# Curing of Epoxy Resin with Poly(*m*-phenylene methylphosphonate)

**Tao Wu,* Andrew M. Piotrowski, Qiang Yao, Sergei V. Levchik**

*Ripplewood Phosphorus, 1 Livingstone Ave., Dobbs Ferry, New York 10522*

Received 08 November 2004; accepted 17 May 2005
DOI 10.1002/app.22966

**ABSTRACT:** The mechanism and kinetics of curing of epoxy resin with poly(*m*-phenylene methylphosphonate) (PMP) was studied by extraction and swelling experiments, DSC, $^{31}$P NMR, and FTIR. It was shown that at linear heating of 20°C/min PMP cures bisphenol A type epoxy resin at 230–300°C, whereas in the presence of catalytic amount of 2-methyl imidazole the curing occurs at 200–230°C. Under isothermal conditions, epoxy resin was cured with PMP after 40–70 min at 150°C. An unusual mechanism of curing due to opening and insertion of epoxy into the phosphonate bond was suggested. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4011–4022, 2006

**Key words:** epoxy resin; phosphonate; curing; NMR; DSC; FTIR

## INTRODUCTION

Epoxy resin is a basic material for manufacturing printed wiring boards and encapsulation of electronic elements. Because of safety concern about accidental short circuits and potential ignition, most epoxy resins in these applications are required to be flame retardant. The commonly used product is tetrabromobisphenol A (TBBA), which is reactive with epoxy and incorporates into the polymer network. Industry has been using TBBA for over thirty years and the product performs well. However, recently TBBA, along with other halogen-containing compounds, is receiving some negative perception, which has stimulated development of new mainly halogen-free flame retardant systems. One of the commonly considered approaches is use the of phosphorus-containing reactive curing agents.

There are a few ways for incorporation of phosphorus-containing species in the epoxy resin network some of which are finding commercial application.[1] Since the P—H bond can add to the epoxy group, this reaction can be used to attach hydrogen phosphonates or phosphinates to epoxy resin. The only example of a commercially available reactant of this type is 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO). It is sold in Japan and Europe and it is recommended as a part of a curing system for halogen-free flame retardant epoxies.[2] However, it has a drawback related to its monofunctionality, and it can be used only in conjunction with other curing agents.

In another approach, phosphorus-containing molecules are synthesized to contain two or more phenolic OH groups. For example, phosphorus-containing novolacs were prepared from DOPO and 4-hydroxy benzaldehyde[3] or terephthaldicarboxaldehyde[4] and subsequently reacting with phenol. Since these products contained multiple phenolic groups in the molecular chain, they were used as a polyfunctional curing agents. In another study,[5] the novolac made out of DOPO and 4-hydroxy benzaldehyde was compared with the product of partial phosphorylation of phenol formaldehyde novolac with diphenyl phosphorochloridate. The first product showed better performance, which was related to its rigid structure and tendency to give a char upon thermal decomposition and combustion.

Another approach is synthesis of phosphorus-containing amines or especially diamines. For example, a phosphorus-containing diamine was synthesized from DOPO and 3-nitrobenzoyl chloride followed by hydrogenation.[6] Diamines containing two DOPO groups were prepared by reacting 2 mol of DOPO with 1 mol of various diaminobenzophenones.[7]

Phosphine oxide structures have been proposed to impart flame retardancy to curing agents, because phosphine oxides are thermally and hydrolytically very stable. Many studies have been reported in the literature concerning curing of epoxy resins with bis(aminophenyl)methylphosphine oxide, as well as thermal and combustion performance of the fire retar-

---

**Present address:* NIST, 100 Bureau Drive, Stop 8542, Gaithersburg, MD 20899, USA.

*Correspondence to:* S. V. Levchik (Sergei.Levchik@akzonobel-chemicals.com).

Journal of Applied Polymer Science, Vol. 101, 4011–4022 (2006)

dant epoxies.[8–15] Because of strong nucleophilic character of the amino groups, it cures epoxy at the relatively low temperature of 150°C.

The use of tris(3-aminophenyl)phosphine oxide as a curing agent for epoxy resins was also reported in the literature.[16] A poly(arylene ether sulfone) phosphine oxide with controlled molecular weight and amine end groups was synthesized, and used as a modifier for bisphenol A based epoxy resins.[17] Liu et al.[18] designed and synthesized a highly stable phosphine oxide containing a secondary diamine, bis(4-cyclohexylaminophenyl)phenylphosphine oxide. This diamine along with a nonphosphorus-containing diamine was then used in the preparation of epoxy networks with improved fire resistance and toughness.

Two series of phosphorus-containing poly(alkylene) amines with or without aromatic groups were synthesized by reacting phosphoryl chloride derivatives with commercially available polyetheramines, ethylenediamine, and *N*-phenyl-1,4-phenylenediamine.[19,20] These amines were successfully copolymerized with epoxy resins and showed improvements in flame retardancy. In another study,[21] the diamine bis(4-aminophenyl) phenyl phosphate was cured with a phosphorus-containing resin, diglycidyl phenyl phosphate. Interestingly, phenylphosphonic acid amides have some reactivity toward epoxy resins and have been proposed as flame-retardant curing agents.[22]

One more approach is related to the direct reaction of acidic P—OH functionalities with epoxies. This approach is not normally used because of relatively high reactivity of phosphoric acids with epoxies and poor control of the process. Phosphorus-containing anhydrides or pyrophosphates are more preferable. For example, a phosphinic acid made by reacting methylphosphorus dichloride with acrylic acid,[23] or the related cyclic anhydride,[24] were used for chain extension of bisphenol A based epoxy resin. Phosphinic diacids were also obtained by reacting the anhydride with aliphatic diols.[24] Epoxy resins-containing the anhydride or diacids were further cured with dicyandiamide.

Propylphosphonic anhydride was shown to cure epoxy resin composed of bisphenol F and bisphenol A diglycidyl ethers and epoxy novolac.[25,26] In another patent,[27] examples were shown of the reaction of *O*-methyl *P*-ethyl-*P*-methylphosphinate or dimethyl methylphosphonate, dimethyl ethylphosphonate or dimethyl propylphosphonate with $P_2O_5$ to make pyrophosphinates or pyrophosphonates, respectively, which were used to cure epoxies. In similar way polyphosphonic and polyphosphoric anhydrates were prepared by Weil et al.,[28] and then used to cure epoxy resins.

There are few publications in the literature, indicating reaction of epoxy with phosphorous ester groups, specifically in phosphonates. For example, Dow Chemicals has patented technology on incorporation of cyclic methylphosphonate into an epoxy resin.[29] According to this process, the phosphonate is prereacted with epoxy resin in the presence of strong base, while an additional cocuring agent is used for final hardening of the epoxy. A novel route of synthesis of polyphosphonates was performed by reacting epoxy resins with diphenyl phenylphosphonate or diphenyl methylphosphonate.[30] This reaction was carried out in the presence of phosphonium salts and linear polymers were made.

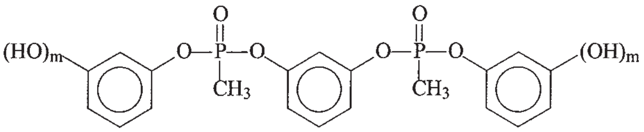


**Figure 1** Structure of Fyrol PMP.

This paper reports data on the curing performance of epoxy resins with poly(*m*-phenylene methylphosphonate) (PMP). This is an innovative and advantageous process, because curing is performed at the temperature and in the time frame usually applied in the circuit board industry. The mechanism of curing was proposed based on the experimental results of swelling test, isothermal curing, DSC kinetically curing, and model system reactions.

## EXPERIMENTAL

### Materials

Poly(*m*-phenylene methylphosphonate) (PMP) Fyrol PMP [31,32] is a newly developed reactive flame retardant (PMP, see structure in Fig. 1). It is an oligomeric product with $M_n$ of 1400 as determined by vapor phase osmometry. PMP contains some phenolic chain ends ($m = 1$ or 0)

Bisphenol A type epoxy resin D.E.R. 331 (DGEBA) was supplied by Dow Chemicals. The curing catalyst, 2-methyl imidazole was provided by Air Products. The chain extension catalyst, ethyltriphenylphosphonium acetate was provided by Cytec. All other chemicals used in this study, for example, triphenylphosphine, 1,2-epoxy-3-phenoxypropane and 1-phenoxyisopropanol were purchased from Aldrich.

