

## A Comparison of Some Imidazole Catalysts as Epoxy Curing Agents

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### Synopsis

Some physical properties of epoxy resins cured with 2-substituted imidazoles, e.g., 2-ethyl-4-methylimidazole (EMI-24), and 1-substituted imidazoles, e.g., 1-methylimidazole (MI-1), were studied in order to determine the effect of additional crosslinking that has been proposed to occur with EMI-24. While these catalysts were found to yield identical physical properties in that system, they were found to behave differently when the epoxy resin was flexibilized with a polysulfide rubber. Evidence from infrared (IR) and nuclear magnetic resonance (NMR) spectra proved that imidazoles unsubstituted in the 2-position were being deactivated through their conversion to a dihydroimidazole compound in a proportion related to the amount of polysulfide rubber present. Hence, only imidazoles substituted in the 2-position will cure epoxy-polysulfide rubber systems.

### INTRODUCTION

2-Ethyl-4-methylimidazole (EMI-24) has been reported<sup>1</sup> to be an excellent catalytic curing agent for epoxy resins. The resulting product shows excellent physical properties, e.g., high heat-distortion temperature, high bond strength, and good chemical resistance.

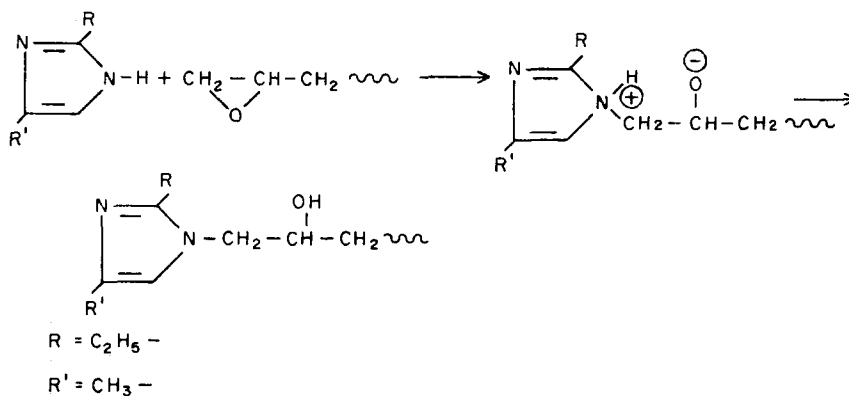
It also has been reported<sup>1</sup> that the mechanism of curing a polyepoxide with EMI-24 involves a two-step process (Fig. 1). Initially the nitrogen with the hydrogen substituent attacks and opens an epoxide ring much as does a normal aliphatic amine curing agent. In the second step, the tertiary-type ring nitrogen attacks and opens an epoxide ring to give an ionic intermediate; the positive charge on the intermediate is stabilized through resonance and the alkoxide ion is the active site for further polymerization.

Since the true catalytic site for polymerization is the latter imine-type ring nitrogen, it was felt that the minimal crosslinking resulting from the initial step involving the active hydrogen of the EMI-24 would not appreciably enhance the physical properties of the polymer. Therefore, the initial goal of the work reported herein was to establish the significance of the initial-step crosslinking by comparing some physical properties of epoxies cured with EMI-24 and with 1-methylimidazole (MI-1) since, in the latter system, the initial step cannot occur.

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During this investigation a system involving a polysulfide rubber flexibilizer was tested. It was observed that EMI-24 behaved as expected in this system while MI-1 was completely ineffective as a catalyst. A con-

STEP A:



STEP B:

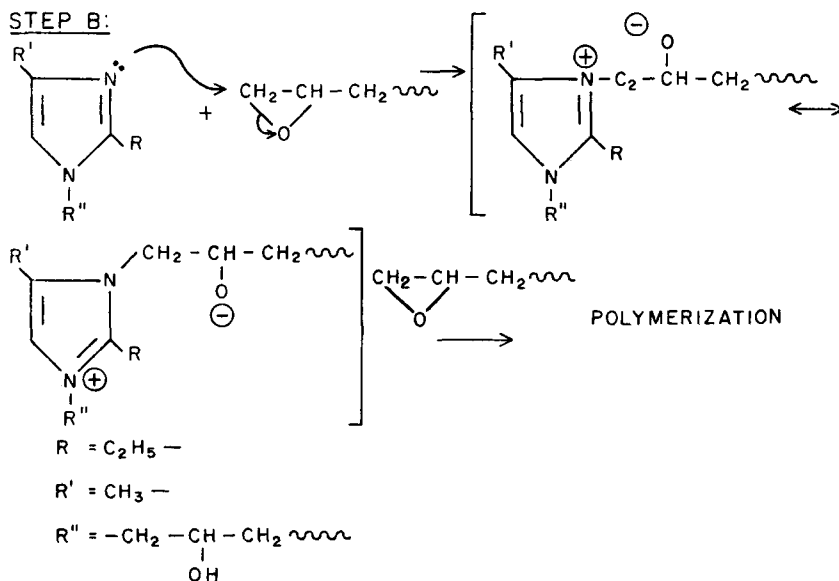


Fig. 1. Mechanism for the polymerization of a polyepoxide with 2-ethyl-4-methylimidazole.<sup>1</sup>

centration study using infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) was undertaken in order to determine the reason for the differences in behavior of EMI-24 and MI-1.

## EXPERIMENTAL

### Materials

The polyepoxide used in this investigation (Epon 828), the 2-ethyl-4-methylimidazole (EMI-24 or curing agent M), phenyl glycidyl ether, and isopropyl glycidyl ether were obtained from Shell Chemical Co. 1-Methylimidazole (MI-1), 2-methylimidazole (MI-2), and 1,2-dimethylimidazole (DMI-12) were obtained from Badische Anilin & Soda-Fabrik, while the 1-benzyl-2-methylimidazole (BMI-12) was a product of Toho-Rayon Co. of Japan. Imidazole was obtained from Eastman Organic Chemicals. Polysulfide rubber (PSR), LP-3, was a product of the Thiokol Chemical Corp. The materials were used as received.

### Procedures

**Physical Measurements.** IR spectra were obtained on a Beckman IR-5 spectrometer. The course of the reactions was followed by placing the reactants between sodium chloride crystals and scanning their spectra at various points in the cure cycle. Except for the special case outlined below, no effort was made to distill the reaction products.

Standard characteristic regions of interest are: 3400–3500  $\text{cm}^{-1}$  ( $-\text{OH}$  and  $-\text{NH}$ ), 2500  $\text{cm}^{-1}$  ( $-\text{SH}$ ), 1650–1700  $\text{cm}^{-1}$  (see discussion section), and 920  $\text{cm}^{-1}$  (oxirane group).

NMR spectra were obtained on a Varian A-60 spectrometer with carbon tetrachloride as a solvent and tetramethylsilane as a reference.

Heat deflection temperatures and bond strengths were obtained according to ASTM D-648-56 and D-2095, respectively.

**Preparation of the Adduct of Phenyl Glycidyl Ether and 1-Methylimidazole.** A solution of 16.0 g (0.2 mole) of 1-methylimidazole and 30.0 g (0.2 mole) of phenyl glycidyl ether in 200 ml of benzene was heated to reflux for 6 hr. The solvent was distilled under reduced pressure and the dark-brown liquid residue heated to 100°C for 2 hr. IR spectra of the product showed no unreacted epoxide.

**Reaction of Isopropyl Glycidyl Ether, 1-Methylimidazole, and Polysulfide Rubber.** A mixture containing 25 g of isopropyl glycidyl ether, 5 g of polysulfide rubber, and 2 g of 1-methylimidazole was allowed to stand at room temperature for two days. The mixture was then heated at 100°C for 4 hr. An epoxy absorption was still present in the IR at 920  $\text{cm}^{-1}$ . Distillation of the reaction mixture yielded 8.0 g of isopropyl glycidyl ether, bp 30°C (2 mm); 0.3 g of an unresolved mixture bp 70°–73°C, (0.2 mm), and 4.7 g of a clear pale-yellow liquid, bp 130–145°C (0.2 mm). No further distillate could be obtained from the residue. The IR spectrum of the highest boiling fraction showed a strong peak at 3450  $\text{cm}^{-1}$  ( $-\text{OH}$ ) and 1665  $\text{cm}^{-1}$  (olefinic).

## RESULTS AND DISCUSSION

The initial studies comparing EMI-24 and MI-1 indicated that they yielded polymers with essentially identical properties (Table I). In comparing the values it should be kept in mind that, due to molecular weight differences, the reactivity of 4 g of EMI-24  $\cong$  to that of 3.0 g of MI-1.

