

Cure Behavior of Epoxy Resins With Different Kinds of Onium Salts as Latent Thermal Catalysts

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Received 4 October 2000; accepted 8 January 2001

ABSTRACT: Two latent thermal catalysts, Dimethyl phenacylsulfonium hexafluoroantimonate, (Benzyl-S), and triphenyl benzyl phosphonium hexafluoroantimonate, (Benzyl-P), were synthesized. Both these synthesized catalysts fulfill requirements for a rapid cure at a moderately elevated temperature in curing the epoxy resins of neat 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate, (EPC), neat 2,2-bis(4-glycidylphenoxy)propane, (EPA), and their hybrid resin. The cure behavior of these resins cured individually with the synthesized catalysts was studied through correlation of the *in situ* FTIR (Fourier transform infrared) spectroscopy and DSC (differential scanning calorimetry) dynamic scanning results. Catalyst Benzyl-S is more effective than Benzyl-P. Resin EPC is significantly more sensitive to the latent thermal catalysts than the EPA resin. Activated chain-end (ACE) and activated monomer (AM) mechanisms are basically adopted. Isomerization occurs in the neat EPA cure system, and transesterification takes place in all systems containing EPC species in the latter curing stage. Most importantly, ester linkages C=O in the hybrid systems have been destroyed at some time during the curing process, but some reformed at the latter curing stage. It is most likely that the C=O linkage in the EPC segments was attacked by the activated chain-end of the epoxide group of EPA species to form a five-membered cyclic acetal. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3539–3551, 2001

Key words: latent catalyst; cycloaliphatic epoxy ester; diglycidyl ether of bisphenol A resin

INTRODUCTION

Epoxy resin is one of the most important thermosetting resins, and is used extensively as a high performance polymer in composite materials, protective coating, and encapsulation materials in the electronics industry. Two major categories of epoxy resins are the cycloaliphatic epoxides and the more familiar glycidyl ethers. Glycidyl ethers are particularly reactive to bases and are especially reactive with polyamine hardener, whereas

cycloaliphatic epoxides are highly reactive to acidic hardeners, such as anhydrides of dibasic acids. Recently, a considerable number of studies have focused on latent catalysts that can generate reactive species to initiate polymerization by appropriate stimulation, for example, through irradiation or heating. Endo and others^{1–5} have reported that benzyl onium salts, such as sulfonium, ammonium, pyridinium, and phosphonium salts, can act as efficient cationic latent catalysts that can polymerize various cationically polymerizable monomers. Some of these onium salts were used as latent catalysts to cure glycidyl ethers^{6–9} and cycloaliphatic epoxides.^{9,10} Cure reactions with onium salts proceed by means of cationic polymerization. The cationic cure of epoxy resins

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Journal of Applied Polymer Science, Vol. 82, 3539–3551 (2001)
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is very rapid and has shown potential in commercially significant industrial processes for liquid reactive systems, which require fast reaction rates.

A perfect latent catalyst for curing liquid epoxy resins should have the following properties: (1) rapid cure at a moderately elevated temperature (100–170°C), (2) indefinite storage life for the catalyzed resin, and (3) no adverse effect on the properties of the cured material. The mentioned onium salts seem to be excellent latent thermal initiators for epoxy resins. These initiators are characterized by easy synthesis and handling due to their reduced hygroscopicity, high dissolvability in the epoxy resin, and a long pot-life. The initiator activity of benzyliodonium salts and benzylphosphonium salts can be enhanced by decreasing the nucleophilicity of the counterion (in this order $\text{BF}_4^- < \text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$).⁸

Differential scanning calorimetry (DSC) is a very effective method for evaluating qualitative and quantitative properties of the cure of thermosetting resins. Two DSC peaks were observed for Epon 828 cured thermally with diphenyliodonium salts.¹¹ It has been suggested that the multiple exotherms were due to two different initiating species that were active at different temperatures. When the catalyst was run with a cycloaliphatic epoxy resin containing no OH group, only one peak was observed in the DSC thermogram, supporting the fact that the reaction of the OH group in the bisphenol A diglycidylether (EPA) resin is responsible for one of the multiple peaks seen. Crivello¹² has also reported that protic impurities such as adventitious moisture can lead to multiple exotherms in the cationic cure of epoxy resins. In the cure reaction of a cycloaliphatic epoxy initiated by a triphenylsulfonium hexafluoroantimonate, a single peak was observed. However, upon addition of water to the formulation, a second higher peak was obtained, indicating that a second chemical reaction took place.

Thermal cationic cure of EPA resin associated with 1-(*p*-methoxybenzyl) tetrahydrothiophenium hexafluoroantimonate was investigated by McGowen et al.⁸ using DSC. The appearance of multiple DSC exotherms reveals a complex cure behavior with the possibility of multiple cure reactions occurring simultaneously or sequentially. Reaction paths in this system including initiation, propagation, transfer, and termination were suggested. Propagation in cationic polymerization of epoxy monomers can proceed by the activated chain-end (ACE) or

activated monomer (AM) mechanism. In addition to the OH group, ACE and AM mechanisms play important roles in the contribution to the multiple peaks of the DSC exotherms. The relative contributions of ACE and AM mechanisms depend on the ratio of monomer to proton donor. Alternatively, peak temperatures and relative size of the exotherms depend strongly on the initiator concentration. Although some transfer reactions were proposed in this cure system, Park et al.¹³ have proved that cationic polymerization using a latent catalyst can be a novel method to suppress the chain-transfer reaction.

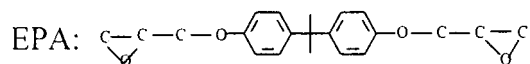
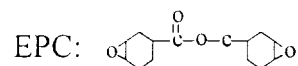
The objectives of this article are to synthesize two kinds of latent thermal catalysts and evaluate the performances of the synthesized catalysts. Cure behavior of different types of epoxy resins (neat liquid cycloaliphatic diepoxide, neat liquid diglycidyl ethers and their hybrid resin) cured individually with the synthesized catalysts were also investigated through correlation of the *in situ* FTIR and DSC dynamic scanning results.

