

DSC and ^{13}C -NMR Studies of the Imidazole-Accelerated Reaction Between Epoxides and Phenols

ARTURO HALE* and CHRISTOPHER W. MACOSKO, *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455*, and HARVEY E. BAIR, *AT & T Bell Laboratories, Murray Hill, New Jersey 07974*

Synopsis

The imidazole-accelerated reaction between epoxides and phenols has been studied through DSC and ^{13}C -NMR of model compounds. The selectivity of the accelerator has been found to be strongly dependent on its concentration. If a low amount of accelerator is used, the reaction takes place almost exclusively through the addition of phenols to epoxides even if the latter are used in excess. However, a larger amount of accelerator will cause the secondary hydroxyls (produced by the main reaction) to react with the epoxides. In any case, the lower reactivity of the secondary hydroxyls prevents them from reacting to any significant extent as long as there are any phenols present. When polyfunctional resins are used, the effect of the selectivity of the reaction on the properties of the crosslinked network is very clear. If a low amount of accelerator is used (to promote only the epoxy-phenol reaction), the maximum glass transition temperature (T_g) occurs when the epoxides and phenols are stoichiometrically balanced, reaching 178°C. However, when an excess of epoxides over phenols is used, along with a larger amount of accelerator, the maximum T_g increases its value to 199°C.

INTRODUCTION

Integrated circuits are commonly packaged by encapsulating a metal lead frame and integrated circuit with a silica filled (70% wt.) thermosetting plastic in a transfer molding operation. Since the early 1970s, epoxy-novolac resins have been used for this purpose,¹⁻³ but only a handful of references have been published on their reaction kinetics or on the change in properties which occur during curing.⁴⁻⁹

In general, the encapsulating resin consists of an epoxy cresol novolac prepolymer and a cresol novolac hardener or a phenol novolac hardener; the average functionality of each of these compounds is typically around 5. The molecular structures of these compounds are shown in Figure 1. Lewis bases are typically used to accelerate the reaction between the epoxides and the phenolic hydroxyls,² the most common being imidazoles.¹⁰

The reaction between epoxides and phenols has been widely studied.¹¹⁻¹⁹ Shechter and Wynstra¹¹ reported that the base-accelerated reaction of epoxides with a stoichiometric amount of phenol takes place almost exclusively through the addition of the phenolic hydroxyl to the epoxide (Fig. 2). The same results have been reported by Enikolopiyan¹² and Shcheblanova et al.¹³ Further work has shown that a second reaction may occur, the importance of which is determined by the nature and concentration of accelerator, as well as

*Present address: AT&T Bell Laboratories, Murray Hill, New Jersey 07974.

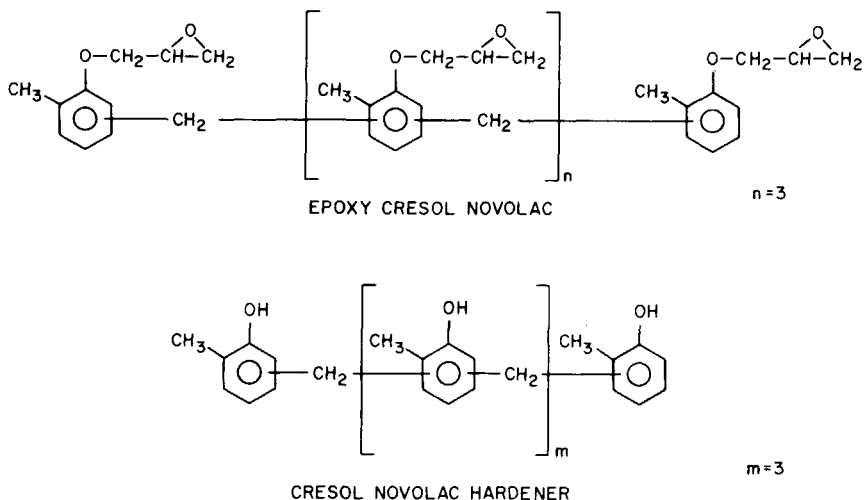


Fig. 1. Molecular structure of epoxy cresol novolac and of cresol novolac hardener.

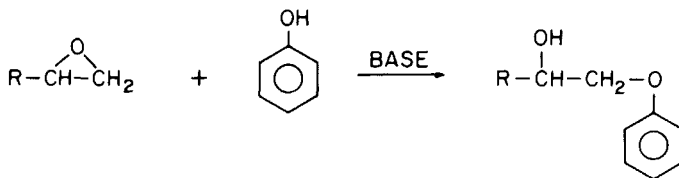


Fig. 2. Epoxide-phenol reaction.

by the temperature.¹⁴⁻¹⁷ Gagnebien and co-workers¹⁷ have shown that the second reaction consists of the secondary hydroxyl (produced by the main reaction) reacting with another epoxide, as shown in Figure 3. Some accelerators, such as triethanol amine, have proven to be very selective towards the main reaction^{14,15}; however, even accelerators with "low" selectivity promote the epoxide-phenol reaction preferentially over the epoxide-secondary hydroxyl reaction.^{14,15}

Despite the importance of imidazoles in the encapsulation of integrated circuits, there is hardly any information in the open literature about the kinetics and selectivity of these accelerators *when used for the epoxide/phenol reaction*, although there is some information about imidazoles used for catalyzing the homopolymerization of epoxies.²⁰⁻²⁴

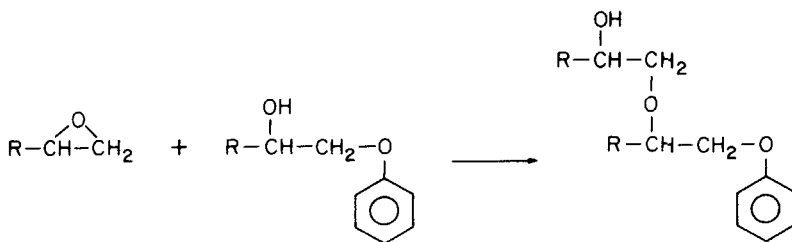


Fig. 3. Epoxide-secondary hydroxyl reaction.