TABLE I  
Comparison of Physical Properties of Epoxy Resins Cured with 2-Ethyl-4-Methylimidazole and 1-Methylimidazole

Curing agent	Bond strength, <sup>a</sup> psi	Heat deflection temperature, <sup>b</sup> °C	Thermal gravimetric analysis 50% wt loss, °C
2-Ethyl-4-methylimidazole			
4 phr	4640	82	450
1-Methylimidazole			
2 phr	4530	79	460
4 phr	4235	87	445

<sup>a</sup> Cured 4 hr at 65°C.

<sup>b</sup> Gelled at room temperature plus 4 hr at 65°C.

In preparing the samples for heat deflection temperature tests, the normal procedure was to allow the resin to gel at room temperature before initiating cure at elevated temperature. This was necessitated by the extent of exothermic reaction that occurs when 30–40 g of the epoxy-imidazole mix is heated to 65°–70°C.

Thermal gravimetric analysis of epoxies cured with EMI-24 and MI-1 gave essentially identical values except for the temperature at which initial weight loss occurred. Resin samples cured with MI-1 lost about 1% of their weight at about 280°C and then lost no more weight until they reached 310°C, whereas resin samples cured with EMI-24 did not lose weight until they reached 310°C. Since the former loss was rapid, and the weight then remained constant up to  $\cong$ 310°C, this loss was attributed to volatile material on the surface of the sample.

### Reaction Between Epoxy Resin, Polysulfide Rubber, and Imidazoles

Up to this point, it appeared that the two imidazole compounds were similar in their ability to cure epoxy resins. However, when they were used to catalyze the polymerization of an epoxy-PSR mix, MI-1 was found to be ineffective as a curing agent. Investigating further, a series of imidazole compounds was mixed with a 70:30 epoxy-PSR mix and heat cured. While EMI-24, DMI-12, MI-2, and BMI-12 were found to be excellent catalysts, imidazole and MI-1 failed to impart a satisfactory cure to the system. The only apparent difference between the two groups of

imidazoles was that the effective ones were substituted in the 2-position of the ring.

In an attempt to establish the difference in results, two imidazoles, one effective and one ineffective, were chosen for more detailed study. In order to prevent step 1 of the mechanism outlined in Figure 1 from occurring, and also for the sake of simplicity, MI-1 and DMI-12 were the catalysts chosen for study. The progress of the reaction was followed by observing the IR spectra.

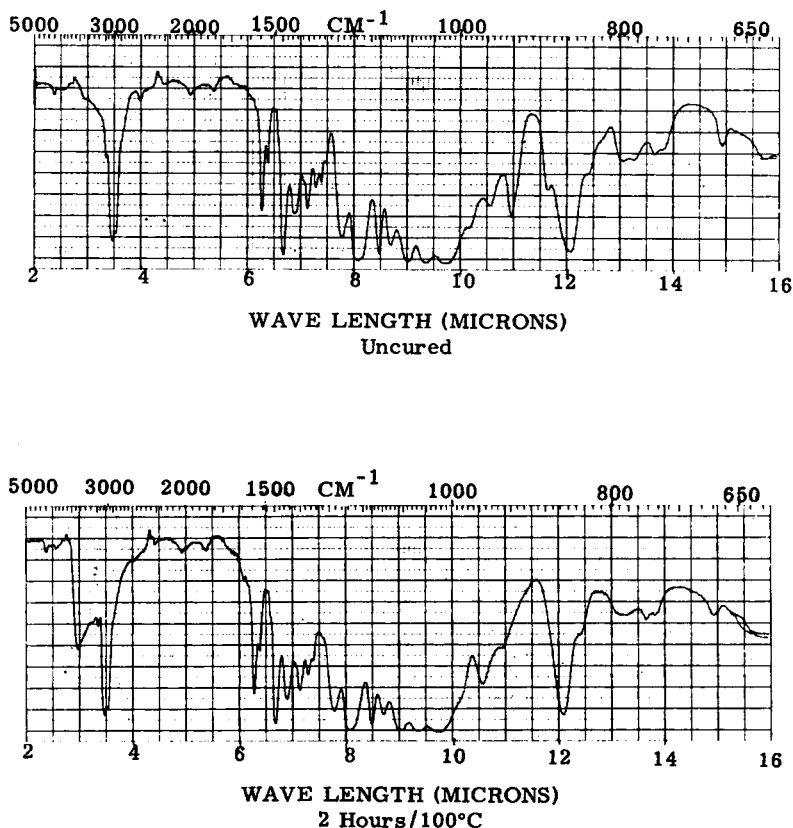


Fig. 2. IR spectra of an epoxy resin, polysulfide rubber, and 1,2-dimethylimidazole mixture before and after curing.