EXPERIMENTAL

Materials

Epoxy Resins

The epoxy resins investigated with the synthesized catalysts were 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (EPC, 252 g/mol), and 2,2-bis(4-glycidyloxyphenyl)propane (EPA, 340.4 g/mol), which were used as purchased (from Union Carbide Corp. U.S.A.; and TCI, Japan, respectively).



Syntheses of Latent Catalysts

Syntheses of the following catalysts arises fundamentally from the methods reported in the literature,^{1,3-5} but with some modifications in this work.

Dimethyl phenacylsulfonium hexafluoroantimonate (Benzyl-S)

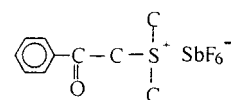
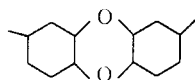


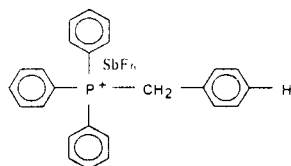
Table I FTIR Spectral Assignments

Chemical Class	Absorbing Group	Wavenumber (cm ⁻¹)
Epoxy resin (EPA)	Epoxide	912
	Ether (AR—O—C)	1247
	—CH ₃	1510
	Aromatic ring	831
Epoxy resin (EPC)	Epoxide	800
	Ester (—COO—)	1731
	—CH ₂ —	1435
	(ester-CH ₂ -cyclohexane)	
Aldehyde	Ether in ester	1243, 1181
	C=O (in —CHO)	1725
Polyether	—O— (Aliphatic)	1075~1160
	ArC—O—C (ali.)	1240
	Ether	880



Phenacyl bromide 9.9525g (0.05 mol) (ϕ -C(=O)—C—Br; Acros Organics, Belgium) and Dimethyl sulfide 3.136g (0.05 mol) (C—S—C; Riedel-de Haen, Germany) were completely dissolved in 50 mL acetonitrile, respectively, then added into a three-neck reactor. Pale-white precipitates appeared after 30 min of reaction at room temperature. The mixture was placed in a refrigerator for 4 h to recrystallize completely. The pure precipitate was obtained by filtrating the resulting mixture, subsequently washed with cold acetonitrile, then dried in a rotatory vacuum. A NaSbF₆ solution and a solution of the pure precipitate were individually prepared by dissolving equal amounts of mole numbers in extra-pure water. The aqueous NaSbF₆ solution was then poured slowly into the solution of the precipitate. After a 1 h reaction at 40°C, the mixture was placed in a refrigerator for 24 h to recrystallize completely. Finally, white crystalline needles emerged from the solution and were obtained by filtrating the solution and drying the crystals.

Triphenyl benzyl phosphonium hexafluoroantimonate (Benzyl-P)



Triphenyl phosphine 13.1145 g (0.05 mol) (ϕ_3 -P; Aldrich Chem. Co., USA) was weighed in and

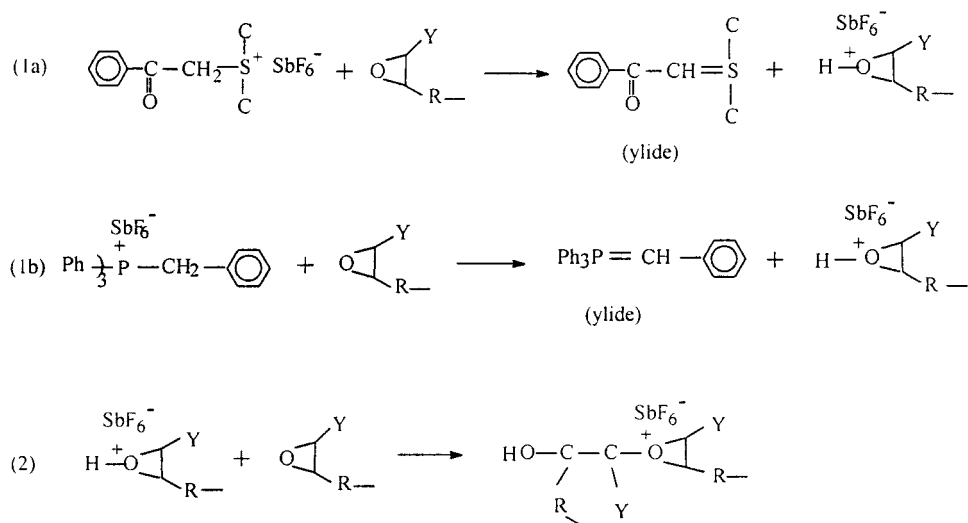
completely dissolved in 35 mL of acetone. Benzyl chloride 9.2785 g (0.05 mol) (ϕ -CH₂Cl; Riedel-de Haen, Germany) was weighed in and poured into the above solution. Reaction proceeded at 50°C for 24 h in a three-neck reactor. The mixture was then placed in a refrigerator for 24 h to recrystallize completely. A white precipitate (P) and a perfect crystal (C) simultaneously appeared. The precipitate (P) was obtained by filtrating the resulting mixture and discarding the perfect crystal, subsequently recrystallized by hot water, and finally dried in a rotatory vacuum. The reaction method for the NaSbF₆ solution with the solution of pure precipitate (P) is virtually the same as described above. The final precipitates were obtained by filtrating the previous mixture, subsequently poured into cold water to remove NaCl, and then filtrated again and dried in the rotatory vacuum.

The crude products were further purified through repeated recrystallization before an ¹H NMR spectrum was taken and an elemental analysis (EA) conducted. Discernible impurity traces were neither identified in the ¹H NMR nor by the EA results. The EA result for Benzyl-S was C÷H = 28.69÷3.18, compared to the theoretical values of C÷H = 28.79÷3.12; for Benzyl-P, C÷H = 50.85÷3.80, compared to the theoretical values of C÷H = 50.96/3.74, all in wt %.

Instrumentation

Differential Scanning Calorimetry (DSC)

Samples approximately 5–8 mg were sealed in hermetic pans and scanned in a differential scan-



Y = H for the EPA resin

Y = CH₂- (a part of cyclohexyl ring containing R) for the EPC resin

Steps 1a and 2 are the initiation steps for the Benzyl-S catalyst

Steps 1b and 2 are the initiation steps for the Benzyl-P catalyst

Scheme 1 Initiation steps in the cure reaction of the EPA and EPC resins initiated by the individually synthesized catalyst (Benzyl-P or Benzyl-S).