The goal of this work is to study the primary and secondary products of the imidazole accelerated epoxy-phenol reaction, as well as the selectivity of the accelerator. This is essential in order to understand the chemorheology and the structure buildup in imidazole-accelerated epoxy-novolac reactions. First the chemistry is studied using model monofunctional compounds; then, the effect of the competing reactions on the glass transition temperature of cured epoxy-novolac systems is analyzed.

EXPERIMENTAL

Materials

The model compounds employed were *o*-cresyl glycidyl ether (Ciba-Geigy Araldite DY023, epoxy equivalent = 199g/eq), phenyl glycidyl ether (Aldrich, 99%, epoxy equivalent = 150 g/eq), *m*-cresol (Aldrich, 99 + %), and *o*-cresol (Aldrich, 99 + %). The accelerators were 2-methyl imidazole (Aldrich, 98%) and 2-ethyl 4-methyl imidazole (Aldrich, 99%). The molecular structures of all these compounds are shown in Figure 4. The polyfunctional epoxy resin used was an epoxy cresol novolac supplied by Ciba-Geigy (Araldite ECN-1273, epoxy equivalent = 215 g/eq, number average functionality = 4.8); the cresol novolac hardener was Ciba-Geigy Araldite HT-9690, number average functionality = 5.1, hydroxyl equivalent = 126 g/eq. All the epoxy equivalents

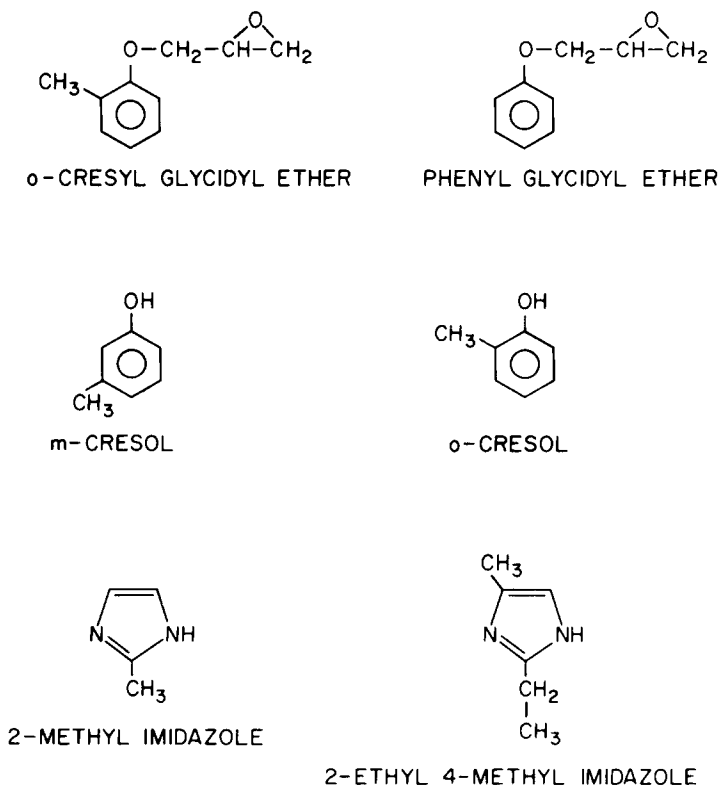


Fig. 4. Molecular structures of model compounds and accelerators.

were determined by titration (ASTM-D1652). The rest of the information was provided by the suppliers. The chemicals were used as received.

Instrumentation

DSC. A Perkin-Elmer differential scanning calorimeter DSC-2 connected to a TADS-3600 data station was used to study the kinetics of the reactions. A Perkin-Elmer DSC-7 was used to study the variation of the glass transition temperature (T_g) as a function of stoichiometry using different levels of accelerator.

NMR. The mixtures containing *o*-cresyl glycidyl ether were run in a Jeol FX90Q Fourier transform spectrometer. A flip angle of 90° was employed, with a pulse delay of 30 s. At least 2000 acquisitions were taken for each spectrum. All the other solution spectra were obtained in a Nicolet NT-300WB spectrometer, using a flip angle of 45° , and a pulse delay of 2 s. At least 400 acquisitions were taken for each spectrum. Deuterated acetone was the solvent in all the cases. The internal reference was tetramethyl silane. The solid state NMR spectrum was obtained in a modified Nicolet NT-150WB spectrometer with magic angle spin and cross polarization capabilities, utilizing a contact time of 2 ms and a repetition time of 10 s. The number of scans was 176.

IR. Transmission spectra were obtained in an IBM IR/40 Fourier transform spectrometer equipped with a mercury cadmium telluride detector. Spectra with a resolution of two wavenumbers were taken, utilizing 500 scans. The epoxide peak used was that at 4530 cm^{-1} .²⁵

PROCEDURE AND RESULTS

Model Compounds

First it was necessary to obtain the heat of reaction between an epoxide and a phenolic hydroxyl. An excess of phenolic hydroxyls was used in order to avoid reaction of the secondary hydroxyls. *o*-Cresyl glycidyl ether (CGE) and *o*-cresol were mixed at room temperature in a 1:2 molar ratio. 2-Ethyl 4-methyl imidazole (EMI) was dissolved in this mixture (1.9 wt%). This solution was reacted in the DSC using a programmed temperature scan from room temperature to 200°C at a rate of $20^\circ\text{C}/\text{min}$. Several samples were reacted isothermally in the DSC at 105 and 125°C . A similar procedure was followed with a 1:2 mixture of *o*-cresyl glycidyl ether and *m*-cresol using 2-methyl imidazole (MI) as accelerator. An average value of -20.7 kcal/mol epoxide was obtained, the discrepancy between different measurements being less than 3%. Bair and Ludwick^{6,7} have reported a figure of -19 kcal/mol for the same reaction, while Enikolopiyan¹² and Rogovina and co-workers¹⁸ have published a value of -18 kcal/mol .

