were used as starting materials with EMI, 2-methylimidazole, and dimethylbenzylamine as catalysts. During the curing of the resin at 50°C., the decrease in the infrared absorption of the epoxy band with time is accompanied by a decrease in the intensity of the imine band of the imidazole moiety, indicating its reaction with the epoxy group and its incorporation into the resin. The measurement of the residual epoxy content after curing for 24 hr. at 50 and 140°C. showed that the imidazoles were not more efficient in completing the epoxy reaction than dimethylbenzylamine. In the experiments with phenyl glycidyl ether the rate of reaction of the epoxy group with EMI was faster than the rate of polymerization, proving that the imidazole becomes permanently attached to the polymer chain. These results also suggest that the true catalytic species is not EMI but some addition product thereof. In comparative rate measurements the compound formed from equimolar quantities of EMI and phenyl glycidyl ether was found to be an excellent catalyst. The NMR analysis of the 1:1 and 1:2 adducts of EMI and phenyl glycidyl ether has shown that the second mole of phenyl glycidyl ether reacts with the ring nitrogen in the 3 position and not with the hydroxyl group of the mono adduct. By forming the bis adduct in this way the imidazole molecule acts as a crosslinking agent and at the same time introduces an alkoxide ion which can initiate further polymerization. It is very likely that this crosslinking is the process that leads to the superior physical and chemical properties (high heat deflection temperature, resistance to chemicals and oxidation) of the resins prepared with imidazoles as catalysts.

### INTRODUCTION

Certain imidazoles have proved to be good curing agents for epoxy resins. Among these 2-ethyl-4(5)-methylimidazole (EMI) is particularly effective and imparts to the resulting resins excellent physical properties, such as resistance to chemicals and oxidation, high heat-distortion temperature, and superior electrical characteristics.<sup>1</sup>

These favorable results were thought to depend somehow on the presence of an active hydrogen in the imidazole molecule, which could react with an epoxy group and thereby become incorporated into the resin.

It was our objective to ascertain the nature of the reactions that cause the curing of epoxy resins in the presence of imidazoles. We sought to

accomplish this objective by comparing the rates of the catalyzed polymerization of an epoxy resin and of phenyl glycidyl ether in the presence of imidazoles and other amine catalysts and by searching for reactions that would indicate the incorporation of the imidazole catalyst into the polymer.

## EXPERIMENTAL

### Materials

Epon 828 of Shell Chemical Company was used as an example of a commercial resin. The phenyl glycidyl ether and dimethylbenzylamine were obtained from Distillation Industries. The 2-ethyl-4(5)-methylimidazole and 2-methylimidazole were products of the Houdry Process & Chemical Co.

### Procedures

**Polymerization of Epon 828.** The rate of polymerization was followed by measuring the decrease in the infrared absorption due to the epoxy group at  $920\text{ cm.}^{-1}$  according to the procedure described by Dannenberg and Harp,<sup>2</sup> Lee,<sup>3</sup> and Lee and Breland.<sup>4</sup>

The curing agents were used at a concentration of 0.47 moles per 1,000 g. of resin. Samples of this mixture were prepared as films 0.025 mm. thick between rock salt plates. The initial curing step was carried out by placing the salt cell containing the resin and catalyst in an oven controlled at  $50^{\circ}\text{C}$ . The cell was removed periodically from the oven and the infrared spectrum scanned. The epoxy concentration at each time interval was determined from the absorbance of  $920\text{ cm.}^{-1}$  with the use of a calibration chart of absorbance versus epoxy concentration of solutions of Epon 828 in benzene.

After 24 hr. at  $50^{\circ}\text{C}$ . the temperature was increased to  $140^{\circ}\text{C}$ ., and the resin was post-cured for 24 hr., during which period the infrared spectrum was again scanned at various time intervals.

The initial epoxy concentration of the resin mix was also determined by chemical analysis according to ASTM Method D-1652-597.

In addition to the  $920\text{ cm.}^{-1}$  region the  $3430\text{ cm.}^{-1}$  region was scanned for each sample, in order to determine the concentration of the free  $\text{>NH}$  groups.