### Swelling experiments to determine degree of curing

PMP was dissolved in the epoxy resin to form a 30 wt % solution, and then samples were heated at 150°C in an oven under nitrogen from 40 to 240 min. After removal from the oven, the samples were cooled down and ground. Since some samples were still flexible, they were cooled down by dry ice and then ground. Standard sieves of 12 and 16 mesh were used to collect particles for extraction experiments. Extraction was carried out in a Soxhlet apparatus over 20 h, using methylethyl ketone (MEK) as a solvent. After the extraction was finished, the sample was removed and MEK was blown out from the surface by cold air. The weight of the swelled epoxy was recorded as a final swelling weight, $W_s$. The sample was left for 12 h in open air and then again for 12 h in a vacuum oven at 70°C to remove all MEK. The weight of this sample was recorded as cured epoxy weight, $W_c$. The degree of swelling $D_s$ was defined as follows:

$$D_s = \frac{W_s - W_c}{W_c} \times 100$$

The degree of curing $D_c$ was defined as follows:

$$D_c = \frac{W_c}{W_o} \times 100$$

where $W_o$ is the sample original weight before extraction.

The extractant was retreated by removing MEK with distillation and weighed (extractant residue weight, $W_R$). Some extractants were analyzed by $^{31}$P NMR.

### Reactions with model compounds

1,2-Epoxy-3-phenoxypropane or 1-phenoxyisopropanol were mixed with PMP in 2:1*M* proportion assuming that every phosphorate ester group of PMP can potentially react with an epoxy or OH group. The mixture was prepared in a two-neck flask. One opening was used for a condenser and another for sampling. The reaction was carried out at 150°C, and the samples were taken after 30, 60, and 120 min.

### Instrumentation

DSC experiments were performed on a Perkin–Elmer DSC 7. Curing was carried in sealed aluminum pans. Each sample contained ~8–9 mg of uncured mixtures. Five samples were prepared for each mixture and run at five different heating rates 2.5, 5, 10, 20, and 40°C/min. Kinetic analysis was performed by the isoconversional method, which allows plotting of the activation energy on the degree of advancement of curing.

FTIR transmission spectra were taken on a Perkin–Elmer Spectrum RX. The samples were dissolved either in acetone or chloroform, and a film was then deposited on KBr disks.

$^{31}$P NMR spectra were recorded on a Germini 2000, 200 MHz Spectrometer. The samples were dissolved in deuterated chloroform, and triphenylphosphine was used as a standard.

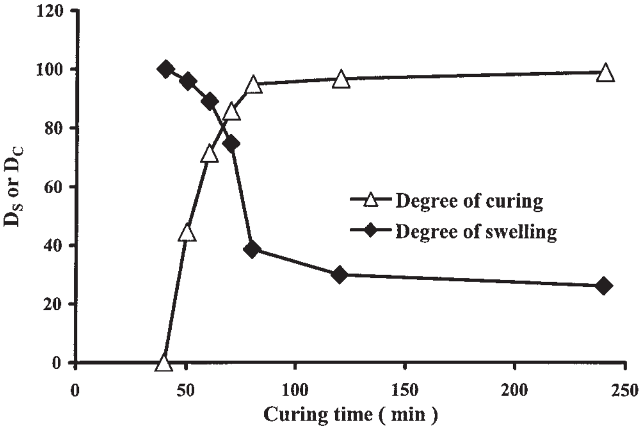


**Figure 2** Degree of epoxy swelling and degree of curing of epoxy/PMP blend heated at 150°C.

## RESULTS AND DISCUSSION

### Isothermal curing

Figure 2 shows the dependency of the degree of epoxy swelling and degree of curing over time. During the first 40 min at 150°C, the mixture of epoxy with PMP does not produce any insoluble material in ME. However, this does not mean that PMP does not react with epoxy at this time. Figures 3 and 4 show $^{31}$P NMR spectra of PMP and PMP heated with epoxy over 40 min. Peaks at 24–26 ppm belong to unreacted PMP, peaks at 28–30 ppm and 32–35 are due to reaction products of PMP with epoxy.

While samples are heated at a constant temperature most of the curing occurs in a time frame between 40 and 70 min, where 86% of the material is crosslinked. The degree of swelling, which reflects density of crosslinks, is also steadily decreasing over this period of time. However, the degree of swelling is still relatively high, which reveals that the network contains a significant portion of free-moving long chains and has some flexibility. In fact, before extraction all samples were hard and brittle, but after extraction these samples became softer and elastic. The elasticity decreases with the longer curing time.

Figure 5 shows the $^{31}$P NMR spectrum of the extracted material from epoxy/PMP heated for 60 min. The spectrum is similar to that of epoxy/PMP cured for 40 min. Interestingly, the extract from the sample heated for 120 min did not show any $^{31}$P NMR peaks meaning that all PMP reacted with epoxy and is not extractable.

Following the fast initial curing, the next step is slower due to limited molecular diffusion as a result of the developing network. Nevertheless, during a short

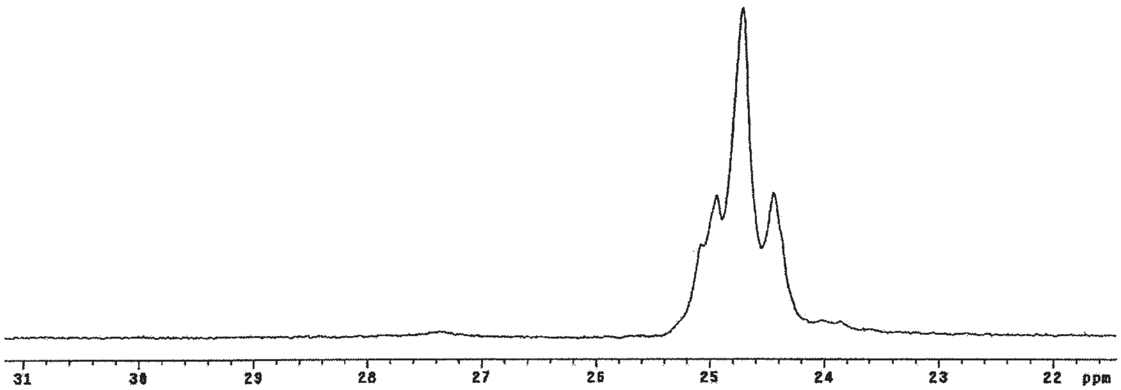


**Figure 3** $^{31}$P NMR spectrum of Fyrol PMP.

period of time (10 min) from 70 to 80 min, a sudden drop of the degree of swelling from 75 to 39% occurs, which corresponds to only a 10% change of the degree of curing. At this period of time, most of the free long chains have been crosslinked.

During further heating up to 240 min, a relatively small increase of the degree of curing and decrease of the degree of swelling has been observed. The degree of curing is approaching but not reaching 100%. There is still some extractable material in the bulk of the cured epoxy. After this material has been removed, the solvent occupies the space and swells the network. There is still about 26% degree of swelling, even after 240 min of curing.