In following the cure of an epoxy-PSR mixture with DMI-12, the expected changes in its IR spectra were observed (Fig. 2). The loss of the mercaptan absorption ( $2525\text{ cm}^{-1}$ ) and of the epoxy absorption ( $3550\text{ cm}^{-1}$ ), along with the formation of an hydroxyl absorption ( $3550\text{ cm}^{-1}$ ), were easily detected.

The IR spectra of an epoxy-PSR mixture heated in the presence of MI-1 also showed the loss of the mercaptan and epoxy absorptions and the formation of an hydroxy absorption (Fig. 3). However, a new strong absorption was observed at  $1665\text{ cm}^{-1}$ . The absorption at  $1665\text{ cm}^{-1}$  also appeared when imidazole was substituted for MI-1.

It was determined by IR analysis that heating any two of the three compounds together did not result in the formation of a peak at  $1665\text{ cm}^{-1}$ . Also it was observed that PSR and the imidazoles do not undergo any reaction and that an epoxy-PSR mix would react only slowly at elevated temperatures.

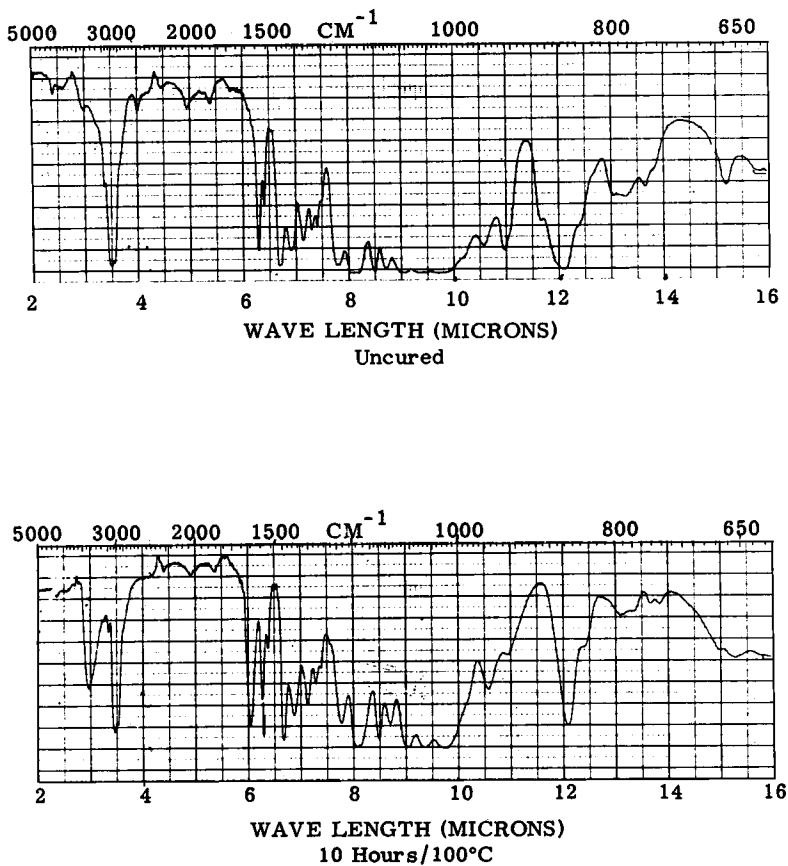


Fig. 3. IR spectra of an epoxy resin, polysulfide rubber, and 1-methylimidazole mixture before and after curing.

A series of studies in which the ratios of epoxy, PSR, and MI-1 were varied was performed. IR spectra showed a peak at  $1665\text{ cm}^{-1}$ , even when small amounts of PSR or MI-1 catalyst were used. On the other hand, if an excess of PSR over epoxy resin was employed (based on molec-