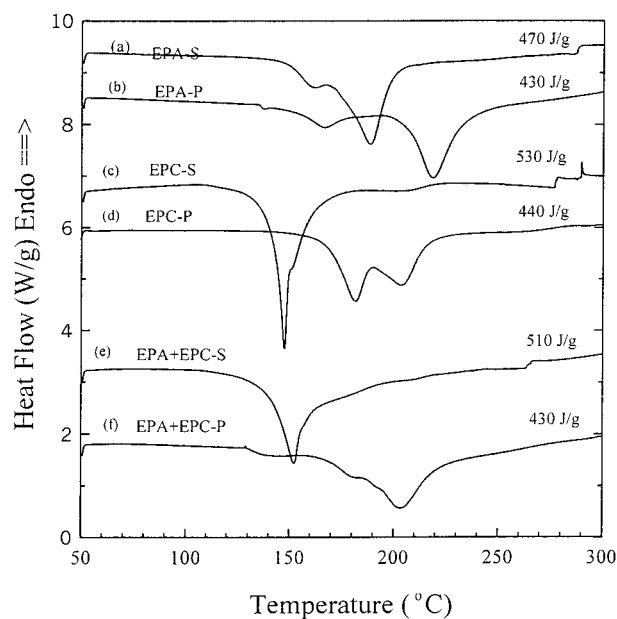


Figure 1 Comparison of DSC thermograms for all cure systems at a heating rate of 5°C/min.

ning calorimeter (Perkin-Elmer DSC-7) calibrated with an indium standard. A stream of nitrogen at a flow rate of 20 mL/min was used to purge the DSC cell.

Fourier-Transform Infrared Spectroscopy (FTIR)

The liquid sample was mixed with KBr powder, pressed into a pellet, and subsequently dried in a desiccator. A Digi-Lab FTS-40 FTIR spectrometer equipped with a temperature-controlled sample holder in a N₂ atmosphere was used to study the cure reaction *in situ*. The cure reaction proceeded at a heating rate of 5°C min⁻¹ in the FTIR cell. Spectra were obtained in an optical range of 400 cm⁻¹–4000 cm⁻¹ by averaging 6 scans at a resolution of 8 cm⁻¹ to minimize the effects of dynamic scanning.

Dynamic Mechanical Analyzer (DMA)

Gel point and gelation time were determined through measurement of the complex viscosity with Perkin-Elmer dynamic mechanical analyzer (DMA-7) equipped with a thermal mechanical analyzer (TMA). Temperature was calibrated with

an indium standard. Temp/time scan mode in parallel plate with tray was used at a heating rate of 5°C/min. The frequency, amplitude, and tension were set 1 Hz, 2 μm , and 105%, respectively. A stream of nitrogen at a flow rate of 30 mL/min was used to purge the DMA cell.

RESULTS AND DISCUSSION

A specified initiator (5 phr) was added to the epoxy resins and mixed thoroughly with a spatula for the sample preparation. Through continuous mixing, the initiator was dissolved slowly in the epoxy resin to a state with no indication of undissolved onium salt. Mixed samples were sealed in hermetic pans for DSC scans and pressed into KBr pellets for FTIR runs. Characteristic infra-

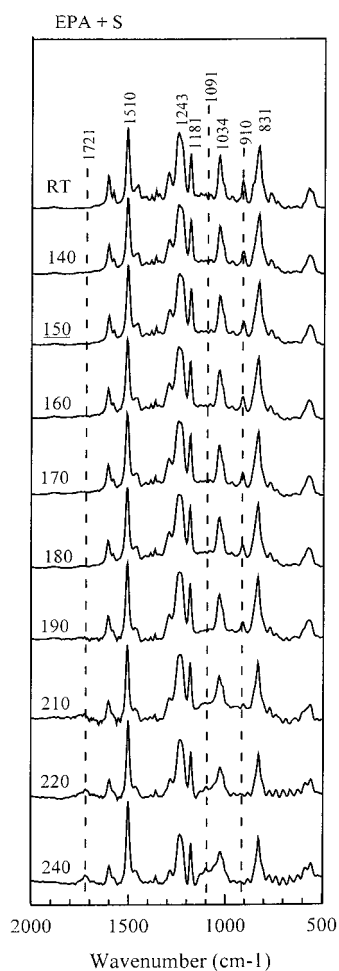


Figure 2 Some crucial representative FTIR spectra for the curing system of neat EPA with Benzyl-S at a heating rate of 5°C/min.

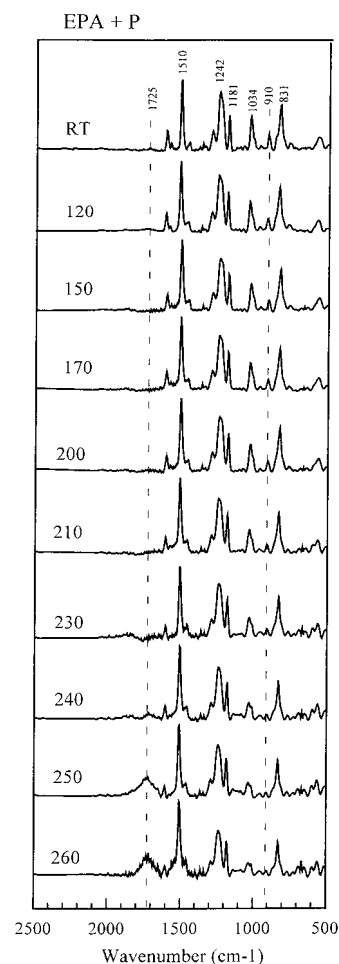
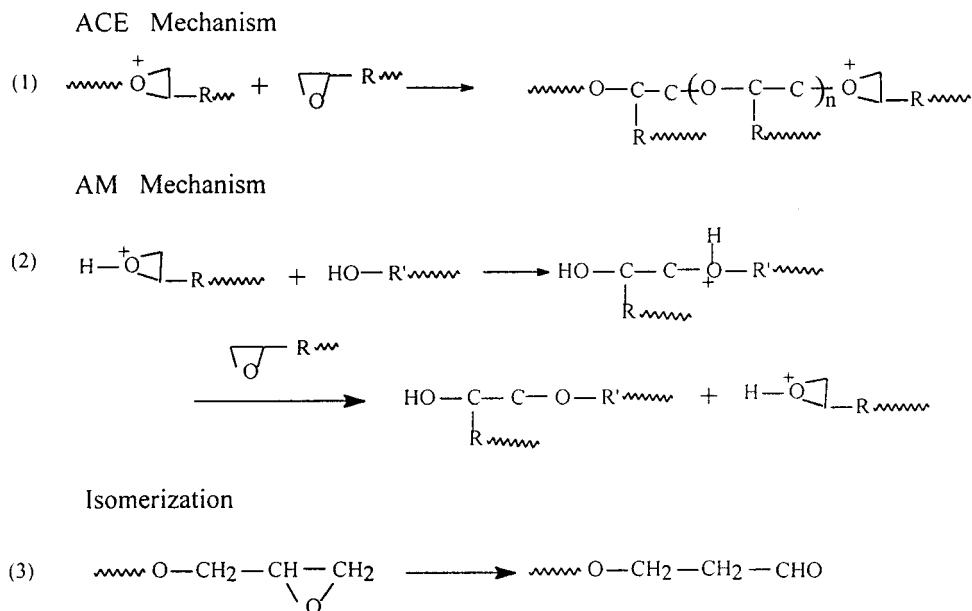