## Kinetics of curing

Figure 6 shows DSC runs of curing epoxy/PMP(30 wt %) either alone or combined with different catalysts at the 2000 ppm level. The mixture without catalyst requires the highest temperature to start curing and the curing process lasts longer. Ethyltriphenylphosphonium acetate and triphenylphosphine show similar behavior, starting curing at a slightly lower tempera-

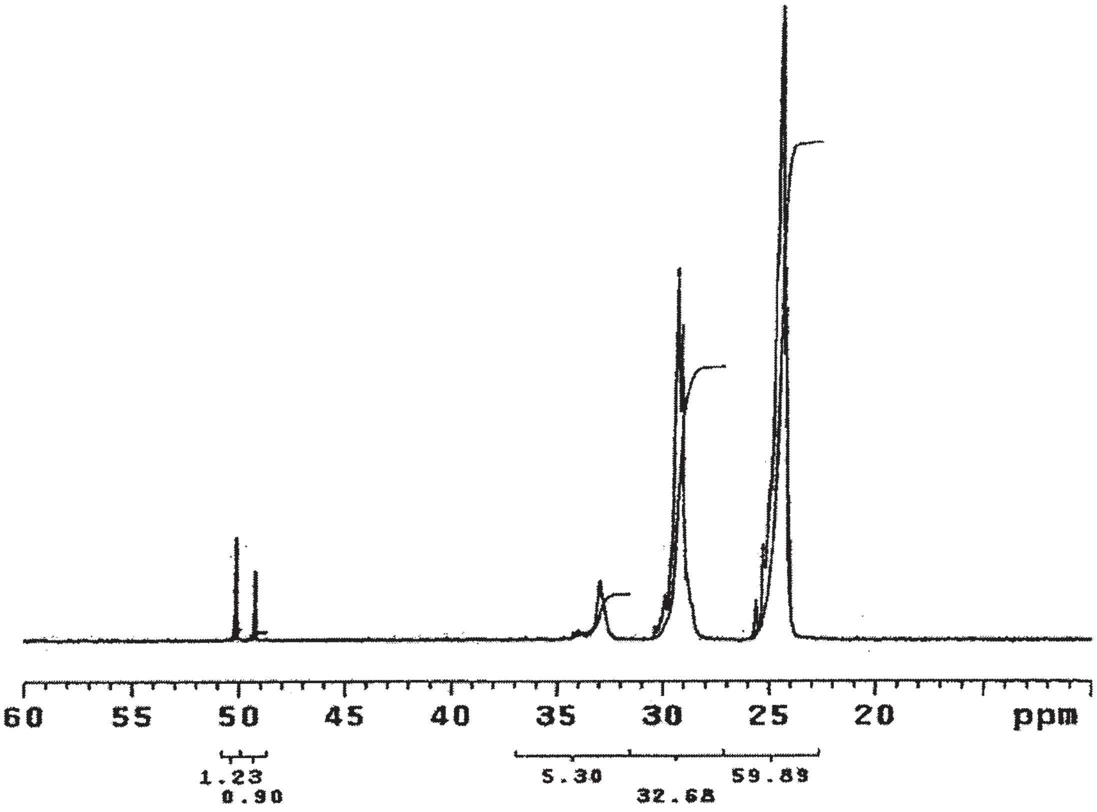


**Figure 4** $^{31}$P NMR spectrum of PMP heated with epoxy over 40 min at 150°C.

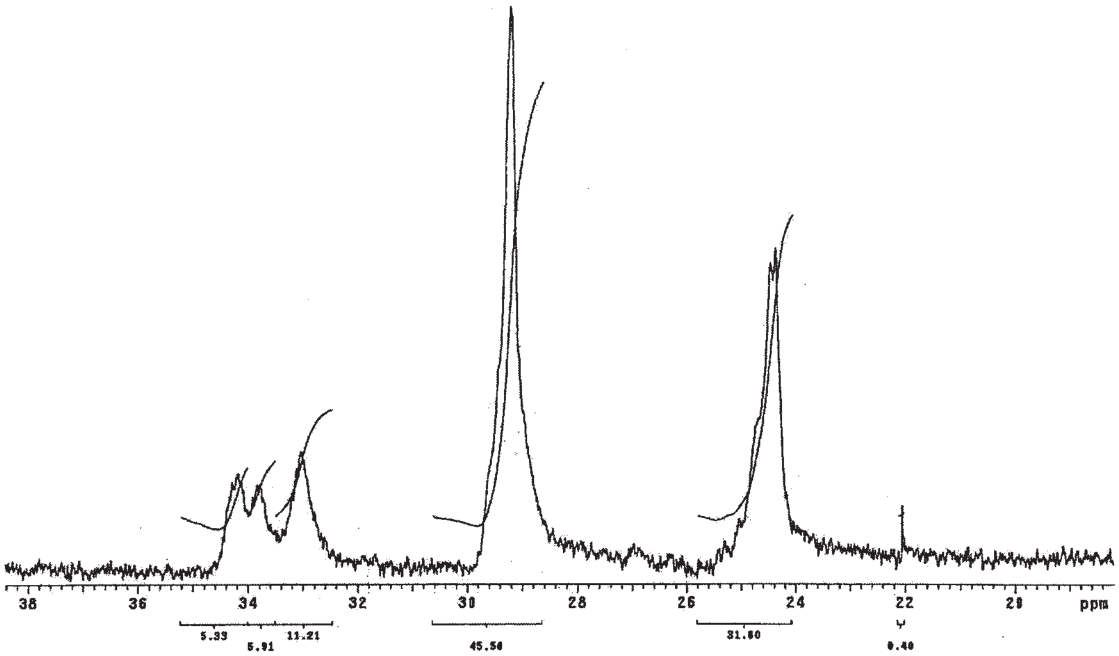


**Figure 5** $^{31}$P NMR spectrum of extract from PMP/epoxy blend heated over 60 min at 150°C.

ture than that without catalyst, but curing proceeds significantly faster. Finally, the blend with 2-methyl imidazole cures at a much lower temperature, with maximum heat release at 213°C. The blend without catalyst or with two phosphine-based catalysts showed a maximum exotherm at about 240°C.

DSC traces of epoxy/PMP added with methyl imidazole are shown in Figure 7. As expected, the exotherm of curing decreases with decrease of heating rate and shifts to lower temperatures. The dependencies of the activation energy ($E_a$) on the degree of curing calculated from the DSC runs at different heating rates for the mixture with 2-methyl imidazole and without catalyst are shown in Figure 8. It is interesting to note that both catalyzed and uncatalyzed systems have similar activation energies at the beginning of