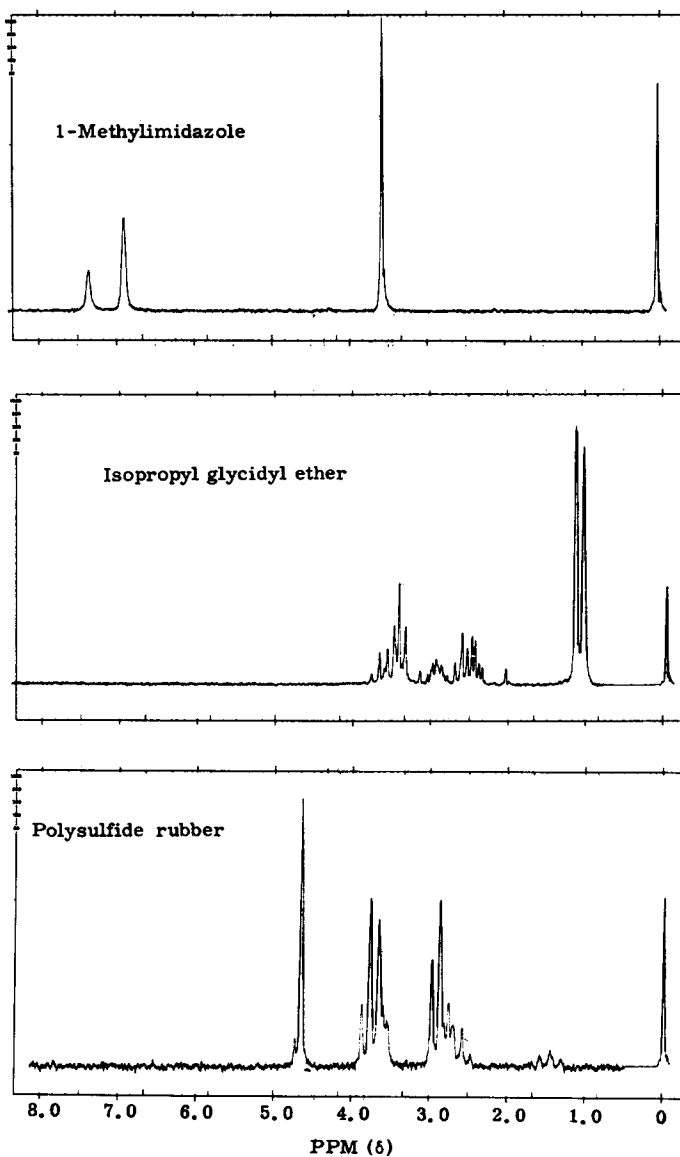
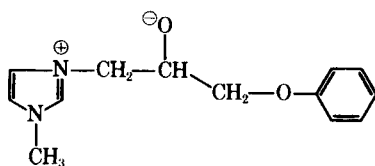


Fig. 4. NMR spectra of the starting materials.

ular weight per reactive function), then the peak at  $1665\text{ cm}^{-1}$  was not evident in the heated mixture. Since there were no carbonyl-containing compounds in the mix, the absorption at  $1665\text{ cm}^{-1}$  was attributed to an olefin-containing compound.

#### Adduct of Phenyl Glycidyl Ether and 1-Methylimidazole

The adduct of phenyl glycidyl ether and 1-methylimidazole (I) was prepared and equal amounts of the adduct and PSR were heated together.



I

The IR spectrum showed virtually no change. However, when the mix containing the adduct and PSR was then treated with phenyl glycidyl ether itself, an exothermic reaction took place and a peak was observed at  $1665\text{ cm}^{-1}$ . This indicates, first, that the initial step in the reaction may be the normal opening of the epoxide ring by the imidazole and, second, that free epoxy resin is necessary in order for the new peak at  $1665\text{ cm}^{-1}$  to appear. Attempted distillation of the reaction mixture was unsuccessful.

#### Reaction Between Isopropyl Glycidyl Ether, 1-Methylimidazole, and Polysulfide Rubber

Since the peak at  $1665\text{ cm}^{-1}$  was indicative of a side reaction in the epoxy-PSR system catalyzed with MI-1, this reaction was attempted using a lower-boiling epoxide, namely isopropyl glycidyl ether, in the hope of isolating the product or products of the side reaction. The mixture was heated until no further changes in its IR spectra were observed. The dark residue was then vacuum distilled and about 30% of unreacted isopropyl glycidyl ether was recovered, together with a small amount of mixed distillate and a higher boiling fraction. The highest boiling fraction ex-