Figure 3 Some crucial representative FTIR spectra for the curing system of neat EPA with Benzyl-P at a heating rate of 5°C/min.

red spectral absorptions for the possible structures in the following systems are listed in Table I. Some of those assignments resulted from FTIR spectra of neat EPC and neat EPA, and some are from Pretsch et al.¹⁴

It has been mentioned that a lot of onium salts can readily polymerize various cationically polymerizable monomers. Initiation steps of EPA by the Benzyl-P have been proposed by Takuma et al.⁷ The initiation species in this polymerization should not be the benzyl cation but a proton liberated from the benzyl methylene, because ease of proton abstraction in the benzyl phosphonium salts increases with an increase of the electron-withdrawing capacity of the substituent of the benzyl group, the stability of the corresponding benzyl phosphonium ylide. Initiation of the Benzyl-S also results in a reversible loss of a proton with the concomitant formation of a resonance-



Scheme 2 Cure reactions for the EPA/Benzyl-S or EPA/Benzyl-P cure systems.

stabilized ylide.¹⁵ The initiation steps in the cure reaction of EPA, EPC and their hybrid resins initiated by the individually synthesized catalysts (Benzyl-P or Benzyl-S) are proposed in Scheme 1.

EPA Cure System

Shown in Figure 1(a) and 1(b) are the DSC thermograms of the EPA resin cured with Benzyl-S and Benzyl-P, respectively, at a heating rate of 5°C/min. Two distinct, but somewhat overlapping, exothermic peaks were observed. The cure reactions of the EPA/Benzyl-S system proceeded at a lower temperature than that of the EPA/Benzyl-P system and the total reaction heat (ΔH) of the EPA/Benzyl-S system (470 J/g) is also slightly larger than that of the EPA/Benzyl-P system (430 J/g), implying that Benzyl-S is more effective than Benzyl-P.

To be able to compare the FTIR spectra and the DSC thermograms, we performed the infrared study for the dynamic cure of this system at the same heating rate (5°C/min) from room temperature to 250°C. Although there is a slight uncertainty as to the exact heating rate used for FTIR work, the progressive temperature increase between the FTIR spectra and the corresponding DSC thermograms is comparable. The FTIR scans were performed at each 10°C incremental sequence of progressively ascending temperature during the heating. Some crucial representative

FTIR spectra of EPA/Benzyl-S (Fig. 2) and EPA/Benzyl-P (Fig. 3), are shown taken during the dynamic heating to compare to the DSC thermograms. Both dynamic FTIR spectra show that the reactions which occurred were virtually identical, except that they might take place in a somewhat different temperatures. Disappearance of the epoxide peak (910 cm^{-1}) occurs earlier in the EPA/Benzyl-S system than in the EPA/Benzyl-P system, a result in accordance with the DSC observations. In the earlier stage, the intensity of the epoxide peak (910 cm^{-1}) gradually declined (as compared with the internal standard peak, $-\text{CH}_3$, 1510 cm^{-1}), but the intensity of an ether linkage formed instead was not apparent due to the fact that it was immersed in the original peak (1242 cm^{-1}). In the latter stage, the absorption peak of $\text{C}=\text{O}$ (1725 cm^{-1}) was emerging, presumably due to the formation of an aldehyde via epoxide isomerization. The possibility of epoxide isomerization to form aldehyde had been proved,¹⁶ especially for the diffusion-controlled regime in the cure system.

To explain the double exotherms in the DSC thermograms, we adopted the ACE and AM mechanisms. In Scheme 2, cure reactions are suggested for the EPA/Benzyl-S cure system. In addition to ACE and AM mechanisms, epoxide isomerization to form aldehyde is also included. The cure reactions of the EPA/Benzyl-P cure system are virtually the same as for the EPA/Ben-

zyl-S. Observed double exotherms were apt to be due to the different contributions of ACE, AM mechanisms and adventitious moisture. Epoxide isomerization occurred, probably due in part to vitrification, but the evolved heat of this reaction was not significantly detectable.

EPC Cure System

Shown in Figure 1(c) and 1(d) are the DSC thermograms of EPC resin cured with Benzyl-S and Benzyl-P, respectively, at a heating rate of 5°C/min. Only one very sharp exotherm was observed in the EPC/Benzyl-S system, but two and somewhat overlapping exotherms were observed for the EPC/Benzyl-P system. The cure reaction of the EPC/Benzyl-S system proceeded at a lower temperature than that of the EPC/Benzyl-P sys-

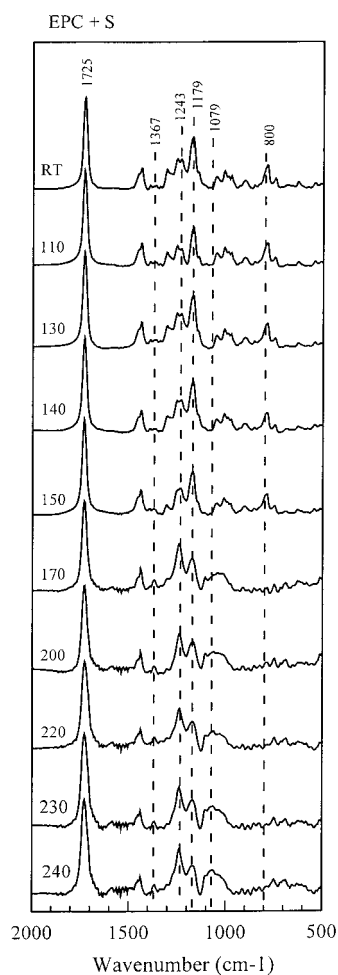


Figure 4 Some crucial representative FTIR spectra for the curing system of neat EPC with Benzyl-S at a heating rate of 5°C/min.