Next, the selectivity of the accelerator was studied following a procedure similar to Alvey's.¹⁴ CGE and *m*-cresol were mixed at room temperature in a 2:1 molar ratio. As the accelerator, 0.75% wt% of MI was added to this mixture, and the reaction was followed by DSC at 125°C . The conversion at each instant was computed by dividing the heat released up to that moment by the total heat of reaction. The results are shown in Figure 5. It can be seen

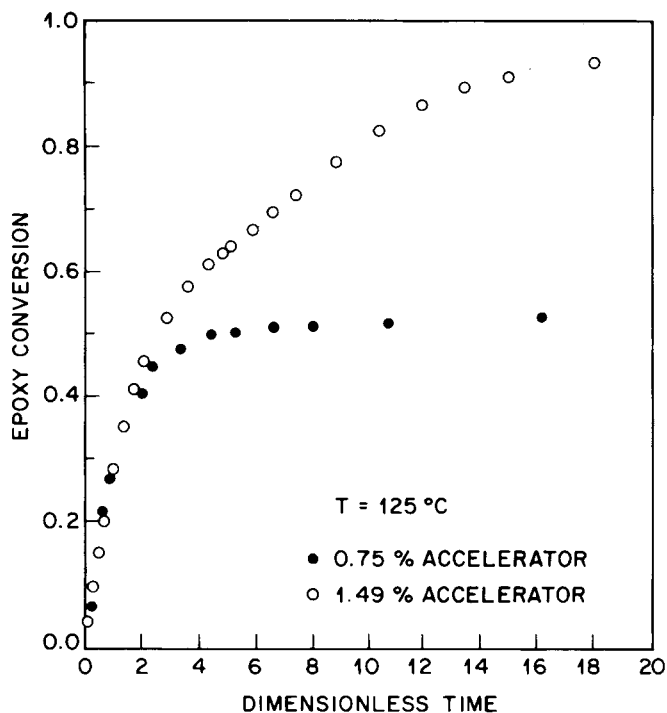


Fig. 5. Epoxy conversion as a function of reaction time using two different levels of accelerator [(●) 0.75% accelerator; (○) 1.49% accelerator]. The reaction mixture consists of a cresyl glycidyl ether-*m*-cresol (2:1 mole) solution. The dimensionless time is defined as reaction time divided by the time needed to achieve 50% conversion of *m*-cresol.

that the reaction levels off at approximately 50% epoxy conversion. This means that when the *m*-cresol is depleted, the reaction slows down very drastically, i.e., any possible side reaction is very sluggish. Similar behavior is observed at 140 and 160°C, although slightly higher values of conversion are achieved. Even though half of the epoxies are still unreacted, they do not react to a significant extent once the phenolic hydroxyls have been consumed. However, if the same procedure is carried out, but with 1.49% of accelerator instead of 0.75%, a different behavior is observed (Fig. 5). Instead of the reaction nearly stopping at around 50% epoxy conversion, the rate of reaction (the slope in the conversion vs. time plot) stays at a constant value from 60 to 80% conversion, and it does not level off until 90% conversion is reached. Since there are enough phenolic hydroxyls to react with only 50% of the epoxides, then it follows that another reaction is taking place. As it will be seen later, our ^{13}C -NMR results show that this secondary reaction occurs between an epoxide and a secondary hydroxyl in agreement with the observations by Gagnebien et al.¹⁷

The sharp dependence of the accelerator selectivity upon its concentration is also seen when EMI is used as accelerator. Figure 6(a) shows the ^{13}C -NMR spectrum of a 2:1 (mole) mixture of CGE and *o*-cresol cured for 90 min in an oven at 125°C using 0.5% EMI as accelerator. Figure 6(b) shows the ^{13}C -NMR spectrum of an equivalent mixture that has been cured at 125°C using 2.6%

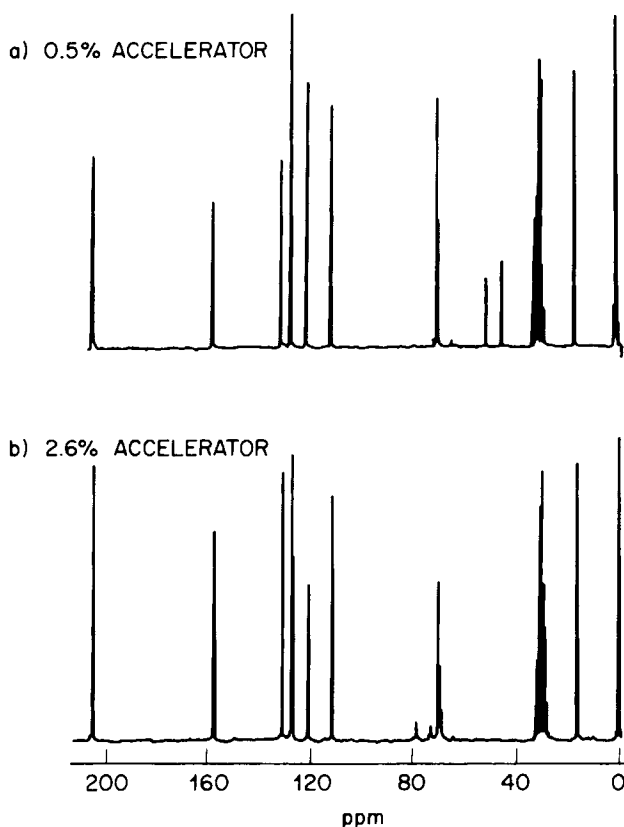
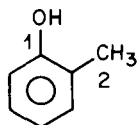