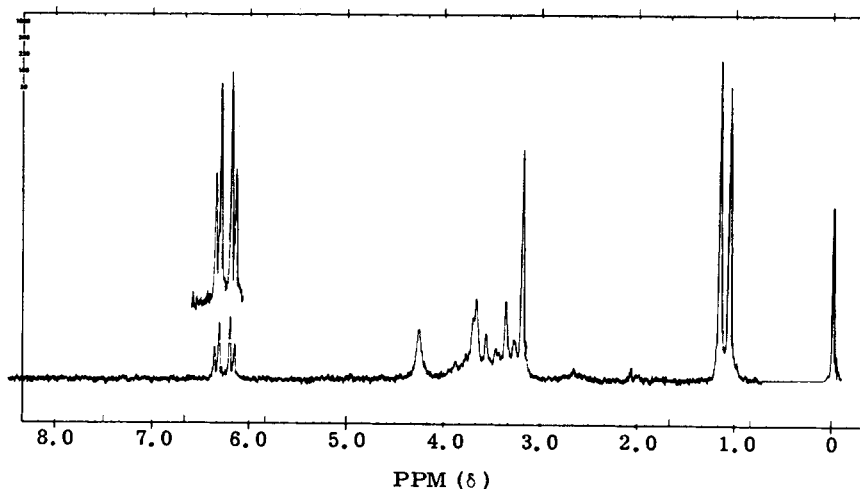


Fig. 5. NMR spectra of the distillate bp  $140^{\circ}$ – $145^{\circ}\text{C}$  (0.2 mm).



hibited IR peaks indicative of the desired product of the side reaction. Thin-layer chromatography on silica gel, using 1:1 benzene-ether, showed it to be mainly one component but four other compounds were also present in very small amounts.

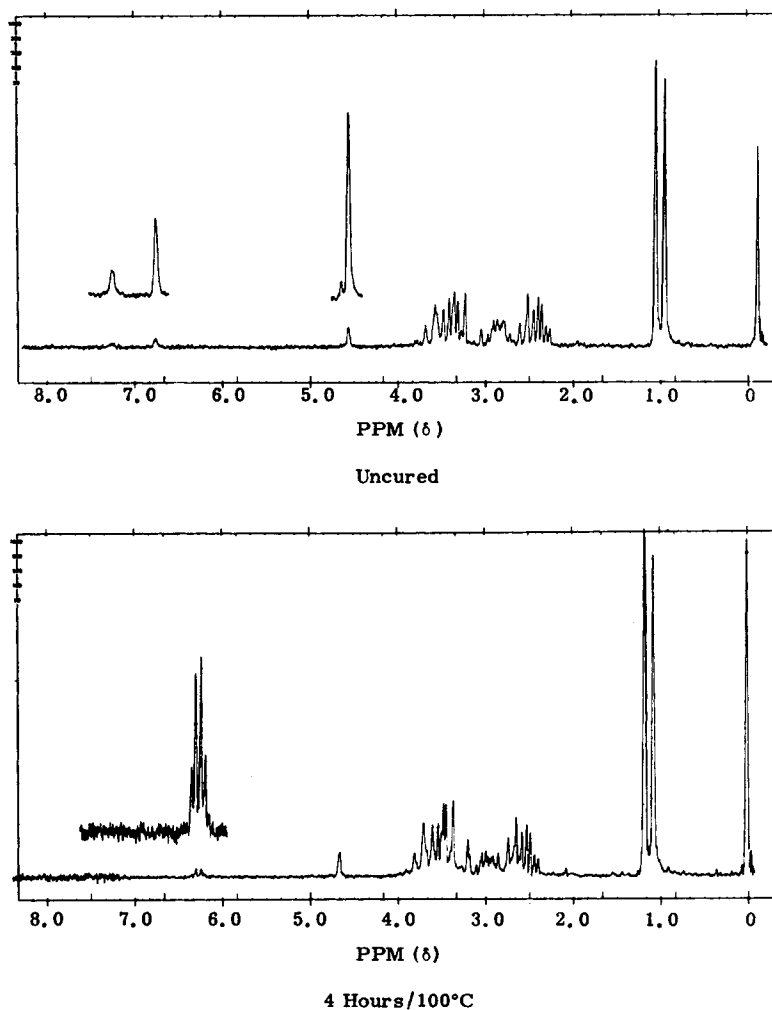


Fig. 6. NMR spectra of isopropyl glycidyl ether-polysulfide rubber-1-methylimidazole (20:4:1).

The NMR spectrum of this distillation fraction was compared with the NMR spectra of the starting materials (Figs. 4 and 5). It can readily be seen that the product contains an isopropyl group (1.0–1.3  $\delta$ ) but is free from unreacted epoxide (2.3–2.7 and 3.6–3.8  $\delta$ ). The aromatic imidazole protons (6.9 and 7.4  $\delta$ ) are absent, but a new distinctive pair of doublets (6.1–6.4  $\delta$ ) is present.