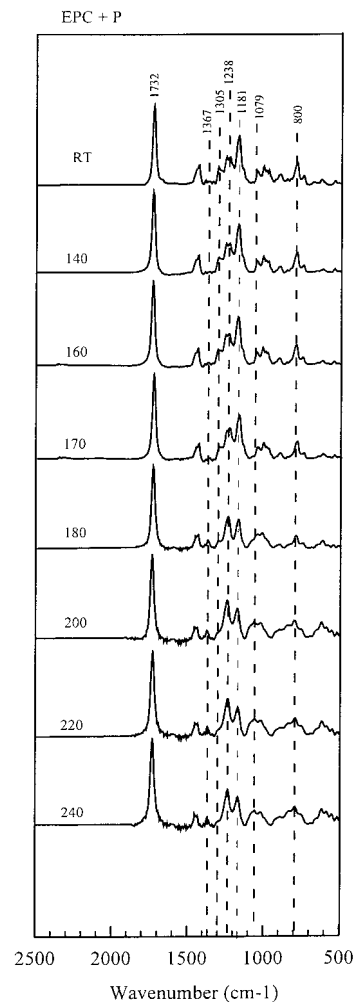
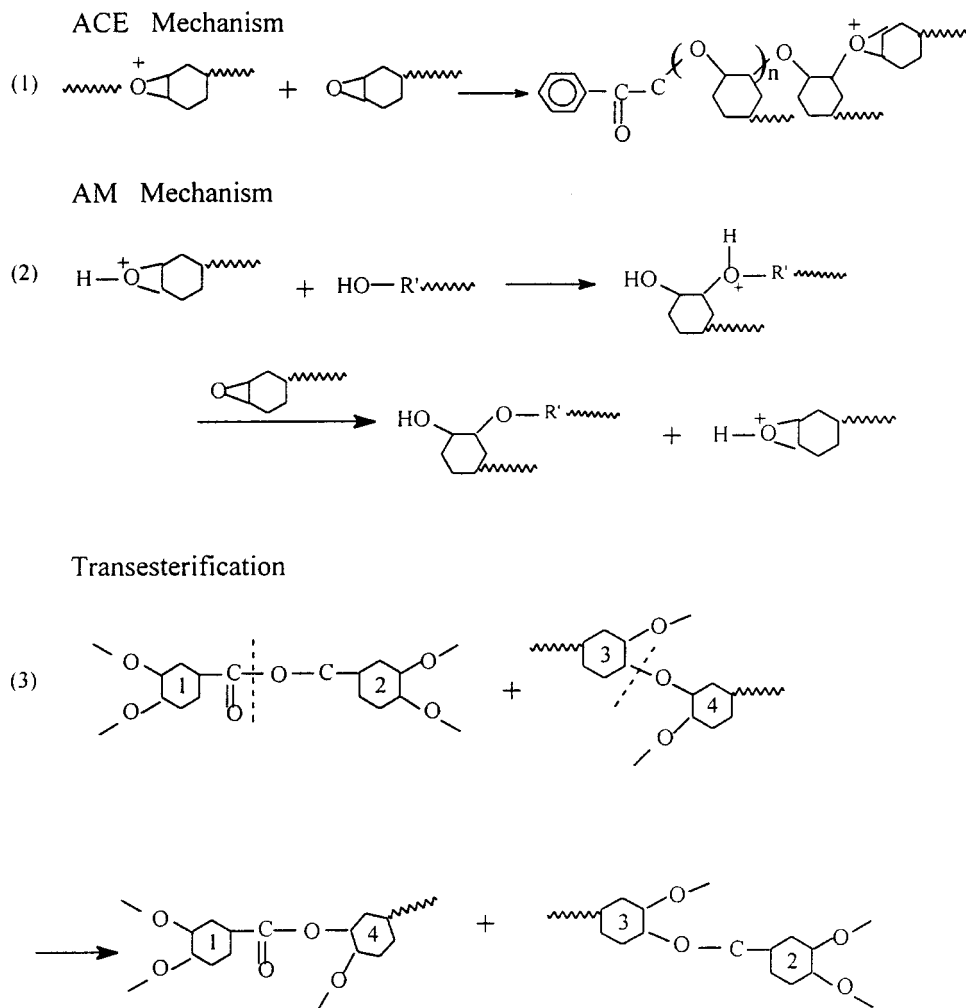


Figure 5 Some crucial representative FTIR spectra for the curing system of neat EPC with Benzyl-P at a heating rate of 5°C/min.

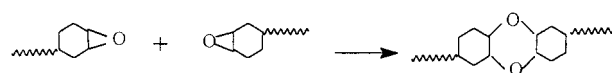
tem. The total reaction heat (ΔH) of the EPC/Benzyl-S system (530 J/g) is larger than that of the EPC/Benzyl-P system (430 J/g). As previously described in the EPA system, Benzyl-S is more effective than Benzyl-P in the EPC system. Some unreacted epoxide groups remained in the EPC/Benzyl-P system due to vitrification, because the cure reactions of this system proceeded at a higher temperature near the vitrification region. Compared to the EPA system, Benzyl-S proved to be more sensitive to EPC resin.

