

Network Formation During Cocure of Phenolic Resins with Vinyl-Ester and Epoxy-Amine Systems for Use in Multifunctional Composites

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Received 27 September 2002; accepted 5 August 2003

ABSTRACT: Traditionally, multilayered composites have been manufactured in multiple steps that involve the fabrication of each layer separately and the bonding them together by using adhesives or secondary bonding. More recently, manufacturing techniques have been developed that enable the manufacture of multilayered hybrid composite parts in a single step. In one such technique known as coinjection resin transfer molding (CIRTM), two or more resins are simultaneously injected into a mold filled with a stationary fiber bed. This method not only cuts down manufacturing costs and time, but also offers the potential of cocure of the adjacent thermosetting resins inside the mold, which could aid in the formation of a tougher interphase between the layers and improve long-term durability. The advantages offered by coinjection are, however, dependent on the successful cocure of the resins involved, and hence, there exists a need to determine compatible resin systems for coinjection. By compatible, it is meant that the resins must cure when in contact with each other, have compatible cure cycles (i.e., cure temperature, cure time, etc.), and result in acceptable physical and mechanical properties. The most commonly used matrix resins are vinyl-ester resins. The cure

of vinyl-ester resin was found to be severely limited by contact with phenolic resin. This necessitates an impermeable separation layer between phenolic and vinyl-ester resins in CIRTM manufacture. A possible candidate for this separation layer was epoxy-amine-based prepregs or adhesive layers. Thus, the cocure of mixtures of phenolic with epoxy-amine was studied, and it was found that phenolic resin significantly affects the cure of epoxy-amines. A model to quantify the effect of phenolic resin on the cure of epoxy-amines has been proposed. By using this model, the fraction of primary amine consumed by the phenolic can be estimated. It was found that increasing the initial amine concentration in the cocure reaction mixture leads to an increase in the epoxy conversion as well as the T_g of the material. Therefore, it is recommended that, in cocure of epoxy-amine and phenolic resins, the initial concentration of amine must be greater than the stoichiometric amount to compensate for the loss of amine to the phenolic resin. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3107–3119, 2004

Key words: resins; composites; curing of polymers

INTRODUCTION

Glass fiber reinforced polymers (GRP) composites based on thermosetting resins, such as vinyl-esters and epoxies, have been used for many years for their strength and lightweight properties. A major application of these materials is in the defense industry for making bodies of aircrafts and armored vehicles. All these applications require resins and GRP composites to have fire-retardant properties along with the excellent physical and mechanical properties that they possess. Phenolic resins and GRP-phenolic composites are inherently fire-retardant materials due to the aromatic ring structure of phenol. They yield low levels of smoke and combustion products under both flaming

and smoldering fire conditions. It is for this reason that phenolics constitute the lining of GRP-composites in armored vehicles and other such applications where fire resistance is a critical requirement.

Traditionally, multilayered composites have been manufactured in multiple steps that involve the fabrication of each layer separately and then the bonding of them together by use of adhesives or secondary bonding. More recently, manufacturing techniques have been developed that enable the manufacture of multilayered hybrid composite parts in a single step. One such technique is called coinjection resin transfer molding (CIRTM).¹ In CIRTM, two or more resins are simultaneously injected into a mold filled with a stationary fiber bed. This method not only cuts down manufacturing costs and time but also offers the potential of cocure of the adjacent thermosetting resins inside the mold, which could aid in the formation of a tougher interphase between the layers and improve long-term durability. Cocure of adjacent layers enhances mechanical properties by improving bonding

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Contract grant sponsor: U.S. Army Research Labs.

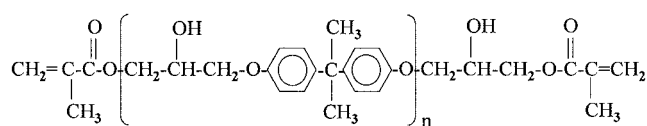
between the layers and also by allowing previously nonstructural layers to provide structural contribution to the part.

The advantages offered by coinjection are, however, dependent on the successful cocure of the resins involved, and hence, there exists a need to determine compatible resin systems for coinjection. By compatible, it is meant that the resins must cure when in contact with each other, have compatible cure cycles (i.e., cure temperature, cure time, etc.), and result in acceptable physical and mechanical properties.