Fig. 6. ^{13}C -NMR spectra of a "completely" reacted 2:1 mixture of cresyl glycidyl ether and *o*-cresol using different concentrations of accelerator.

accelerator. In both cases the reaction had practically stopped after 90 min. The most striking difference between these two spectra is the fact that epoxy peaks (44.3 and 50.7 ppm) are still present in Figure 6(a), but have disappeared in Figure 6(b). Another interesting feature is the appearance in Figure 6(a) of new peaks at 72.9 and 78.4 ppm. These peaks are due to the reaction of an epoxide with a secondary hydroxyl. This is consistent with the DSC observations: When a low amount of accelerator is used [Fig. 6(a)], the excess epoxides do not react significantly after the phenols have been depleted; however, if a larger amount of accelerator is employed [Fig. 6(b)] the epoxies react completely, first with the phenols, and then with the secondary hydroxyls. Figure 7 shows the ^{13}C -NMR assignments of the relevant peaks of the products of the aforementioned reactions.

The dependence of the selectivity of the imidazole accelerator on the concentration was further proved by curing phenyl glycidyl ether (PGE) with *o*-cresol. A 2:1 (mole) solution of PGE and *o*-cresol was mixed with different amounts of EMI. A solution with 0.05% EMI was cured in an oven at 120°C under nitrogen for 32 h. The PGE-cresol mixture was also reacted with 0.25% EMI and with 2% EMI for 5 h at 120°C under nitrogen. Again, for the lowest

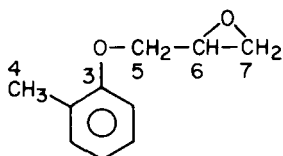
(a) *o*-CRESOL



CARBON δ (ppm)

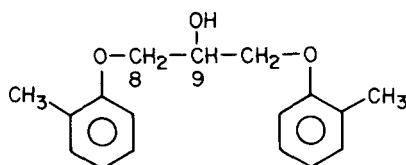
| | |
|---|-------|
| 1 | 156.2 |
| 2 | 16.2 |

(b) *o*-CRESYL GLYCIDYL ETHER



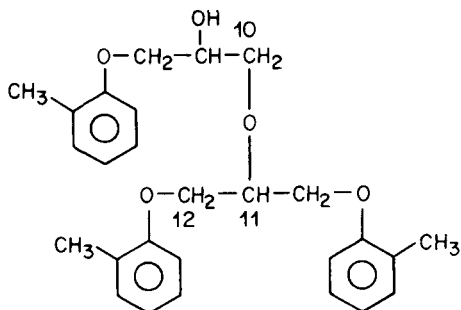
| | |
|---|-------|
| 3 | 157.6 |
| 4 | 16.3 |
| 5 | 69.8 |
| 6 | 50.7 |
| 7 | 44.3 |

(c) a + b



| | |
|---|------|
| 8 | 70.0 |
| 9 | 69.3 |

(d) b + c



| | |
|----|------|
| 10 | 72.9 |
| 11 | 78.4 |
| 12 | 68.5 |

Fig. 7. ^{13}C -NMR peak assignment of reactants and products of the reaction between *o*-cresyl glycidyl ether and *o*-cresol.

amount of accelerator (0.05%) the ^{13}C -NMR spectrum (not shown here) exhibits a significant amount of unreacted epoxides (44.4, 50.5 ppm) and very little reaction with the secondary hydroxyls (small ether peaks at 72.8 and 78.4 ppm). The main product of this reaction is shown in Figure 8, together with the peak assignment. When a larger amount of accelerator (0.25%) is used, there are still epoxides left, but it is clear that some secondary hydroxyls have reacted, as can be seen from the ether peaks at 72.8 and 78.4 ppm.

Figure 9 shows the peak assignments of the product of the reaction between the secondary hydroxyls and the epoxies. With the largest amount of accelerator (2%), the epoxides are depleted. The corresponding ^{13}C -NMR spectrum is shown in Figure 10. Besides the now familiar ether peaks at 72.8 and

| CARBON | SHIFT (ppm) |
|--------|-------------|
| 1 | 159.7 |
| 2 | 115.2 |
| 3 | 130.0 |
| 4,6 | 69.9, 70.0 |
| 5 | 69.2 |
| 7 | 157.6 |
| 8 | 127.0 |

Fig. 8. ^{13}C -NMR peak assignment of 1-(2-methyl phenoxy) 3-phenoxy 2-propanol, the product of the addition of *o*-cresol to phenyl glycidyl ether.

78.4 ppm, there are new small ether peaks at 72.4 and 79.05 ppm. These are due to the reaction between the compound shown in Figure 9 and an epoxide. The resulting species, together with the peak assignment, is shown in Figure 11. The identification of the CH—OH peaks in the crowded region around 69 ppm has been achieved using an “attached proton test” (APT) pulsing sequence. Since Gagnebien and co-workers could not detect any reaction between a “second generation” secondary hydroxyl (such as that in Fig. 9) and epoxides,¹⁷ our hypothesis that the peaks at 72.4 and 79.05 ppm are due to such reaction needs further evidence. A 3 : 1 solution of PGE and *o*-cresol was mixed with 1.8% EMI and cured in an oven under nitrogen at 125°C for 5 h. The corresponding NMR spectrum is shown in Figure 12. Although there are still epoxides left (44.4, 50.5 ppm), they are nearly depleted. If the “second

| CARBON | SHIFT (ppm) |
|--------|-------------|
| 1, 3 | 68.4 |
| 2 | 78.4 |
| 4 | 72.8 |
| 5 | 69.7 |

Fig. 9. ^{13}C -NMR peak assignment of the product of the reaction between phenyl glycidyl ether and 1-*o*-toluoxy-3-phenoxy 2-propanol. A “second generation” secondary hydroxyl has been created.