Microanalysis indicated 53.1% carbon, 8.6% hydrogen, 10.3% nitrogen, and trace amounts of sulfur in the distillate. The presence of nitrogen in the distillate indicated that 1-methylimidazole, or a derivative, was present but, as stated above, the NMR spectrum showed no peaks attributable to

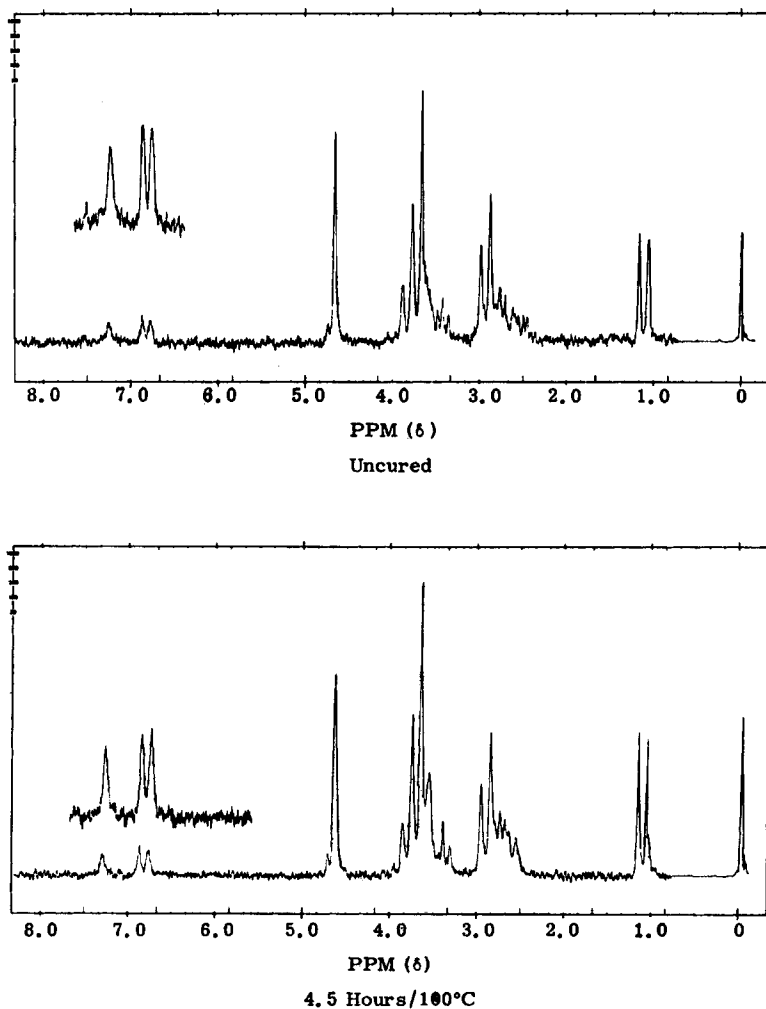
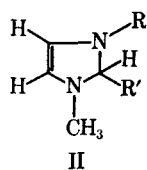


Fig. 7. NMR spectra of isopropyl glycidyl ether-polysulfide rubber-1-methylimidazole (7:30:5).

imidazole protons. It was then apparent that the pair of doublets found at 6.1 to 6.45  $\delta$  was due to the vinyl protons of a dihydroimidazole compounds (II). This is also indicated by a shift in the peak attributed to the N-methyl group from 3.6 to 3.2  $\delta$ .



Several formulations of epoxy-PSR-MI-1 were prepared and their NMR spectra before and after curing were obtained (Figs. 6, 7, and 8). Figure 6