**Polymerization of Phenyl Glycidyl Ether.** Samples of a mixture of 0.01 mole of phenyl glycidyl ether and 0.0008 mole of EMI or of the curing agents were placed in a bath held at  $50^{\circ}\text{C}$ . At various time intervals a sample was removed and diluted to  $100\text{ cm.}^3$  with benzene in a volumetric flask. The infrared spectrum of this solution was then scanned with pure benzene as reference. The concentration of phenyl glycidyl ether was determined by measuring the intensity of the epoxy band at  $920\text{ cm.}^{-1}$ .

For each of the samples from EMI runs the intensity of the band at  $3430\text{ cm.}^{-1}$  was also measured, to follow the reaction with the  $\text{>NH}$  hydrogen.

**Reaction of 2-Ethyl-4(5)-methylimidazole with Phenyl Glycidyl Ether.**

The 1:1 adduct, a mixture of 2-ethyl-3-( $\beta$ -hydroxy- $\gamma$ -phenoxypropyl)-4- and 5-methylimidazoles, was prepared by reacting 22 g. (0.2 mole) of 2-ethyl-4(5)-methylimidazole dissolved in benzene with 30 g. of phenyl glycidyl ether (0.2 mole) for 3 hr., removing the benzene by distillation and then drying the residue in a vacuum oven at  $40^\circ\text{C.}$  for 24 hr. The infrared spectrum of this viscous material had a hydroxyl band at  $3600\text{ cm.}^{-1}$  and no epoxy absorption at  $920\text{ cm.}^{-1}$ . The NMR spectrum showed the presence of two isomers.

The procedure used for the synthesis of the 1:2 adduct was essentially the same as that used in the procedure described above, except that 0.4 mole (60 g.) of phenyl glycidyl ether was added to 0.2 mole of EMI. The product that remained after the removal of the benzene was a dark viscous liquid. Its NMR spectrum showed only one imidazole proton peak at 6.60 ppm, indicating that the second molecule of phenyl glycidyl ether added on to the second nitrogen and not to the hydroxyl group.

**NMR Spectra.** The NMR spectra were determined in  $\text{CDCl}_3$  on a Varian A60A spectrometer. The NMR resonances are reported in parts per million with tetramethylsilane as reference.

## RESULTS AND DISCUSSION

### Polymerization of Epon 828

The rate of polymerization of Epon 828 was measured in the presence of 2-ethyl-4(5)-methylimidazole, 2-methylimidazole, and dimethylbenzylamine. The epoxy concentrations in the sample films, as determined from the absorption at  $920\text{ cm.}^{-1}$ , are shown in Table I as a function of the curing time at  $50^\circ\text{C.}$ , together with the final epoxy concentrations reached after a post-cure period of an additional 24 hr. at  $140^\circ\text{C.}$

It will be noted that among the catalysts tested EMI was the slowest and dimethylbenzylamine the fastest.

The epoxy concentrations reached after 24 hr. at  $50^\circ\text{C.}$  and after 24 hr. at  $140^\circ\text{C.}$  were almost identical for all three curing agents except the value for 2-methylimidazole at 24 hr. and  $50^\circ\text{C.}$  On the basis of these results it appears very unlikely that the superior physical properties observed in epoxy resins prepared with imidazole curing agents are a consequence of faster or more complete polymerization.

On the adding of EMI to Epon 828 a new band appears to  $3330\text{ cm.}^{-1}$ , which is displaced to  $3450\text{ cm.}^{-1}$  on dilution with benzene. Since the same band also occurs in solutions of EMI alone, but not in Epon 828, we assign these bands to the  $\text{>NH}$  group in EMI. This conclusion is con-

TABLE I  
Curing of Epon 828 Films in the Presence of 2-Ethyl-4(5)-methylimidazole (EMI), 2-Methylimidazole (2-MI), and Dimethylbenzylamine (DMBA)