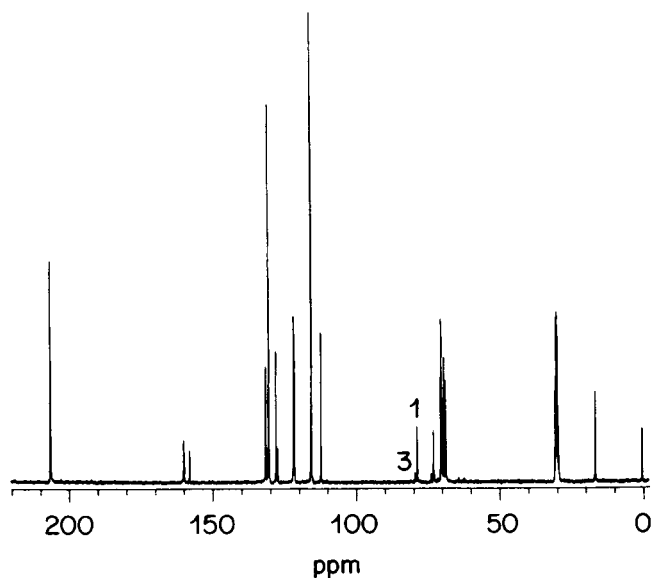
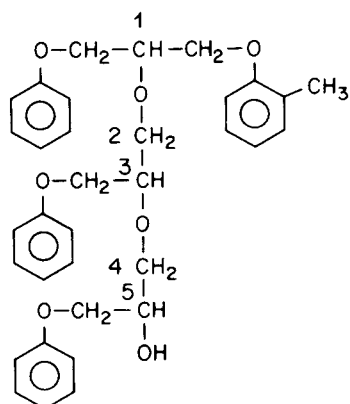


Fig. 10. ^{13}C -NMR spectrum of the product of phenyl glycidyl ether and *o*-cresol (2 : 1) using 2% accelerator. The labeled peaks are assigned in Figure 11.



| CARBON | SHIFT (ppm) |
|--------|-------------|
| 1 | 78.2 |
| 2 | 72.4 |
| 3 | 79.05 |
| 4 | 72.8 |
| 5 | 69.7 |

Fig. 11. ^{13}C -NMR peak assignments of the product of the reaction between a "second generation" hydroxyl (Fig. 10) and an epoxide.

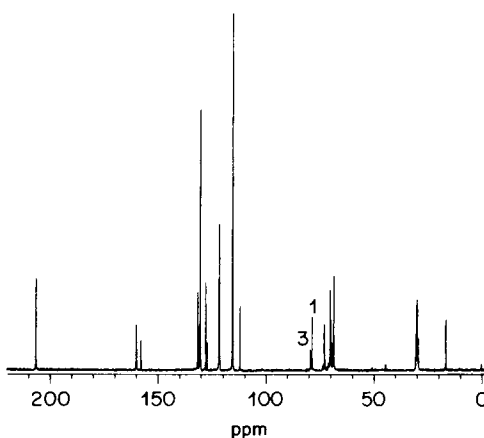


Fig. 12. ¹³C-NMR spectrum of the product of phenyl glycidyl ether and *o*-cresol (3:1) using 1.8% accelerator. The labeled peaks are assigned in Figure 11.

generation" hydroxyls did not react, then there would be a significant amount of unreacted epoxides. The very low amount of epoxides left, together with the new peaks at 72.4 and 79.05 ppm, suggest that these "second generation" hydroxyls indeed react, forming the product shown in Figure 11. Although it could be argued that the consumption of epoxides might be due to homopolymerization, this is not the case, as will be shown shortly.

In order to further corroborate that the formation of the species shown in Figures 9 and 11 takes place through the reaction of epoxides with the product of the epoxide-phenol reaction, the following procedure was followed. A 1:1 solution of PGE and *o*-cresol was mixed with 0.05 wt% of EMI. The mixture was reacted for 48 h at 100°C under nitrogen. The low amount of accelerator utilized was appropriate to ensure that the reaction would proceed cleanly through the addition of the phenols to the epoxides. The NMR spectrum of the product, 1-(2-methyl phenoxy) 3-phenoxy 2-propanol (MPPP), is shown in Figure 13. The peaks have already been assigned in Figure 8. MPPP was then reacted with PGE in a 1:1 (mole) ratio, using 2.8% of EMI as accelerator. The reaction was carried out in an oven at 120°C under nitrogen for 4 h. The NMR spectrum of the product is practically identical with the one shown in Figure 10, which corresponds to the product of reacting a 2:1 mixture of PGE:*o*-cresol using a large amount of accelerator. Similarly, the spectrum of a reacted 2:1 mixture of MPPP and PGE is basically identical with that of the product of a 3:1 solution of PGE:*o*-cresol, shown previously in Figure 12. These results suggest that the epoxides react first with *o*-cresol to form MPPP, which in turn reacts with the remaining epoxies. Figure 14 summarizes this conclusion.