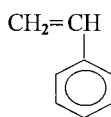
The study presented here is part of ongoing work directed toward investigating phenolic resins and their compatibility with other matrix resins used for GRP composite manufacture through CIRTM. Vinyl-ester resins are commonly used matrix materials for use in resin transfer molding applications. In this work, the cure of vinyl-ester resin was found to be severely limited by contact with resole phenolic systems. This necessitates a practically impermeable separation layer between phenolic and vinyl-ester resins in CIRTM manufacture. Possible candidates for this separation layer include epoxy-amine-based prepregs or adhesive layers. Thus, the cocure of phenolic with epoxy-amine was studied, and it was found that phenolic resin significantly affects the cure of epoxy-amines.

MATERIALS

The phenolic resin used was BPJ2027L, containing 70–80% phenol-formaldehyde solids, 11–12% water, 7–10% free phenol, and 1–2.5% formaldehyde. The complete characterization of this resin using solution ^{13}C -NMR is presented elsewhere.² The catalyst used in this study was BP Phencat 381, which is a delayed

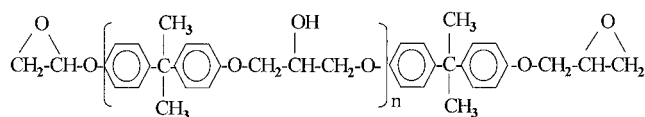


(a) vinyl-ester

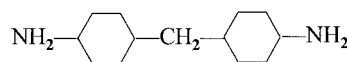


(b) Styrene

Figure 1 Chemical structure of (a) vinyl-ester monomer derived from diglycidyl ether of bisphenol A (DGEBA) and methacrylic acid and (b) styrene monomer.



(a) DGEBA



(b) PACM 20

Figure 2 Chemical structures for (a) DGEBA-based epoxy resin. EPON 828 resin is a DGEBA-based system having an average n value of 2 and (b) cycloaliphatic amine curing agent PACM 20 [bis(*para*-amino-cyclohexyl)-methane].

action catalyst. The major constituent of this catalyst is *p*-toluenesulfonic acid. The delayed action of this catalyst affords enough time after mixing for injection into the mold, making it ideal for use in VARTM. Concentration of the catalyst was 4 wt % of phenolic resin in all cases.

The vinyl-ester resin used in this study, Derakane 411-C50, was supplied by Dow Chemical Co. This resin contains 45% styrene by weight. Figure 1 shows the structure of the vinyl ester and styrene monomers. The free-radical initiator used in the reactions was Trigonox, purchased from Akzo Co. It contains 45 wt % cumyl hydroperoxide, 45 wt % carboxylic ester, and 10 wt % cumyl acid. The concentration of the initiator was maintained at 2% by weight of the resin in all cases. Cobalt Napthenate (CoNap, 0.2 wt %), containing 6 wt % cobalt, was used as an accelerator to induce decomposition of the initiator at low curing temperatures.

The epoxy resin, EPON 828, based on diglycidyl ether of bisphenol-A (DGEBA), was purchased from Shell and the amine curing agent PACM 20 [bis(*para*-amino-cyclohexyl)-methane] was supplied by Air Products and Chemicals. The chemical structures of DGEBA and PACM 20 are shown in Figure 2.

The compositions of the two cocure systems in the experiments performed were as follows: different concentrations of BPJ2027 containing 4% by its weight of Phencat 381 were mixed with vinyl-ester 411-C50 containing 2% by its weight of Trigonox and 0.2% CoNap for the vinyl-ester/phenolic cocure experiments. To conduct experiments on the epoxy-amine/phenolic cocure system, EPON 828, with a stoichiometric amount of PACM 20, was mixed with different concentrations of phenolic resin also containing 4% of its weight of Phencat 381. A stoichiometric amount of PACM 20 in Epon 828 means that there is one-half mole of PACM 20 for each mole of Epon 828, because

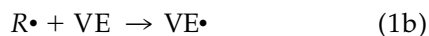
each amine group can react with two epoxy groups. The molecular weights of PACM 20 and EPON 828 are 210 and 368 g/mol, respectively. Thus, well-mixed blends of epoxy-amine containing 0, 5, 10, 20, 50, and 60 wt % phenolic were investigated. All the experiments were conducted at 60°C.