Shown in Figure 4 and Figure 5 are some crucial representative FTIR spectra of EPC/Benzyl-S and EPC/Benzyl-P, respectively, taken during the dynamic heating. Both dynamic FTIR spectra show that the reactions which occurred were essentially the same except that they might take



Scheme 3 Cure reactions for the EPC/Benzyl-S cure system.

place in a somewhat different temperature. As the temperature gradually increased, the epoxide peak (800 cm^{-1}) disappeared, and peaks emerged at 1376 , 1243 , $1070\sim 1100\text{ cm}^{-1}$ and declined at 1179 cm^{-1} (as compared with the internal standard peak, ester $-\text{C}(\text{O})-\text{O}-$, 1725 cm^{-1}). These peaks resulted from the formations of various ethers in the different environments. In Scheme 3, cure reactions are proposed for the EPC/Benzyl-S cure system, including the ACE, AM mechanisms and a transesterification. The ether peak at 1243 cm^{-1} resulted from the ACE and AM reactions, whereas the increasing peaks at 1376 , $1070\sim 1100\text{ cm}^{-1}$, and the decreasing peak at 1179 cm^{-1} came from the transesterification. The cure reactions for the EPC/Benzyl-P cure system are almost the same as for the EPA/Benzyl-S cure system, except for the cycloetherification.



The absorption band at 880 cm^{-1} in the EPC/Benzyl-P cure system probably arose from the formation of a six-membered cycloether via a head-to-head method. Cycloetherification seems reasonable at the elevated temperature, because some unreacted epoxide groups still remain under vitrification conditions.

EPA/EPC Hybrid System

A hybrid system of EPA/EPC in a weight ratio of 1:1 (mol ratio of 0.74:1) was prepared to study the reaction behavior through correlation of the dynamic FTIR spectra and DSC thermograms. Shown in Figure 1(e) and 1(f) are the DSC ther-

mograms of the EPA/EPC hybrid resin cured with Benzyl-S and Benzyl-P, respectively, at a heating rate of 5°C/min. Only one exotherm was observed in the EPA/EPC/Benzyl-S system, but multiple broad exothermic peaks were observed for the EPA/EPC/Benzyl-P system. As previously described, Benzyl-S is still more effective than Benzyl-P in this hybrid system. The peak temperature of the DSC exotherm in the EPA/EPC/Benzyl-S system is located at 153°C, whereas that of the EPA/EPC/Benzyl-P system is at 204°C.

Shown in Figure 6 and Figure 7 are some crucial representative FTIR spectra of EPA/EPC/Benzyl-S and EPA/EPC/Benzyl-P, respectively, taken during the dynamic heating. In these spectra, the peak of $-\text{CH}_3$ groups (1509 cm^{-1}) in the EPA segments was taken as the internal stan-

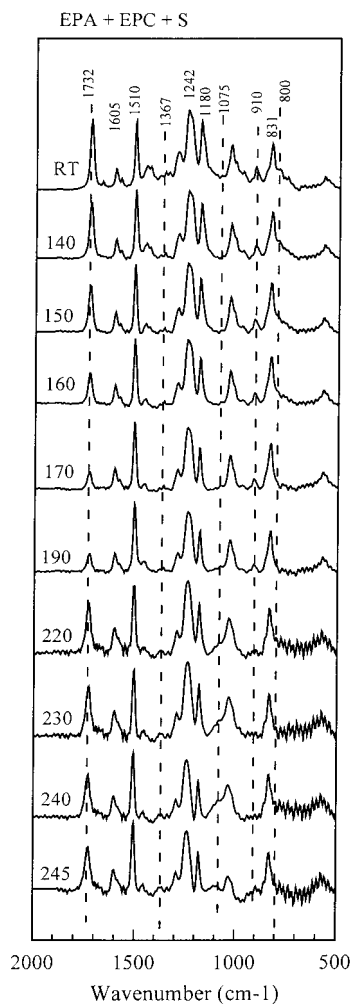


Figure 6 Some crucial representative FTIR spectra for the curing system of EPA/EPC hybrid resin (weight ratio 1:1) with Benzyl-S at a heating rate of 5°C/min.

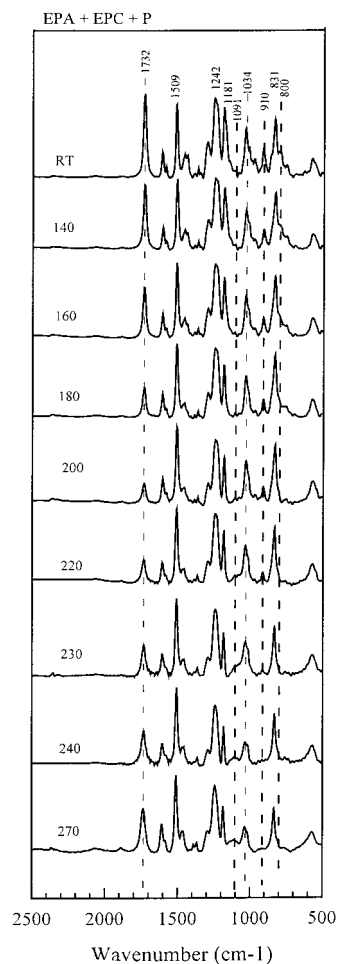
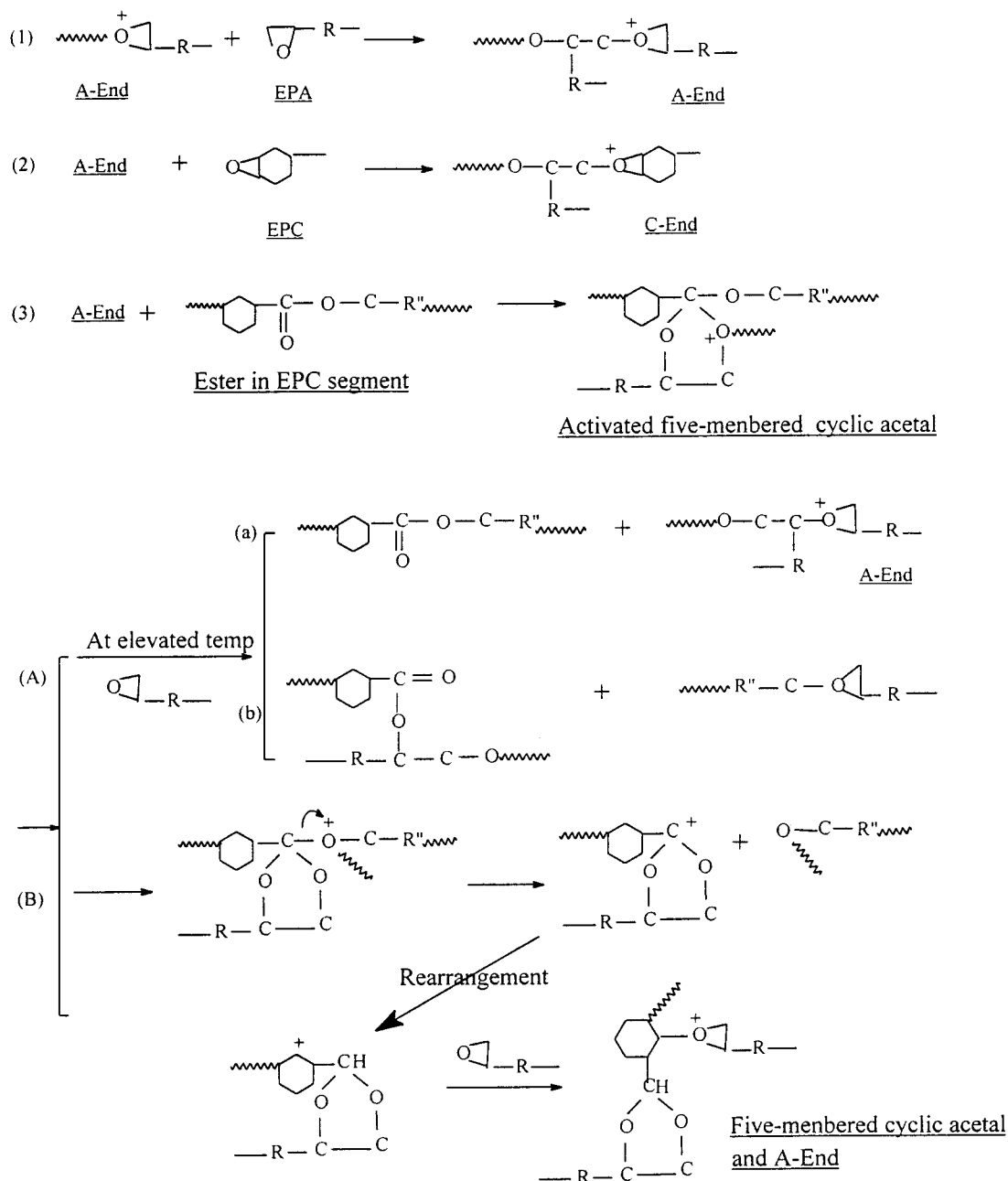