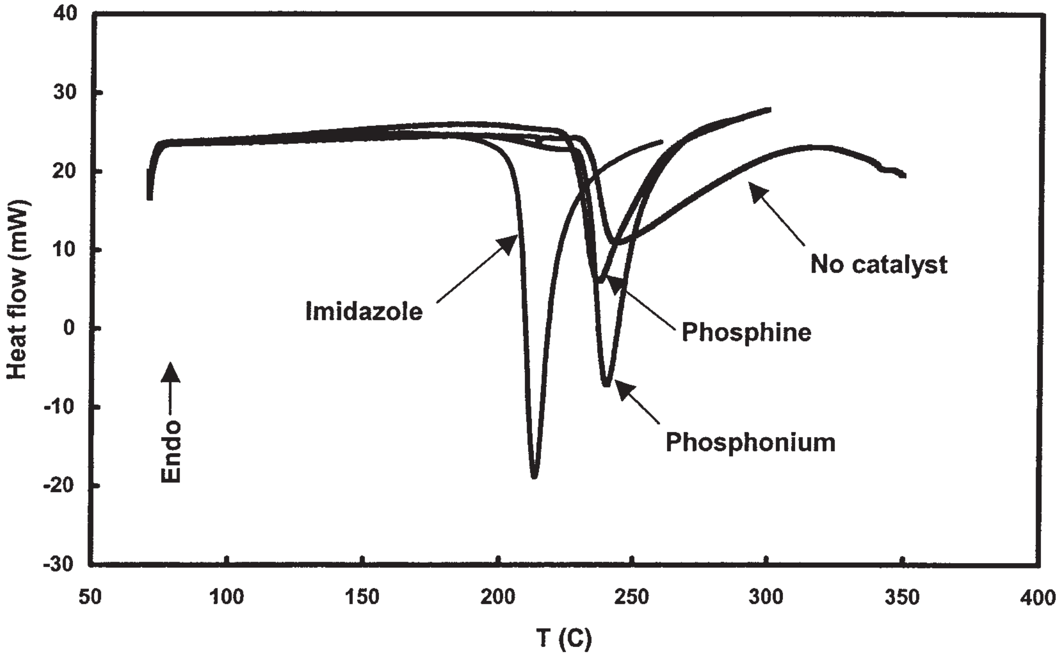


**Figure 6** DSC curves of PMP/epoxy and PMP/epoxy with different catalysts. Heating rate 20°C/min, sealed pans.

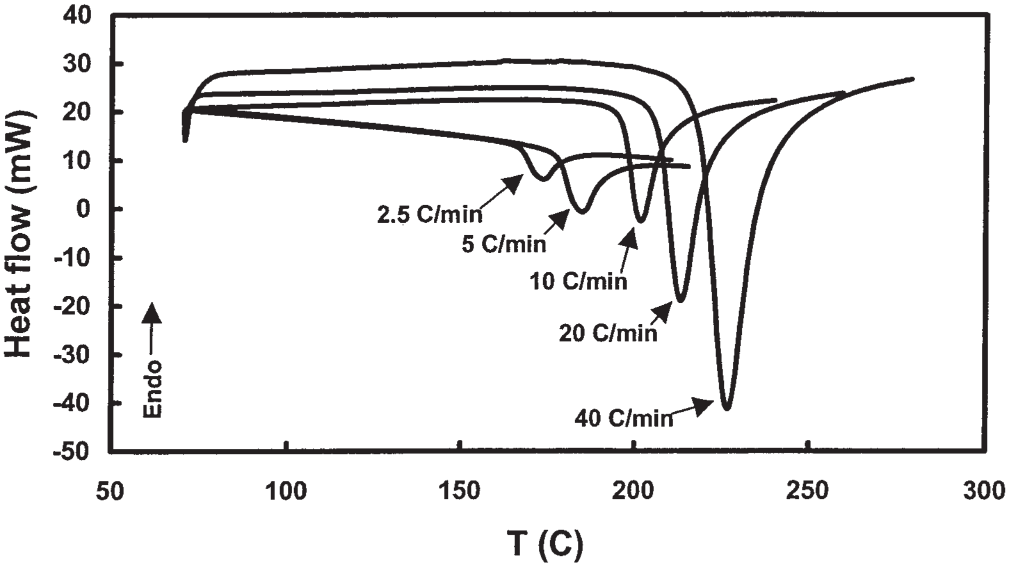


**Figure 7** DSC curves of PMP/epoxy with 2000 ppm of 2-methyl imidazole at different heating rates.

curing; however, with the progress of crosslinking the activation energy of the uncatalyzed system increases, thus slowing curing, whereas the activation energy of the catalyzed system decreases, thus accelerating curing.

## Model reactions

An attempt to react 1-phenoxy-2-propanol with PMP was made to simulate possible transesterification reaction of PMP with secondary alcohol groups present in the commercial bisphenol A type epoxies. At room temperature, PMP does not dissolve in 1-phenoxy-2-propanol; however, after melting it becomes miscible with the alcohol. After 30 min of heating at 150°C without catalyst, PMP solidifies and precipitates out when the sample is cooled down to the room temperature. In contrast, if 2-methyl imidazole is used as a catalyst, PMP does not precipitate already, only after 15 min of reaction.

Figures 9 and 10 show $^{31}$P NMR spectra for the reaction products between PMP and 1-phenoxy-2-propanol after 120 min without catalyst and with 2000 ppm 2-methyl-imidazole, respectively. The peaks in

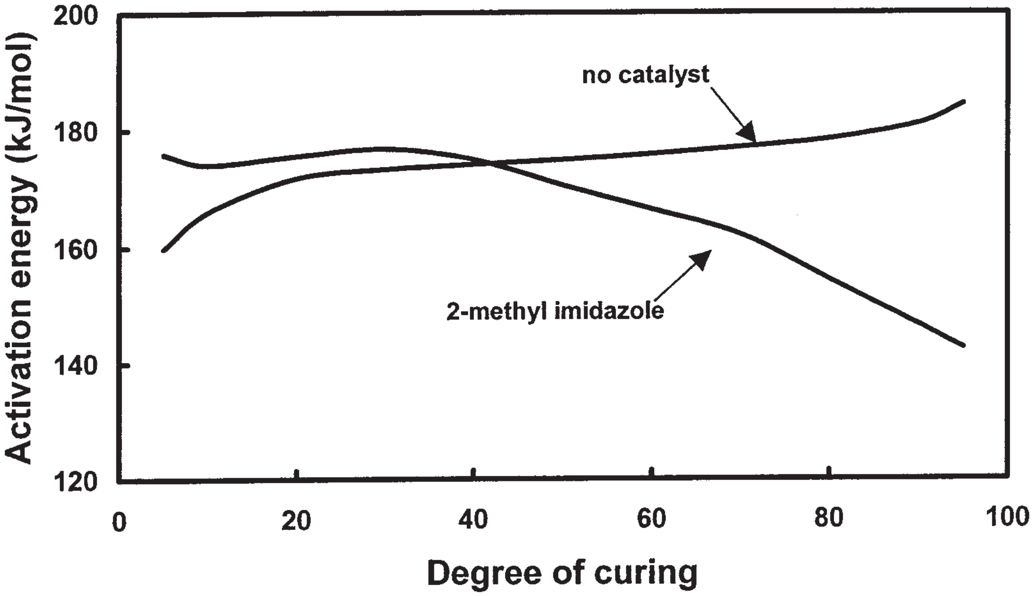


**Figure 8** Dependencies of activation energy on degree of curing for PMP/epoxy and PMP/epoxy with 2000 ppm of 2-methyl imidazole.

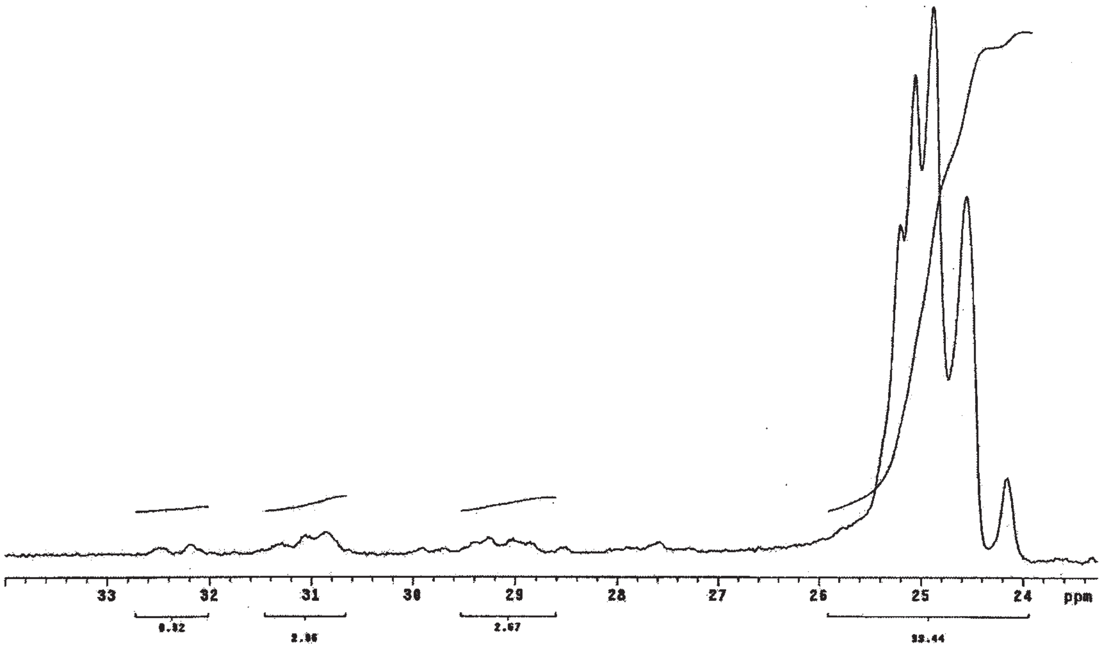


**Figure 9** $^{31}$P NMR spectrum of products of interaction between PMP and 1-phenoxy-2-propanol heated at 150°C over 120 min.

the range of 29–33 ppm are indicative of various products of cleavage of PMP chains. Although with 2-methyl imidazole the conversion rate is almost doubled, the transesterification reaction between PMP and secondary alcohol is still very slow, because in all cases about 90%, PMP remains unreacted after 120 min. The solubility of PMP in alcohol after heating with 2-methyl imidazole could be explained by the cleavage of PMP chains to smaller molecules, which are liquid or soluble in 1-phenoxy-2-propanol.