At this point the question arises whether any reaction between epoxides and secondary hydroxyls takes place if there are phenols present, even when a large amount of accelerator is used. A 1:2 PGE:*o*-cresol mixture was mixed with a "large" (2.5%) amount of EMI and reacted for 5 h at 120°C under nitrogen. The corresponding NMR spectrum is shown in Figure 15. It can be appreciated that all the epoxies have been consumed (44.4 and 50.5 ppm), but there is no sign of the product between MPPP and epoxides (no ether peaks at

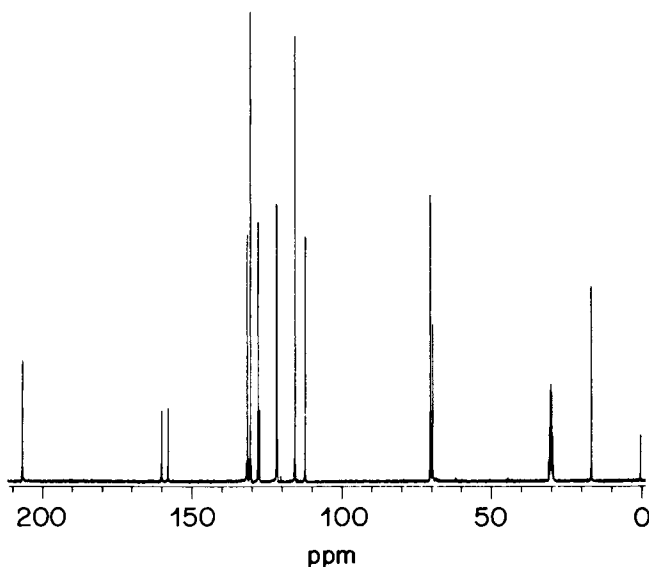


Fig. 13. ^{13}C -NMR spectrum of the product of the reaction between phenyl glycidyl ether and *o*-cresol (1 : 1), 1-(2-methyl phenoxy) 3-phenoxy 2-propanol.

72.8 and 78.4 ppm, and no CH peak at 69.7 ppm), which means that the epoxides have not reacted with the secondary hydroxyls to a detectable extent. The same behavior takes place when PGE and *o*-cresol are reacted in a 1 : 1 ratio. In both cases there is, however, a very small peak at 78.9 ppm, which is possibly due to a slight homopolymerization of the epoxy. A peak in exactly the same position was detected when PGE was homopolymerized using 2.5 wt% of EMI as accelerator. The spectrum of the homopolymerized PGE (after 5 h at 120°C) is shown in Figure 16. The CH—O— region around 79 ppm shows a more complex pattern than in any of the previous spectra.

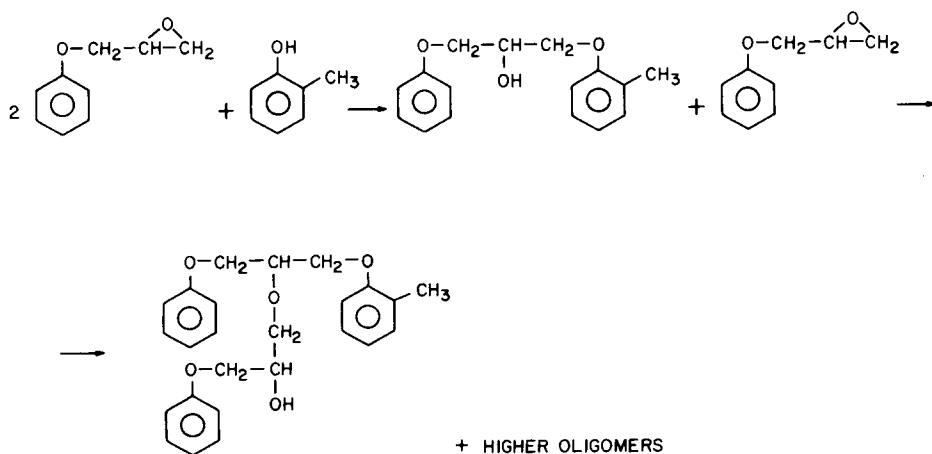


Fig. 14. The epoxide groups react first with the phenolic hydroxyls. After the phenols have been consumed, the remaining epoxides react with the secondary hydroxyls.

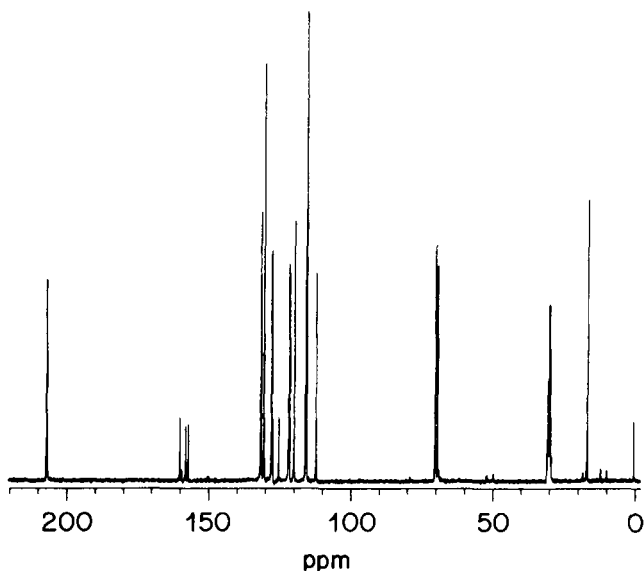


Fig. 15. ¹³C-NMR spectrum of the product of the reaction between phenyl glycidyl ether and *o*-cresol (1:2) using 2.5% accelerator.