Cure chemistry of the resins

It is important to introduce the cure chemistry of the three resins systems under investigation and also the chemistry of cocure and possible mutual interactions of vinyl-ester/phenolic and epoxy-amine/phenolic systems before going into the experimental details.

Free-radical cure of vinyl-ester resins and the effect of inhibitors

The vinyl-ester cure process is a free-radical chain growth bulk copolymerization. For such systems, the course of polymerization can be broken down into three stages: initiation, propagation, and termination. The initiation steps for the polymerization can be depicted as follows for simplicity:



In the above representation, I refers to the initiator, while $R\cdot$ refers to the primary free radical. VE and ST refer to the vinyl-ester and styrene monomers, respectively, while $VE\cdot$ and $ST\cdot$ refer to the monomer radicals. Not all of the radicals released in step (1a) yield chain reactions. Some of them may be lost through side reactions with inhibitors. Inhibitors present in the reaction mixture may consume the primary or monomer radicals. These inhibitors react very rapidly by combining with the initiating free radicals through their unpaired electron, thus converting them to lower reactivity species that are not capable of initiating chain growth. This severely reduces the rate of polymerization until the inhibitor is completely consumed in the process. The efficiency of an inhibitor depends on the following three factors: (1) the chain transfer constant of an inhibitor with respect to a particular monomer; (2) the reactivity of the inhibitor radical that forms; and (3) the reactivity of the particular monomer.

Once the concentration of free radicals produced exceeds the inhibitor concentration and all the inhibitor is consumed, the polymerization rate increases because of the propagation of monomer radicals, as follows:

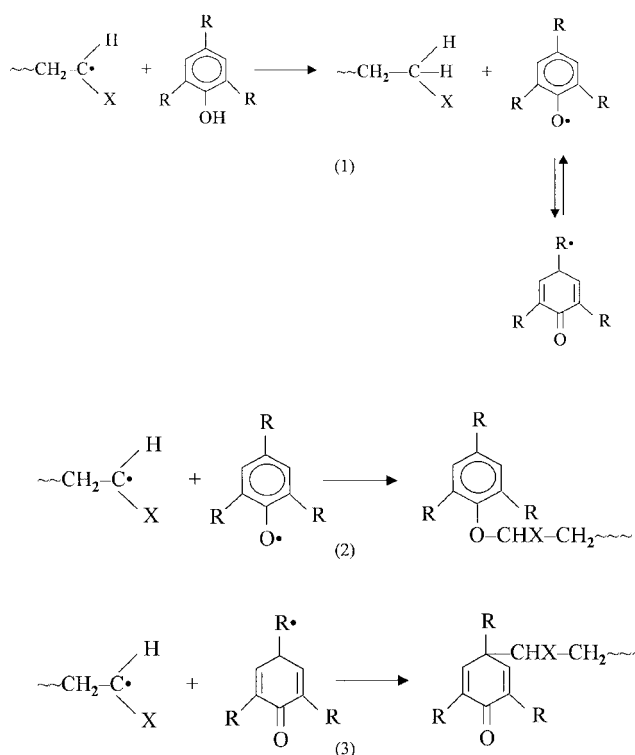
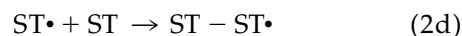
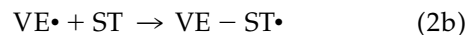
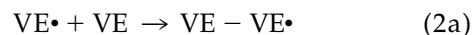


Figure 3 Three proposed schemes for the inhibition of free-radical polymerization by phenols.⁴



Termination involves the reaction of two radicals and can occur by combination and disproportionation. These reactions are discussed in detail elsewhere.³

The most important point to consider in the above discussion is that it is essential for the inhibitor species to be consumed from the reaction mixture before the free radicals can actually initiate a chain growth polymerization. Phenols and arylamines are the most common chain transfer inhibitors. The reaction of phenols, although not fully elucidated, is believed to be as shown in Figure 3.⁴ Phenolic resin is therefore expected to have a detrimental effect on the cure of vinyl-ester resin.