Figure 7 Some crucial representative FTIR spectra for the curing system of EPA/EPC hybrid resin (weight ratio 1:1) with Benzyl-P at a heating rate of 5°C/min.

dard peak. Changes in intensities of all corresponding peaks for both dynamic FTIR spectra were virtually the same. Although mol numbers of EPC epoxide groups were larger than that of EPA epoxide groups, EPC epoxide groups were always completely consumed earlier than EPA epoxide groups, indicating that the EPC epoxide groups were more active than the EPA groups using these latent thermal catalysts. Taking the EPA/EPC/Benzyl-P system as an example, we found that the EPC epoxide groups were completely consumed at 200°C, whereas the EPA epoxide groups were only completely consumed at 240°C. In contrast to the DSC results, although the total reaction heat (ΔH) of the EPA/EPC/Benzyl-S system (510 J/g) was substantially larger than that of the EPA/EPC/Benzyl-P system (430 J/g), we did not find unreacted epoxide groups remaining in the FTIR spectra for the latter sys-

ACE Mechanism



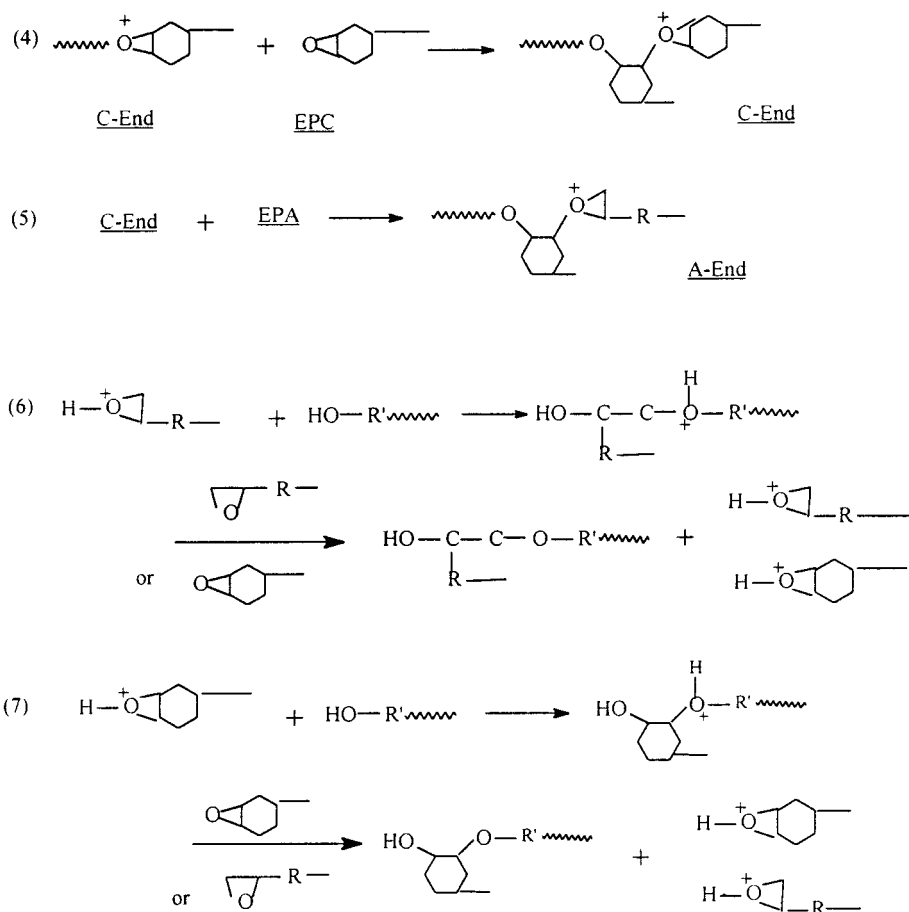
Scheme 4 Cure reactions for the EPA/EPC hybrid resin cured with Benzyl-S or with Benzyl-P.

tem. The reason for this is not clear; it could be due to a complex kinetic behavior.