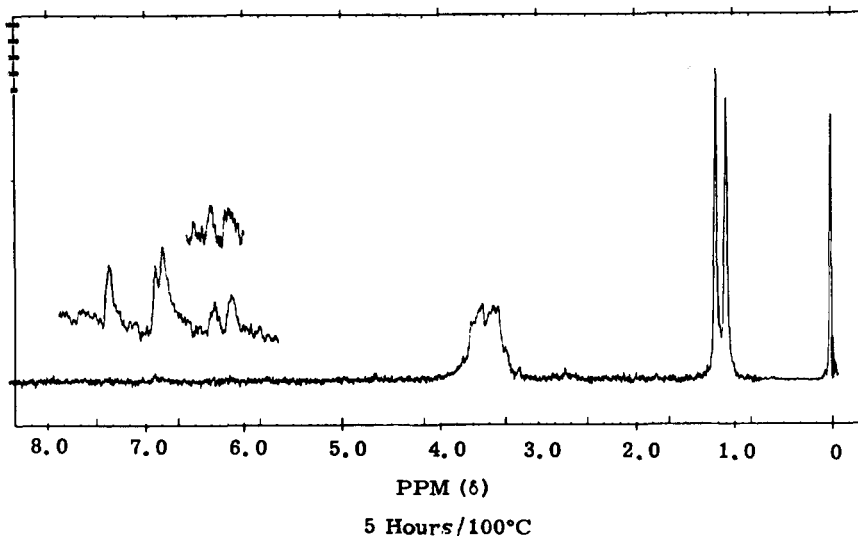
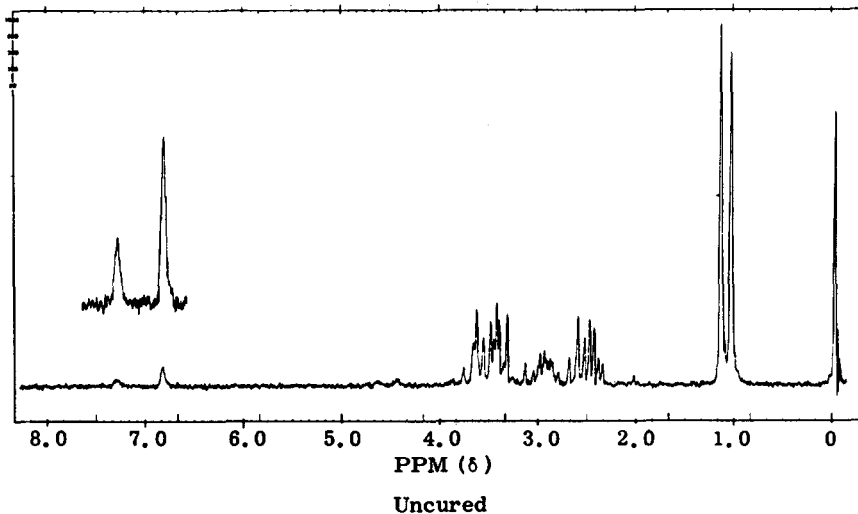


Fig. 8. NMR spectra of isopropyl glycidyl ether-polysulfide rubber-1-methylimidazole (20:1:2).

shows the case in which a slight excess of PSR over MI-1 was used; it can be seen from the region between 5.5–7.5  $\delta$  that all of the MI-1 has been converted to the dihydroimidazole compound. In Figure 7, where an excess of PSR over both epoxy and MI-1 was used, very little change was noted after heating for 4–5 hr at 100°C; by D<sub>2</sub>O exchange a new peak at 3.5  $\delta$  was shown to be —OH and was a result of some opening of epoxy rings by the PSR. In Figure 8, where an excess of MI-1 over PSR was used and the mixture was heated for 5 hr at 100°C, the NMR spectra showed peaks for both the MI-1 and the dihydroimidazole compound (6.6–7.3  $\delta$  and 5.9–6.3  $\delta$ , respectively).

While a mechanism cannot be written at this time, the results of the concentration studies indicate that the amount of MI-1 converted to the dihydroimidazole (II) is directly related to the PSR. The microanalysis indicates that the PSR does not become an integral part of the product formed in the side reaction. It is also of interest that when an excess of PSR over epoxy is employed, neither polymerization nor formation of the dihydroimidazole occurs.

The effect of the alkyl substituent in the 2-position of the imidazole ring is apparently steric in nature.

Noteworthy of mention is the fact that epoxy coatings cured with MI-1 have exhibited surface tackiness. This could be the result of atmospheric moisture behaving much like PSR and inhibiting the cure at the surface of the coatings.

## CONCLUSIONS

The comparison of EMI-24 and MI-1 as epoxy curing agents showed that they give polymers with essentially identical physical properties.

When the epoxy was modified with polysulfide rubber, only imidazole compounds that were substituted in the 2-position acted as effective catalysts. Spectral evidence indicated that the ineffective imidazole compounds were being deactivated through the formation of the corresponding dihydroimidazole compound. A concentration study showed that the amount of deactivation was directly related to the amount of polysulfide rubber present.

## Reference

1. A. Farkas and P. Strohm, *J. Appl. Polym. Sci.*, **12**, 159 (1968).

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