Time, hr.	Curing temp., °C.	Epoxy content, mole/l.		
		EMI	2-MI	DMBA
0	50	5.36 <sup>a</sup>	5.38 <sup>a</sup>	5.56 <sup>a</sup>
1.00			4.82	
1.25		4.50		
1.75				3.66
2.00			4.57	
2.25		4.12		
2.75		4.07		2.76
3.25			3.44	
3.75				2.07
24.0		1.68	2.06	1.53
24.0	140	0.42	0.54	0.37

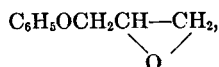
<sup>a</sup> Obtained by chemical analysis.

firmed by the presence of these bands in solutions of EMI, or of 2-methylimidazole, in phenyl glycidyl ether and its absence in benzene solutions of 1-hydroxyethyl- or of 1-(2'-hydroxy-3'-phenoxypropyl)-2-ethyl-4-methylimidazole.

We have found that the 3430 cm.<sup>-1</sup> band diminishes in intensity during the initial curing stage at 50°C., showing that EMI reacts with the epoxy group of the resin. After 2.5 hr. at 50°C. the band disappears almost completely, and there is only a slight shoulder on the adjacent CH<sub>2</sub> band at 3000 cm.<sup>-1</sup>.

### Polymerization of Phenyl Glycidyl Ether

Phenyl glycidyl ether,



was selected as a model compound for this part of the study, in order to avoid the complication caused by the reaction of hydroxyl groups and of two epoxy functions present in each molecule of such epoxy resin ingredients as Epon 828.

The polymerization of this compound in the presence of EMI was studied at 50°C. by using the infrared technique for measuring the intensity of the epoxy band at 920 cm.<sup>-1</sup>.

As shown by the data of Table II, the initial rate of reaction is 0.0003–0.0004 mole/hr. A slower rate was found for dimethylbenzylamine.

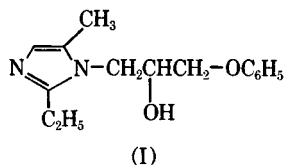
Again, we observed the appearance of the >NH band of EMI at 3430 cm.<sup>-1</sup> in the initial reaction mixture and its gradual disappearance during the curing. After approximately 4 hr. at 50°C. all of the EMI (0.0008*M*) had reacted. Since this conversion is approximately equivalent to the

TABLE II

Polymerization of 0.01M Phenyl Glycidyl Ether (PGE) in the Presence of 0.0008M 2-Ethyl-4(5)-methylimidazole (EMI) and of 0.0008M Dimethylbenzylamine (DMBA) at 50°C.

Time, hr.	Residual PGE, moles	
	EMI	DMBA
0	0.0095	0.0098
0.75	0.0092	
1.50		0.0102
2.25	0.0087	
3.0		0.0096
4.5	0.0082	
5.0		0.0087
24	0.0018	

amount of glycidyl ether consumed (0.0013M) during the period, it appears that the first step in the polymerization of the epoxy ether is its reaction with the NH group of the imidazole molecule. Consequently, we have to conclude that in the later stages of the polymerization the true catalyst is not the unsubstituted imidazole molecule but the product of its addition with phenyl glycidyl ether, such as (I).



To check this conclusion, the 1:1 adduct of EMI and phenyl glycidyl ether was prepared and evaluated as a curing agent. As shown by the data in Table III, this adduct was indeed an excellent curing agent for the

TABLE III

Polymerization of 0.01M Phenyl Glycidyl Ether (PGE) in the Presence of 0.0008M of the 1:1 Adduct of PGE and 2-Ethyl-4(5)-methylimidazole at 50°C.

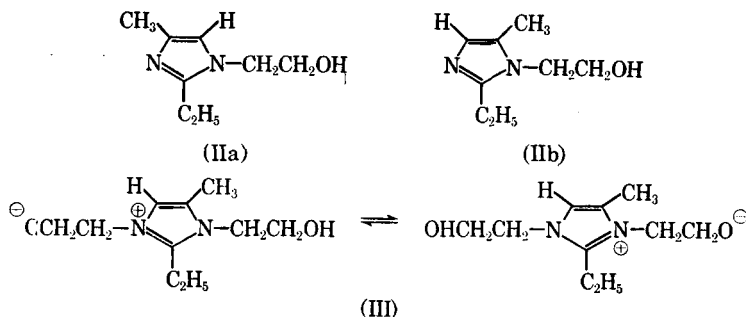
Time, hr.	Residual PGE, moles
0	0.0090
2	0.0084
4	0.0067
6	0.0033

polymerization of the glycidyl ether.