The reaction between PMP and 1,2-epoxy-3-phenoxy propane was performed without catalyst and with 2000 ppm 2-methyl imidazole. Figures 11–13 show $^{31}$P NMR spectra of the product of reaction

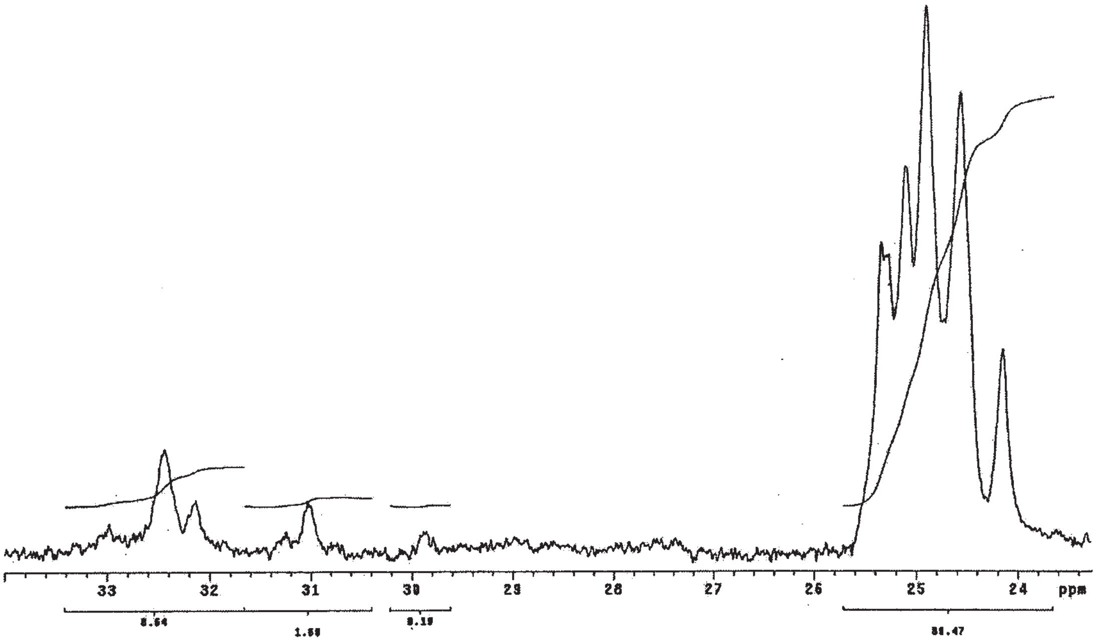


**Figure 10** $^{31}$P NMR spectrum of products of interaction between PMP and 1-phenoxy-2-propanol in the presence of 2000 ppm 2-methyl imidazole heated at 150°C over 120 min.

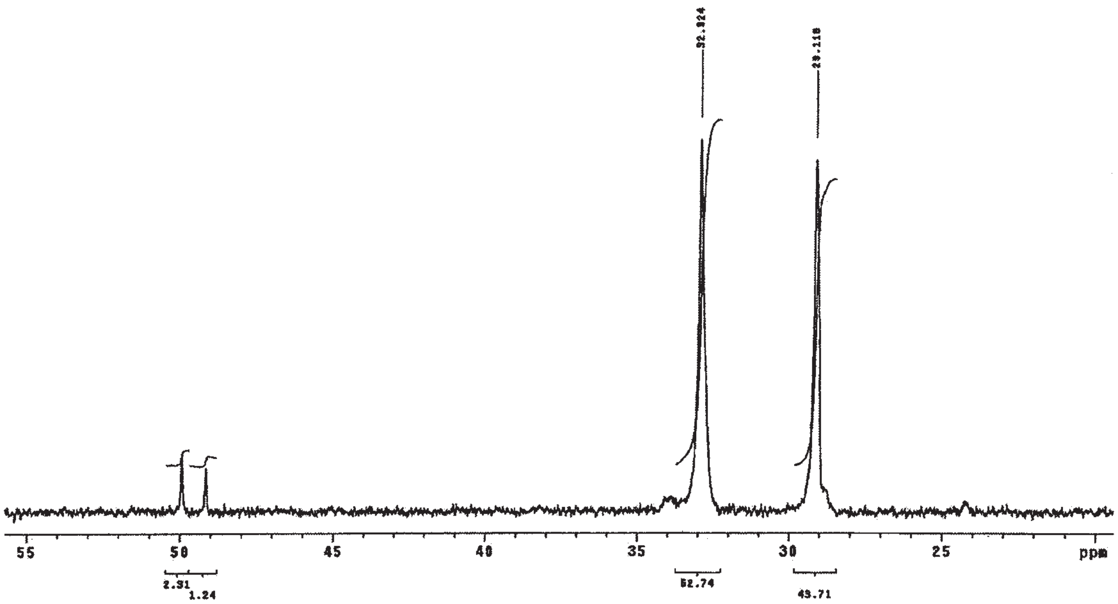


**Figure 11** $^{31}$P NMR spectrum of products of interaction between PMP and 1,2-epoxy-3-phenoxy propane in the presence of 2000 ppm 2-methyl imidazole heated at 150°C over 30 min.

between PMP and 1,2-epoxy-3-phenoxy propane in the presence of catalyst after 30, 60, and 120 min of heating, respectively. There are three major peaks in each spectrum: the peaks at 24–26 ppm are attributed to methylphosphonate surrounded by two phenyl groups (original PMP structure), the peaks at 28–30 ppm to the phosphonate with one phenyl group and one alkyl group, and the peaks at 32–35 ppm to the phosphonate with two alkyl groups. Two small peaks at about 50 ppm are attributed to cyclic phosphonates.[33] From this set of spectra, it is obvious that PMP progressively reacts with epoxy by gradually converting to dialkyl methylphosphonate. The cyclic phosphonate structures quickly formed at the beginning of curing slowly decline.

Figure 14 presents $^{31}$P NMR spectrum of the products of reaction of PMP and 1,2-epoxy-3-phenoxypropane without catalyst. Although the degree of reaction is also high in this case, the concentration for surviving diphenyl methylphosphonate structures is 20%,

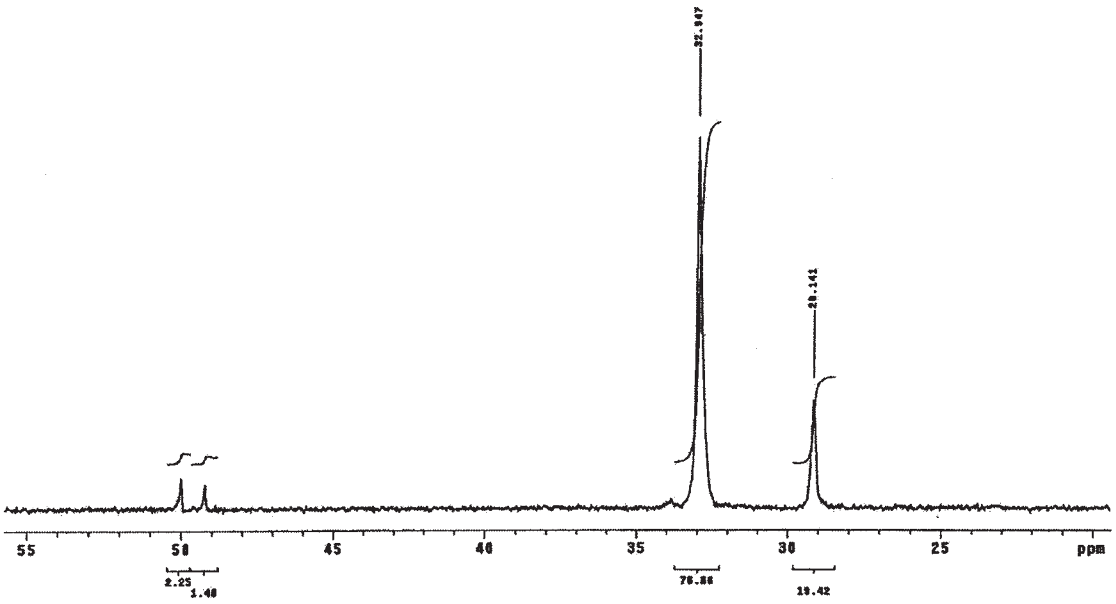


**Figure 12** $^{31}$P NMR spectrum of products of interaction between PMP and 1,2-epoxy-3-phenoxy propane in the presence of 2000 ppm 2-methyl imidazole heated at 150°C over 60 min.