Diminishing of epoxide peaks (910 cm^{-1} for EPA and 800 cm^{-1} for EPC) was accompanied by the emerging peaks at 1376 , $1070\sim 1100\text{ cm}^{-1}$ and a declining peak at 1179 cm^{-1} . As for 1242 cm^{-1} , the change was not visible since the peak

was immersed in the original peak as described in the EPA system. Most of the phenomena observed here can be attributed to the behavior of a combined neat EPA and neat EPC system. But surprisingly, intensity of ester band at 1732 cm^{-1} significantly varied with the scanning temperature. Initially, this band is reduced by a factor of

AM Mechanism



Transesterification

(8) the same as eq. (3) in Scheme 3

Scheme 4 (Continued from previous page)

about 4 and then increases gradually to some extent (about half of the original value) in the latter stage. This phenomenon was not observed in the neat EPC cure system, indicating that the decrease in the intensity of C=O did not result from H-bonding. These results indicate that some of C=O in the ester linkages have been destroyed during the curing process. This could mean that the C=O in the ester linkages within the EPC segments were attacked by the activated chain-end of epoxide group of EPA species to form an activated five-membered cyclic acetal, shown in Equation 3 in Scheme 4, then followed by the

other two main paths. One main path is the recovery of the ester linkages C=O from this unstable five-membered cyclic acetal, shown in Equation 3A. The other main path is the formation of a stable five-membered cyclic acetal from the unstable five-membered cyclic acetal via rearrangement, shown in Equation 3B, illuminating the permanent disappearance of the ester linkages C=O. These inferences can explain the fact that the intensity of the C=O band was substantially reduced in the early stage and then recovered gradually to some extent (but never completely). There are two ways for the recovery of

the ester linkages C=O from this unstable five-membered cyclic acetal, shown in Equations 3Aa and 3Ab. The position of the peak of C=O did obviously not shift, implying that the environment of the recovered ester linkage did not change; Equation 3Aa predominated. Scheme 4 proposes the reaction paths for the hybrid systems (both EPA/EPC/Benzyl-S and EPA/EPC/Benzyl-P cure systems), including ACE, AM mechanisms and transesterification. We cannot distinguish which reaction or reactions in Scheme 4 are predominant in these hybrid systems. But, it should be pointed out that Equation 3 in Scheme 4 always plays an important role in these hybrid systems. Incidentally, the isomerization in the EPA system and the cycloetherification in the EPC/Benzyl-P cure system were not observed in this hybrid system. The inferred structure of the five-membered cyclic acetal will be further verified using model compounds and solid-state ^{13}C -NMR in our laboratory.

Evaluation of the Pot-Life and Vitrification Time of the Prepared Samples

Pot-lives of both types of epoxy resins mixed either with Benzyl-S or with Benzyl-P were longer than five months. No viscosity change was observed during this period of storage time. Gelation time was defined here as the time starting from the onset point of gelation to the state of

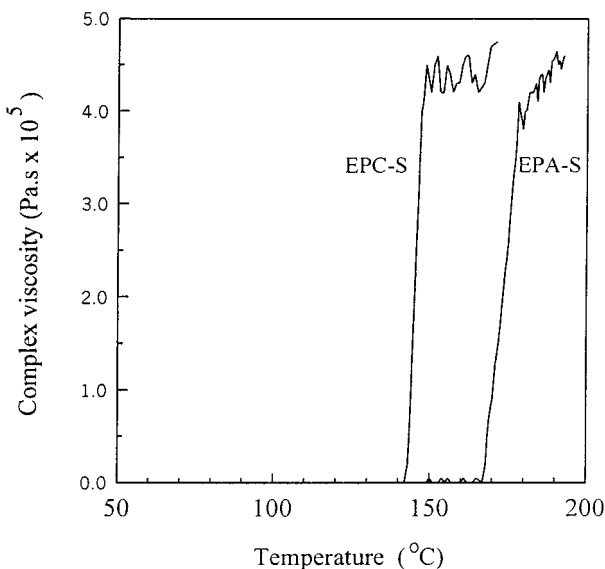


Figure 8 DMA plot of complex viscosity versus temperature for the EPC/Benzyl-S and EPA/Benzyl-P, respectively, using a heating rate of 5°C/min.

Table II Some Physical Properties for the Various Curing Systems

Curing System	Gelation Temp. (°C)	Gelation Time (min)	T_g (°C)
EPA/Benzyl-S	167	110	271
EPA/Benzyl-P	208	150	285
EPC/Benzyl-S	143	55	265
EPC/Benzyl-P	174	170	282
EPA/EPC/Benzyl-S	146	60	265
EPA/EPC/Benzyl-P	180	180	283

infinite viscosity. Shown in Figure 8 is the DMA plot of complex viscosity versus temperature for the EPC/Benzyl-S and EPA/Benzyl-P systems, respectively, using a heating rate of 5°C/min. The gelation temperatures, gelation times and glass-transition temperatures (T_g) for the various cure systems are listed in Table II. Rapid cure at this moderately elevated temperature matches one of the requirements of a perfect latent catalyst.

CONCLUSIONS

Latent thermal catalyst Benzyl-S is a very efficient initiator for EPC resin to undergo cure reaction. It shows rapid cure (vitrification time ca. 45 s) when the temperature of this system reaches 148°C by a heating rate of 10°C/min. Catalyst Benzyl-S is more effective than Benzyl-P. This can probably be partially attributed to the melting point of Benzyl-S, which is lower than that of Benzyl-P. Resin EPC is significantly more sensitive to the latent thermal catalysts than EPA. By the same token, resin EPC is a very promising liquid epoxy resin for future use as an encapsulation material.

In addition to traditional ACE and AM reaction paths, some minor reactions were observed in the latter stage for some of the specified cure systems. Isomerization occurs in the neat EPA cure system, and transesterification takes place in all systems containing EPC species. More surprisingly, ester linkages C=O in the hybrid systems have been destroyed at some time during the curing process; but some reformed at the latter curing stage, which can probably be attributed to the formation of a five-membered cyclic acetal via the cure reaction.

The financial support of the National Science Council under contract number NSC-88-2216-E-151-003 is gratefully acknowledged.

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