#### Reaction of 2-Ethyl-4(5)-methylimidazole with Phenyl Glycidyl Ether

In a previous study in our laboratories<sup>5</sup> the nature of the products formed in the reaction of 1 mole of EMI with 1 and 2 moles of ethylene oxide was examined by NMR spectroscopy. It was found that, while

the first mole of ethylene oxide reacted, as expected, to yield two isomeric 1-hydroxyethyl derivatives, (IIa) and (IIb) as evidenced by two different imidazole protons in the NMR spectrum of the reaction product, the second mole of ethylene oxide did not add to the OH group but rather



added to the ring nitrogen to form the equilibrium mixture (III), in which the —OH proton is undergoing rapid exchange.

We have prepared the corresponding reaction products of EMI with phenyl glycidyl ether and examined them by using the same NMR technique.

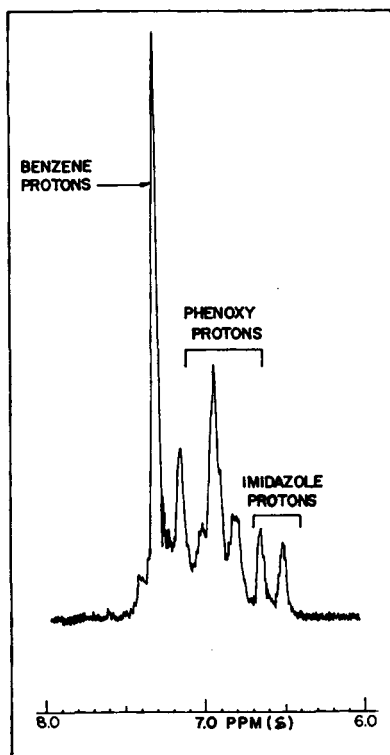


Fig. 1. NMR spectrum of 1-( $\beta$ -hydroxy- $\gamma$ -phenoxypropyl)-2-ethyl-4(5)-methylimidazole showing ring protons.

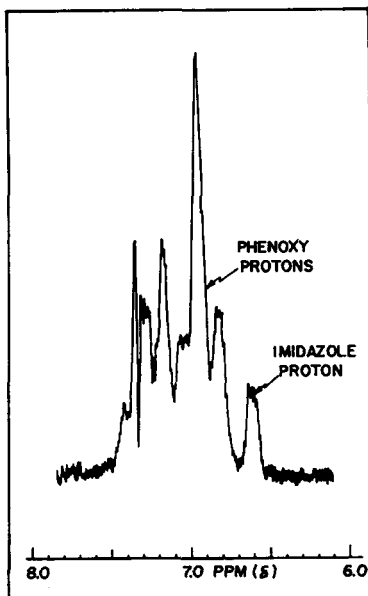
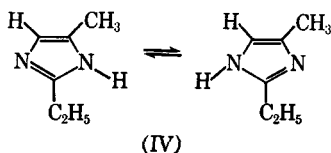
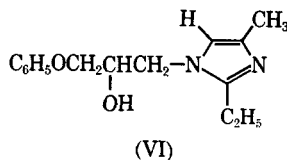
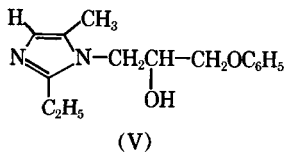


Fig. 2. NMR spectrum of the adduct formed from 2 moles of phenyl glycidyl ether and 1 mole of 2-ethyl-4(5)-methylimidazole, showing ring proton region.

The NMR spectrum of EMI shows the ring proton chemical shift at 6.65 ppm in deuterated chloroform. This signal appears as a singlet because of the rapid exchange experienced by the amine hydrogen.