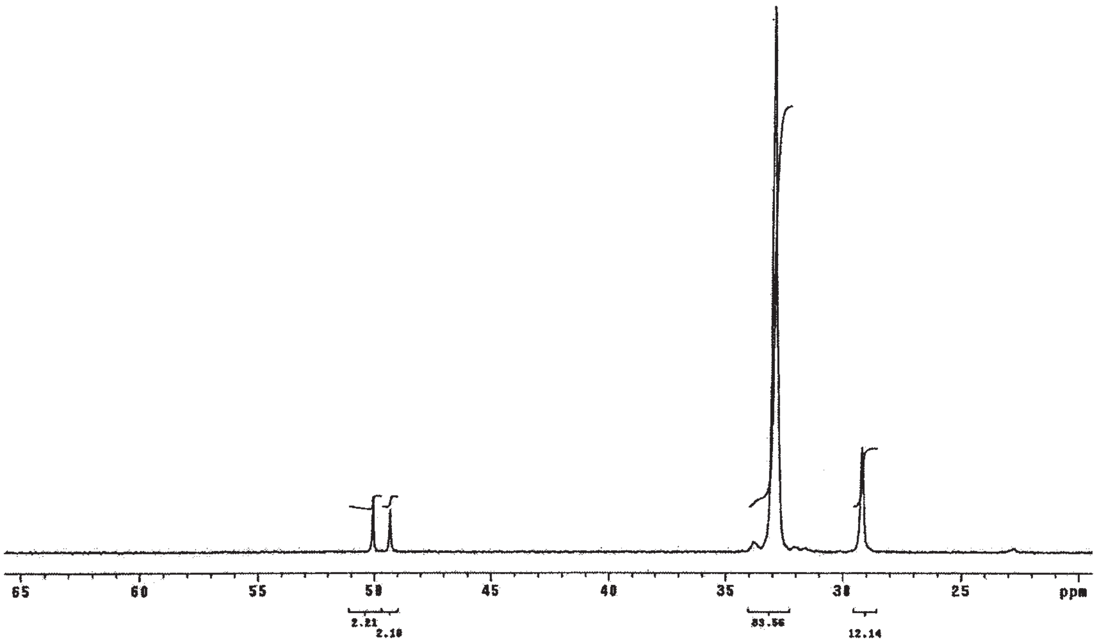


**Figure 13** $^{31}$P NMR spectrum of products of interaction between PMP and 1,2-epoxy-3-phenoxy propane in the presence of 2000 ppm 2-methyl imidazole heated at 150°C over 120 min.

whereas there are no such structures in the mixture containing 2-methyl imidazole (Fig. 13). After 120 min exposure to 150°C, the product of reaction containing 2-methyl imidazole becomes solid after cooling down to room temperature, whereas the product of reaction without catalyst is still a very viscous liquid.

Further identification of the products of reaction between PMP and 1,2-epoxy-3-phenoxy propane was done by infrared. Figures 15 and 16 show the spectrum of the initial blend of PMP with 1,2-epoxy-3-phenoxy propane and 2000 ppm 2-methyl imidazole, and the spectrum of the blend after 120 min heating,

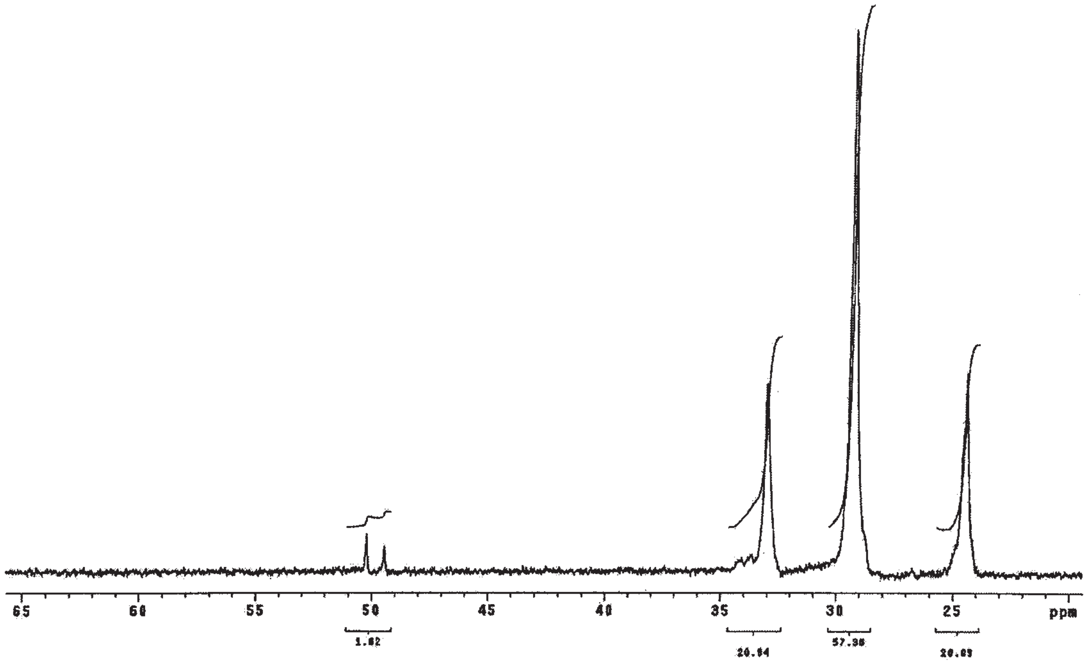


**Figure 14** $^{31}$P NMR spectrum of products of interaction between PMP and 1,2-epoxy-3-phenoxy propane heated without catalyst at 150°C over 120 min.

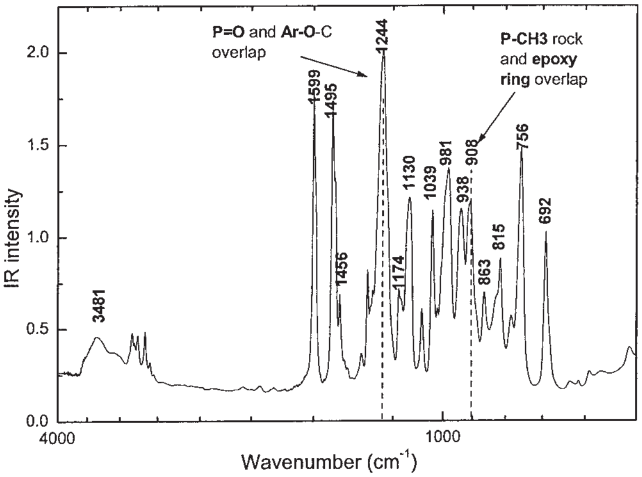


**Figure 15** FTIR spectrum of the blend of PMP and 1,2-epoxy-3-phenoxy propane 2000 ppm 2-methyl imidazole.

respectively. New peaks at 987 and 999 $cm^{-1}$ appeared after heating are attributed to O—C stretching in P—O—CHR.[34] There are two peaks, because R can be different depending on how the epoxy ring opens. The peak at 1130 $cm^{-1}$ in Figure 15 attributed to P—O—Ar significantly decreases in the cured sample.

### Mechanism of curing

Based on DSC, $^{31}$P NMR, and FTIR data for model compounds as well as for commercial epoxy resin, the mechanism of curing with PMP can be suggested. Because strong base type catalyst, 2-methyl imidazole, accelerates curing, it is likely that opening of epoxy ring proceeds through an ionic mechanism. The values of the activation energies in the range of 160–180 kJ/mol are also in favor of this type of mechanism. The scheme of reaction of epoxy and PMP in the presence of 2-methyl imidazole is shown in Figure 17.