This spectrum also shows peaks at 70.5 ppm which do not show in any of the other spectra. Hence it follows that the depletion of epoxides after all the phenols have been consumed [Figs. 6(b), 10] is not due to epoxy homopolymerization, once more confirming that the reaction of secondary hydroxyls is responsible for this. It seems that the small amount of homopolymerization of epoxides detected (78.9 ppm) takes place at the beginning of the reaction. This

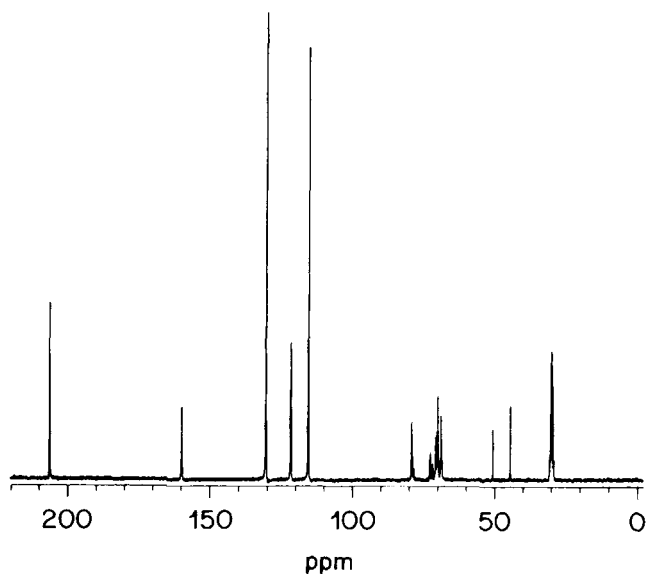


Fig. 16. ¹³C-NMR spectrum of homopolymerized phenyl glycidyl ether.

has also been observed by Bantle and Burchard²⁶ in the reaction between bisphenol-A and diglycidyl ether of bisphenol-A accelerated with tetrabutylammonium hydroxide (a very selective accelerator towards the epoxide-phenol reaction). Since the true catalyst in the base-accelerated reaction of epoxides with phenols has been proposed to be a three-member intermediate formed by the epoxide, the phenol, and the base,^{17,19} it is likely that some epoxy homopolymerization competes with the formation of this complex; however, once the complex is formed, the reaction with phenols is much faster, so that the homopolymerization does not reach a significant extent. The fact that a small amount of bound imidazole can be detected in Figure 15 ($\text{CH}_2\text{-N}$ peaks at 49 and 52 ppm) supports the hypothesis that the imidazole is not a true catalyst for the reaction between epoxides and phenols, since it is not regenerated.

Polyfunctional Resins

The presence or absence of the reaction between epoxides and secondary hydroxyls may drastically change the network structure of a crosslinked system. The high functionality of the epoxy resin and the novolac hardener used in the encapsulation of integrated circuits (Fig. 1) leads to an early gelation (at around 25% conversion of reactive groups); the insolubility of the gel prevents us from obtaining solution NMR spectra. Cross-polarization magic angle spin (CP-MAS) techniques have been employed to obtain ^{13}C -NMR spectra of our highly crosslinked resins. A typical spectrum is shown in Figure 17. There is not enough resolution in the region between 70 and 80 ppm to determine whether the secondary hydroxyls have reacted or not. The low resolution is probably caused by identical nuclei having different local environments in the amorphous sample due to disorder in the molecular environment; this cannot be averaged out by magic-angle spinning.²⁷ An attempt was made to improve the resolution by swelling the polymer in THF, with the

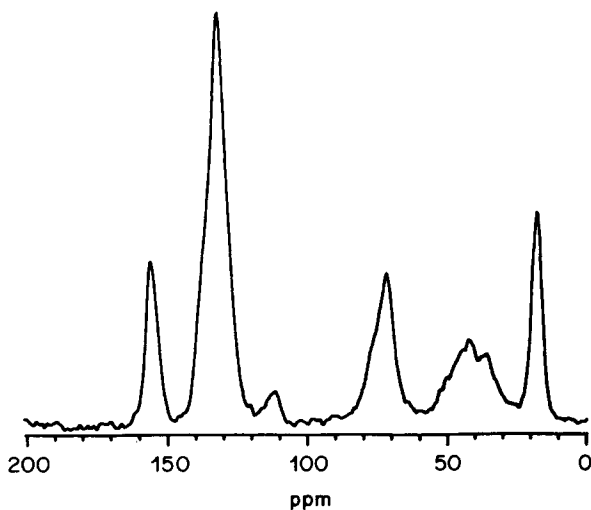


Fig. 17. CP-MAS ^{13}C -NMR spectrum of "completely" reacted epoxy cresol novolac and cresol novolac hardener (1 : 1).

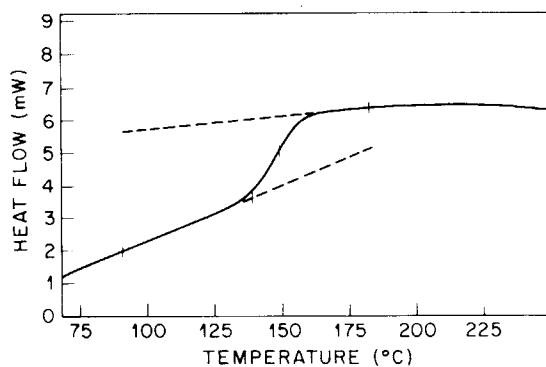


Fig. 18. DSC scan of a reacted mixture consisting of epoxy cresol novolac and cresol novolac hardener (1 : 2) using 0.74% accelerator. $T_g = 139^\circ\text{C}$.

hope that swelling would make the sample more homogeneous and remove some of the differences in the local environments. The CP-MAS ^{13}C -NMR spectrum of the swollen sample did not show any significant improvement. Probably the only option left would be to obtain a spectrum above T_g , but this would imply operating at temperatures of around 220°C , which cannot be achieved with our instrumentation.