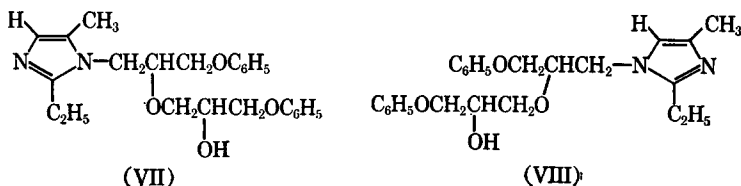
In the NMR spectrum of the reaction product of 1 mole of EMI with 1 mole of phenyl glycidyl ether the ring hydrogen chemical shift appears as two peaks, one at 6.50 ppm and the other at 6.66 ppm (see Fig. 1). The complex pattern from 6.7 to 7.5 ppm results from the phenyl group and the presence of residual benzene, used as the solvent. Two imidazole ring protons are observed, because two distinct N-substituted derivatives, (V) and (VI), are formed from (IV).



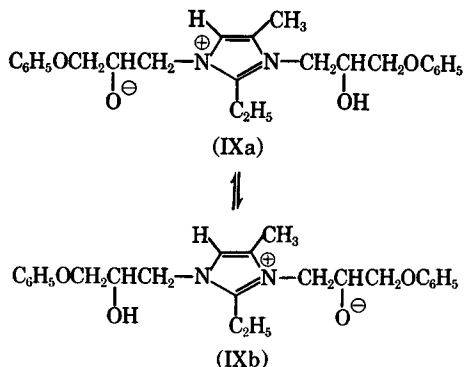
When the isomeric mixture of (V) and (VI) reacts with an equimolar quantity of phenyl glycidyl ether, a product is formed, the NMR spectrum

of which shows a broad singlet at 6.61 ppm for the imidazole proton (see Fig. 2).

If the second mole of the phenyl glycidyl ether had reacted with the hydroxyl groups of (V) and (VI), two isomers, (VII) and (VIII), would have formed, and two ring proton peaks would have been observed in the NMR spectrum.

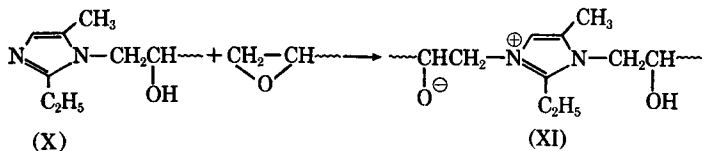


Accordingly, one must conclude that the second molecule of phenyl glycidyl ether is attached by the nitrogen in the 3 position, giving rise to the products (IXa) and (IXb).



One would expect a rapid proton exchange between (IXa) and (IXb), which would lead to an NMR spectrum of the mixture showing just one resonance for the imidazole ring proton.

It is very probable that EMI reacts with epoxy groups during the curing reaction in a similar manner and that the mono adduct (X) formed in the initial reaction subsequently reacts with another epoxy group, giving (XI).



The alkoxide ion in (XI) is an effective catalytic center, which can attack another epoxy group and thus can continue the polymerization reaction, the alkoxide ion remaining in the neighborhood of the positive nitrogen by bending of the polymer chains.



By this reaction sequence EMI becomes part of the polymer, maintains its catalytic activity, and can cause extensive chain branching and thus lead to highly crosslinked resins of superior physical properties and resistance to chemicals.

We take much pleasure in acknowledging our indebtedness to G. A. Mills for his interest in this study and to Leon Mandell for his helpful discussions.