The product (I) prevails in the cured epoxy at the early stage of curing, and the $^{31}$P NMR peak at 28–30 ppm corresponds to this product. Isothermal curing and swelling experiments showed that this type of structure is most likely created during first 30–40 min of curing. Upon advancement of curing more and more epoxy groups are inserted in P—O—Ph bonds, and eventually Alk—O—P—O—Alk and Alk—OPh—O—Alk bridges will be formed in the crosslinked epoxy (II) as shown in Figure 18. $^{31}$P NMR peak at 32–35 ppm corresponds to Alk—O—P—O—Alk bridges. As it is seen from Figures 11–13, the concentration of these bridges is increasing with increase in the duration of curing. Eventually PMP creates very highly crosslinked network, as has been shown by swelling experiments.

Phenolic chain ends present in original PMP most likely also participate in the curing reactions. Because the phosphorus-containing network formed with these chain ends is not distinguishable from the structures (I) and (II), it is difficult to assess if curing reaction actually starts with cleavage of P—O—Ph bonds, as shown in Figure 17 or with the opening of epoxy ring by Ph—OH chain ends.

In the commercial PMP, there is always some low concentration of phosphonic acidic chain ends. Some phosphonic acid chain ends can be also formed by interaction with aliphatic alcohol groups present in the commercial epoxy resins. Upon heating with epoxy, these phosphonic acids quickly react with epoxy forming aliphatic phosphonate groups and aliphatic alcohol groups (Fig. 19, product (III)). Aliphatic alcohol transesterifies P—O—Ph bond and thus cyclic phosphonate structures are formed (IV). These cyclic phosphonates are evidenced by $^{31}$P NMR peaks at about 50 ppm.

## CONCLUSIONS

Most of the curing of epoxy with PMP occurs from 40 to 70 min of heating at 150°C. At this time, 86% of the material is involved in the crosslinking or branching. From 70 to 80 min of heating, a sudden drop of the degree of swelling from 75 to 39% occurs, which corresponds to only 10% change of the degree of curing. At this period of time, most of the free-moving branched chains have been crosslinked.

At linear heating of 20°C/min, PMP cures bisphenol A type epoxy resin in the temperature interval of 230–300°C, whereas in the presence of catalytic amount of 2-methyl imidazole, the curing occurs at 200–230°C. Kinetic analysis showed both catalyzed and uncatalyzed systems have similar activation ener-

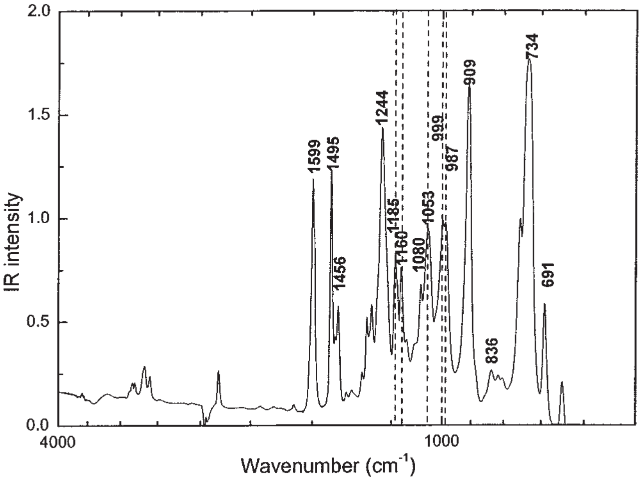
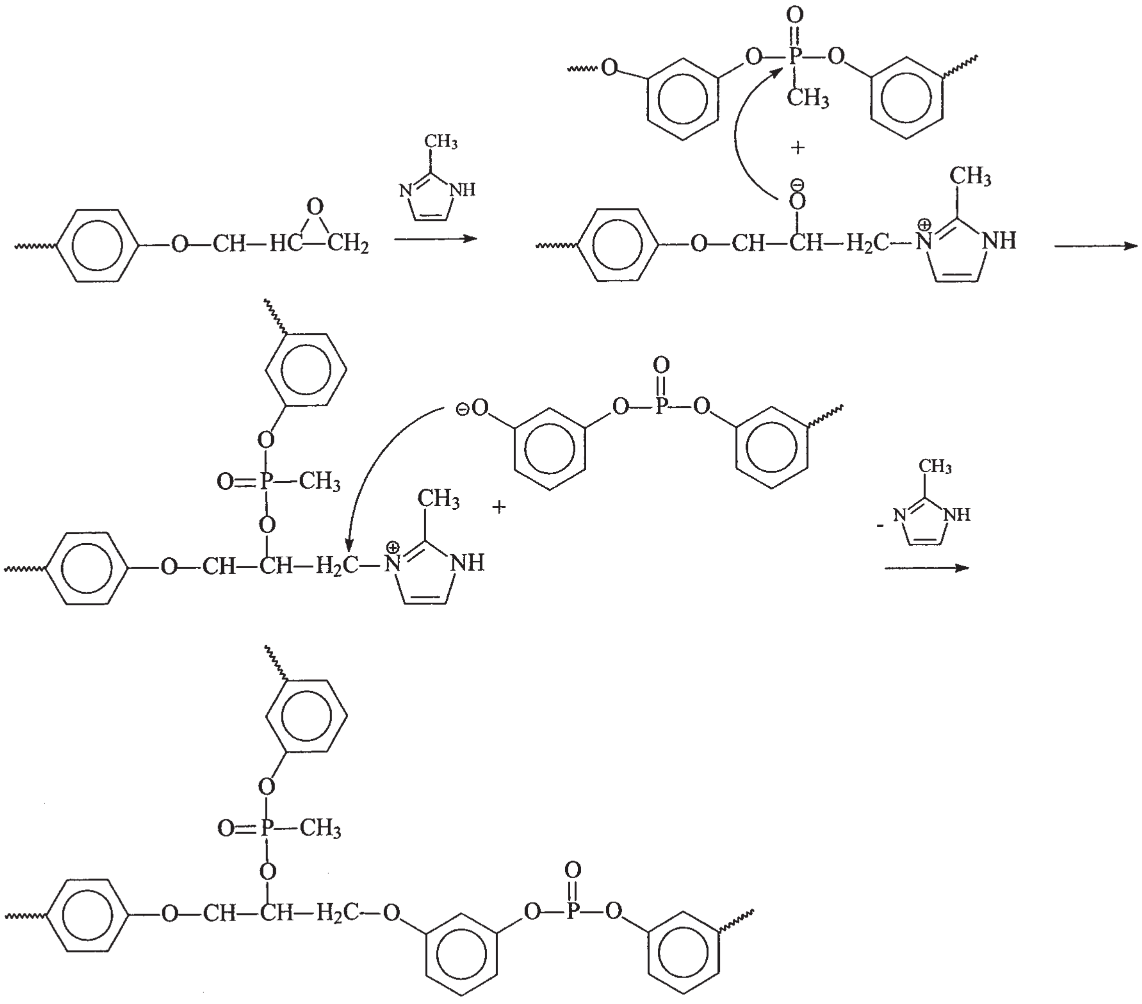


**Figure 16** FTIR spectrum of products of interaction between PMP and 1,2-epoxy-3-phenoxy propane in the presence of 2000 ppm 2-methyl imidazole heated at 150°C over 120 min.