Hence an indirect approach was taken to try to detect whether the secondary hydroxyls react or not. Different ratios of the epoxy resin and the novolac hardener were mixed at 110°C , and a low amount of EMI (typically less than 0.06 wt%) was dissolved in each mixture. The mixtures were then cured under nitrogen in an oven at 235°C for 36 h. After letting them cool to room temperature, the samples were scanned in the DSC at $20^\circ\text{C}/\text{min}$ up to 250°C , quenched to room temperature, and then rescanned. The T_g results reported here correspond to the second scan. They were taken as the intersection between an extrapolation of the baseline in the glassy region and a tangent drawn through the inflection point. Figure 18 shows a typical DSC scan. Another set of epoxy-novolac samples was prepared following the same procedure but with a larger amount of EMI (0.74 wt%). A plot of T_g vs. the stoichiometric imbalance r , defined as the initial number of epoxide groups divided by the phenolic hydroxyl groups, is shown in Figure 19. One can clearly see that, in the case of low accelerator, T_g shows a pronounced maximum at $r = 1$, reaching 178°C . This indicates that the reaction proceeds cleanly through the addition of phenols to epoxides, since at stoichiometric balance the number of chain ends will be minimized. IR spectra of these samples show unreacted epoxies when $r \geq 1$; no unreacted epoxies could be detected when $r < 1$. On the other hand, when a larger amount of accelerator is used (0.74%), the maximum in T_g does not occur at $r = 1$, but it is shifted to higher values of r . When $r \leq 1$, the T_g of the samples with large amount of accelerator fall on the same curve as those of the samples with low amounts of accelerator. However, when an excess of epoxides is used in the high accelerator case, T_g keeps on increasing until reaching 199°C at $r = 2$. This reflects a higher crosslink density. No epoxides were detected in the IR spectrum when $r = 2$, indicating that the epoxies kept on reacting even after the phenolic

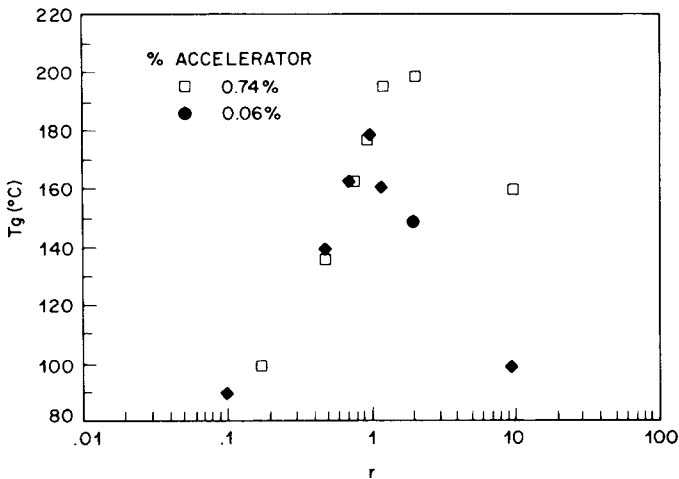


Fig. 19. T_g as a function of stoichiometric imbalance for a reacted epoxy cresol novolac-cresol novolac hardener system using two different levels of accelerator: (□) 0.74%; (◆) 0.06%.

hydroxyls were depleted. The information obtained from model compounds suggests that this behavior is due to the reaction between the excess epoxides and the secondary hydroxyls. Figure 20 shows how a new crosslink would be generated every time a secondary hydroxyl reacted. This reaction, however, is slow, and so when a much larger excess of epoxides is used (10:1 over the

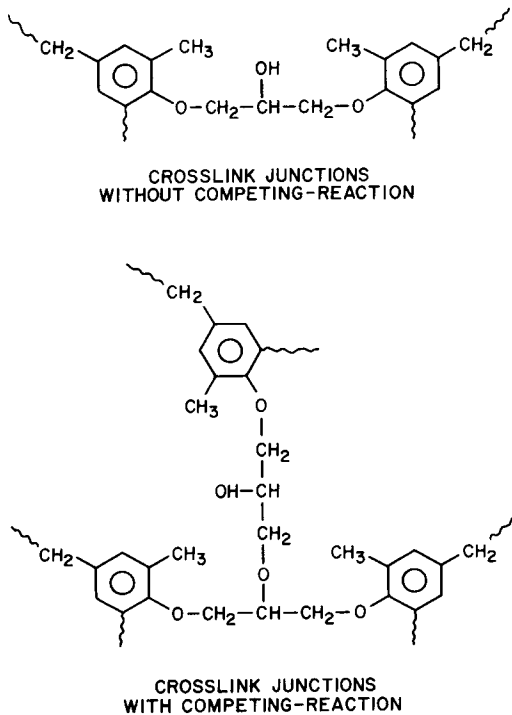


Fig. 20. Crosslink junctions in the absence and in the presence of competing reactions.

phenols), 36 h is not enough time for all the epoxies to react, and the T_g drops again. This is confirmed by IR spectroscopy, which shows unreacted epoxies when $r = 10$.

CONCLUSIONS

The selectivity of imidazole accelerators used to accelerate the epoxy-phenol reaction is strongly dependent on their concentration. A low accelerator concentration will promote almost exclusively the reaction of epoxides with phenolic hydroxyls. When an excess of epoxides is utilized, any reaction between epoxides and secondary hydroxyls is very sluggish even after the phenols are depleted. On the other hand, a high accelerator concentration will promote the reaction between epoxides and secondary hydroxyls; however, this reaction will not take place to any significant extent until the phenols have been consumed.

When polyfunctional resins are used, the effect of the selectivity of the reaction on the properties of the crosslinked network is very clear. If a low amount of accelerator is used, the reaction proceeds cleanly through the addition of phenolic hydroxyls to epoxides, and the maximum glass transition temperature (T_g) of 178°C occurs when the epoxides and phenols are stoichiometrically balanced. However, a larger amount of accelerator causes the maximum T_g to increase to 199°C when an excess of epoxides over phenols is used. This is due to a higher crosslink density caused by the reaction of secondary hydroxyls with the epoxies that remain after the phenols have been consumed.

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