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### Résumé

L'activité catalytique élevée des imidazoles, et en particulier du 2-éthyl-4-méthylimidazole (EMI), pour le traitement des résines époxy et les propriétés des résines résultantes a hâté la présente étude concernant la nature de la réaction de post-traitement. La résine époxy Epon 828 et le composé modèle, l'éther phénylglycidyle ont été utilisés comme matériaux de départ avec l'EMI, le 2-méthylimidazole et la diméthylbenzylamine comme catalyseurs. Au cours du traitement de la résine à 50°C, la diminution de l'absorption infrarouge de la bande époxy avec le temps s'accompagne d'une diminution de l'intensité de la bande imine de la partie imidazolique, ce qui indique une réaction de celle-ci avec le groupe époxy et son incorporation dans la résine. La mesure de la teneur en résine époxy résiduelle après traitement de 24 heures à 50°C et à 140°C, montrait que les imidazoles n'étaient pas plus efficaces pour compléter la réaction époxy que la diméthylbenzylamine. Dans les expériences avec l'éther phénylglycidyle la vitesse de réaction du groupe époxy avec l'EMI était plus rapide que les vitesses de polymérisation ce qui prouve que l'imidazole est attaché de façon définitive à la chaîne polymérique. Ces résultats suggèrent également que l'espèce catalytique vraie n'est pas l'EMI mais certains produits d'addition de celui-ci. Lors de mesures de vitesse comparatives, le composé résultant de quantités équimoléculaires de l'EMI et d'éther phénylglycidyle a été trouvé être un catalyseur excellent. L'analyse NMR du produit 1:1 et 1:2 de EMI avec l'éther phénylglycidyle montrait que la seconde molécule d'éther phénylglycidyle réagit avec l'azote cyclique en position 3 et non pas avec le groupe hydroxylé du produit de monoaddition. En formant un produit d'addition double, de cette façon, la molécule imidazolique réagit comme un agent pontant et simultanément introduit un anion alcoxyde qui peut initié la polymérisation ultérieure. Il est très probable que ce pontage est le processus qui conduit à des propriétés physiques et chimiques supérieures (température de déflexion à chaleur élevée, résistance aux agents chimiques et à l'oxydation) des résines préparées avec des imidazoles comme catalyseurs.

### Zusammenfassung

Die grosse katalytische Aktivität von Imidazolen, und besonders von 2-Äthyl-4-methylimidazol (EMI), in bezug auf die Härtung von Epoxyharzen und die Eigenschaften der entstandenen Harze waren der Anlass zu dieser Untersuchung über das Wesen der Härtungsreaktion. Das Epoxyharz Epon-828 und die Modellverbindung Phenylglycidyläther wurden als Ausgangsmaterialien mit EMI, 2-Methylimidazol und Dimethylbenzylamin als Katalysatoren verwendet. Die während der Härtung des Harzes bei

50°C mit der Zeit abnehmende Infrarotabsorption der Epoxybande wird von einer Intensitätsabnahme der Iminobande der Imidazol-Einheit begleitet, wodurch dessen Reaktion mit der Epoxy-Gruppe und dessen Einbau in das Harz angezeigt wird. Die Messung des restlichen Epoxy-Gehalts nach 24-stündiger Härtung bei 50° und bei 140°C zeigte, dass sich die Imidazole wirksamer als Dimethylbenzylamin hinsichtlich der Vollständigkeit der Epoxy-Reaktion zeigten. In den Versuchen mit Phenylglycidyläther war die Reaktionsgeschwindigkeit der Epoxy-Gruppe mit EMI grösser als die Polymerisationsgeschwindigkeit, wodurch bewiesen wird, dass das Imidazol mit der Polymerkette eine dauernde Bindung eingeht. Diese Ergebnisse deuten auch darauf hin, dass die wahre katalytische Spezies nicht EMI, sondern irgendein Additionsprodukt desselben ist. Bei vergleichenden Geschwindigkeitsmessungen stellte sich heraus, dass die Verbindung aus äquimolaren Mengen EMI und Phenylglycidyläther ein ausgezeichnete Katalysator ist. Die NMR-Analyse der 1:1 und 1:2 Addukte von EMI und Phenylglycidyläther zeigte, dass das zweite Mol Phenylglycidyläther mit dem Ringstickstoff in 3-Stellung und nicht mit der Hydroxylgruppe des Monoaddukts reagiert. Dadurch, dass das Imidazol-Molekül auf diese Weise das bis-Addukt bildet, verhält es sich wie ein Vernetzer und führt gleichzeitig ein Alkoxyd-Ion ein, das weitere Polymerisation starten kann. Es ist sehr wahrscheinlich, dass diese Vernetzung derjenige Vorgang ist, der zu den günstigen physikalischen und chemischen Eigenschaften (grosse Hitzebeständigkeit, Resistenz gegenüber Chemikalien und Oxydation) des mit Imidazol-Katalysatoren hergestellten Harzes führt.

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