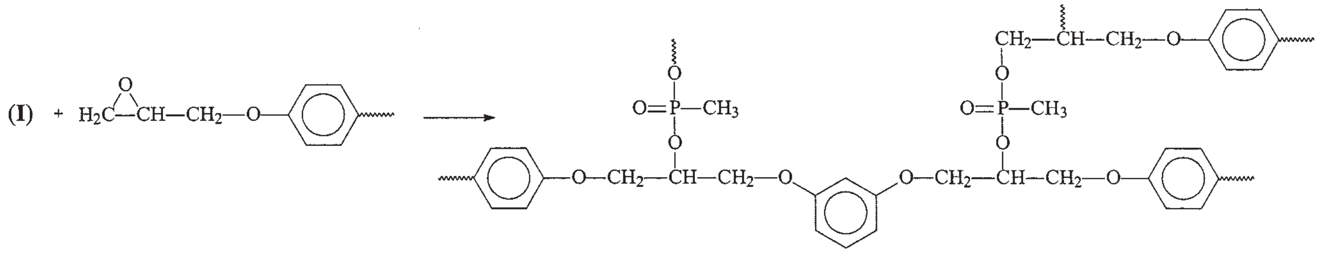


**(I)**

**Figure 17** Scheme of the initial reaction of epoxy with PMP.

gies at the beginning of curing; however, with the progress of crosslinking the activation energy of the uncatalyzed system increases, thus slowing curing, whereas of catalyzed system decreases, thus accelerating curing.

The reaction of PMP with the model compound **1**-phenoxy-2-propanol revealed that although PMP can be transesterified with the secondary alcohol groups present in the commercial epoxy resins, this process is relatively slow and cannot be responsible for curing epoxy with PMP. On the other hand, 1,2-epoxy-3-phenoxy propane simulating epoxy functionality of the commercial epoxy resin reacts with PMP relatively fast, especially in the presence of 2-methyl



**(II)**

**Figure 18** Scheme of advanced curing of epoxy with PMP.

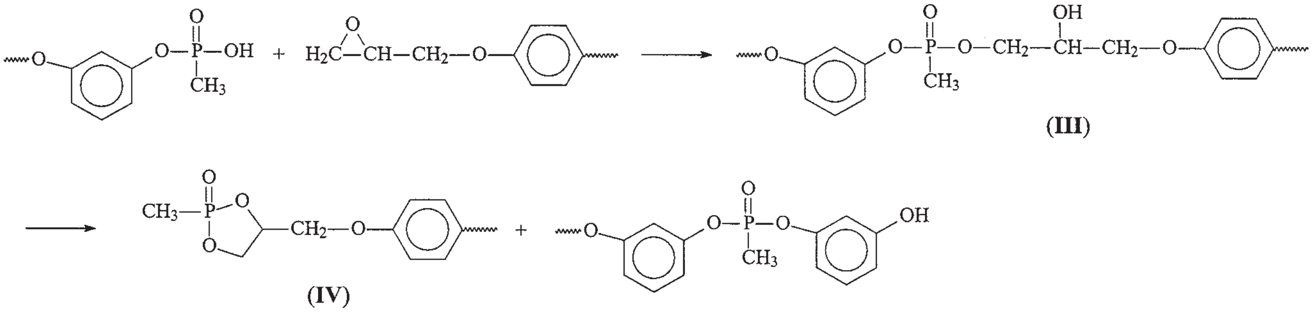


**Figure 19** Scheme of formation of cyclic phosphonates during curing of epoxy with PMP.

imidazole. It was suggested that epoxy groups open and insert into phosphorate ester bonds. This process continues until highly crosslinked structure with Alk—O—P—O—Alk and Alk—O—Ph—O—Alk bridges is formed.

Valuable discussion with Prof. Edward Weil of Polytechnic University of New York is greatly appreciated.

## References

1. Levchik, S. V.; Weil, E. D. Polym Int 2004.
2. Lengsfeld, H.; Altstadt, V.; Sprenger, S.; Utz, R. Kunststoffe 2001, 91, 37.
3. Liu, Y.-L.; Wu, C. S.; Hsu, K. Y.; Chang, T. C. J Polym Sci Polym Chem 2002, 40, 2329.
4. Liu, Y. L. Polymer 2001, 42, 3445.
5. Shieh, J.-Y.; Wang, C.-S. J Appl Polym Sci 2000, 78, 1636.
6. Wang, C.-S.; Lin, C.-H. J Appl Polym Sci 1998, 74, 1635.
7. Chiu, Y.-S.; Jiang, M.-D.; Liu, Y.-L. (to Chung-Chan Institute of Science and Technology, Taiwan), US Patent 6,441,067,2002.
8. Chin, W.-K.; Shau, M.-D.; Tsai, W.-C. J Polym Sci Polym Chem 1995, 33, 373.
9. La Rosa, A. D.; Recca, A.; Carter, J. T.; McGrail, P. T. Polymer 1999, 40, 4093.
10. Shau, M.-D.; Wang, T.-S. J Polym Sci Polym Chem Ed 1996, 34, 387.
11. Varma, I. D.; Gupta, U. J Macromol Sci Chem 1986, A23, 19.
12. Levchik, S. V.; Camino, G.; Luda, M. P.; Costa, L.; Muller, G.; Costes, B.; Henry, Y. Polym Adv Technol 1996, 7, 823.
13. Levchik, S. V.; Camino, G.; Costa, L.; Luda, M. P. Polym Degrad Stab 1996, 54, 317.
14. Levchik, S. V.; Camino, G.; Luda, M. P.; Costa, L.; Muller, G.; Costes, B. Polym Degrad Stab 1996, 60, 169.
15. Tchatchoua, C.; Ji, Q.; Srinivasan, S. A.; Ghassemi, H.; Yoon, T. H.; Martinez-Nunez, M.; Kashtwagi, T.; McGrath, J. E. Polym Prepr 1997, 38, 113.
16. Wang, T.-S.; Yeh, J.-F.; Shau, M.-D. J Appl Polym Sci 1996, 59, 215.
17. Jeong, K. U.; Park, I. Y.; Kim, I. C.; Yoon, T. H. J Appl Polym Sci 2001, 30, 1198.
18. Liu, Y. N.; Ji, Q.; McGrath, J. E. Polym Prepr 1997, 38, 223.
19. Jeng, R.-J.; Shau, S.-M.; Lin, J.-J.; Su, W.-C.; Chiu, Y.-S. Eur Polym Mater 2002, 38, 683.
20. Jeng, R.-J.; Wang, J.-R.; Lin, J.-J.; Liu, Y.-L.; Chiu, Y.-S.; Su, W.-C. J Appl Polym Sci 2001, 32, 3526.
21. Liu, Y.-L.; Hsiue, G.-H.; Lan, C.-W.; Chiule, T.-S. Polym Degrad Stab 1997, 56, 291.
22. Kuo, P.-L.; Wang, J.-S.; Chen, P.-C.; Chen, L.-W. Macromol Chem Phys 2001, 202, 2175.
23. Hoerold, S. (to Clariant). Ger. Pat. Appl. 196,13,067 (1998).
24. Hoerold, S.; Schmitz, H.-P. (to Clariant). Eur. Pat. 0,799,848 (2001).
25. Plundrich, W.; Wipperder, E. (to Siemens). PCT Pat. Appl. 99/45061 (1999).
26. Wipfelder, E.; Plundrich, W. (to Siemens). US Pat. 5,811,486 (1998).
27. Hoerold, S.; Scholz, G. (to Hoechst). Eur. Pat. Appl. 0,794,205 (1997).
28. Weil, E. D.; Tomko, J.; Jaffe, F. (to Akzo America). US Pat. 4,952,646 (1990).
29. Gan, J.; Goodson, A.; Koenig, R.; Everett, J. P. (to Dow Chemicals). PCT Pat. Publ. 99/00451 (1999).
30. Minegishi, S.; Komatsu, S.; Kameyama, A.; Nishikubo, T. J Polym Sci Polym Chem 1999, 37, 959.
31. Levchik, S. V.; Weil, E. D. In Proceedings of 15th Conference on Recent Adv in Flame Retardancy of Polymeric Materials, Stamford, CT, 2004.
32. Levchik, S. V.; Dashevsky, S.; Weil, E. D.; Yao, Q. (to Akzo Nobel). PCT Pat. Appl. 03/029258 (2003).
33. Gorenstein, D. G. In Phosphorus-31 NMR. Principles and Applications; Gorenstein, D. G., Ed.; Academic Press: Orlando, 1984; pp 7–36.
34. Lin-Vien, D.; Colthup, N. B.; Fateley, W. J.; Grasselli, J. G. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press: Boston, 1991.