Epoxy resins and their cure with amines

Primary cure reactions for the epoxy-amine systems involve epoxy ring opening by primary and secondary amines. Ring opening reactions that lead to crosslinking are illustrated in Figure 4. The intrinsic rate of the

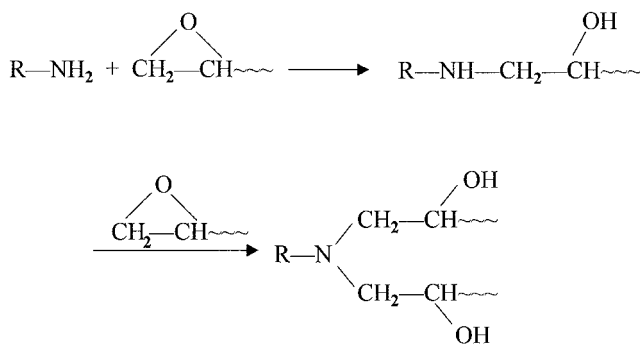


Figure 4 Ring opening of epoxy with primary amines and secondary amines.

epoxy-amine reaction depends not only on the monomer type but also on whether the reaction occurs with primary or secondary amines. Although the reaction rate of secondary amines is often found to be lower than that of the primary amines, the ratio of reactivity of primary to secondary amines depends on the type of amine. Furthermore, proton donors, such as water, phenols, or alcohols, act as catalysts and accelerate the epoxy-amine ring-opening.⁵ Figure 5 illustrates the mechanism for acceleration. Because the reaction of epoxy and amine results in the formation of hydroxyl groups, many epoxy-amine systems exhibit autocatalytic cure behavior. Side reactions for the epoxy-amine systems include the etherification reaction described in Figure 6. Some epoxy-amine systems such as the EPON 828 based on DGEBA and PACM 20 [bis(*para*-amino-cyclohexyl)-methane] combination exhibit little side reaction at low cure temperature. This is, therefore, the system of choice for the compatibility studies reported in this work.

Cocure of epoxy-amine and phenolic resins

The most important effect of cocuring epoxy-amine resins with phenolic resins is the acceleration of the epoxy ring opening due to hydroxyl groups present in the phenolic resin, which has been discussed in the

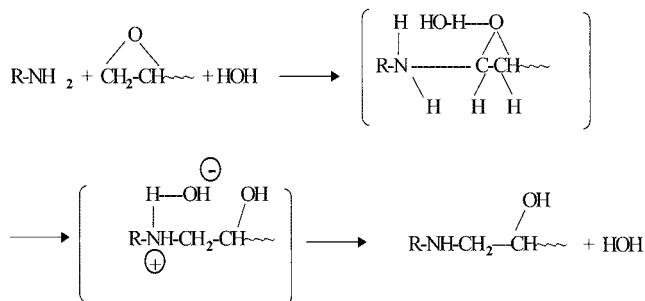


Figure 5 Acceleration of epoxy ring opening and crosslinking of epoxy resin in the presence of proton donors.⁵

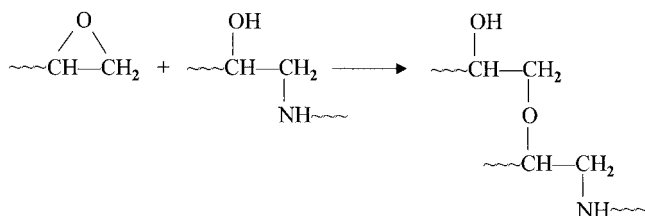


Figure 6 The etherification side reaction common to epoxy systems cured at temperatures greater than 100°C.

previous section. The hydroxyl groups of the phenol as well as their hydroxymethyl substituents are expected to accelerate the crosslinking reactions of epoxy-amines. Another possibility during cocure is the reaction of amine groups with hydroxymethyl substituents of the phenolic resin to form benzylamine linkages, as illustrated in Figure 7.⁶ Trace amounts of the amine would also go into neutralizing the acid catalyst of the phenolic resin system according to the reaction shown in Figure 8. The etherification side reaction mentioned before is not believed to play a very important role in this case because it does not typically occur below 100°C, whereas the cure temperatures used in the study are 60 and 80°C.

EXPERIMENTAL

Fourier transform IR spectroscopy, both in the mid-IR as well as near the IR range, was used to study reaction kinetics of cocure. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were also used to evaluate the cocured samples. By cocuring in this work, we mean the curing of homogeneous mixtures of two resin systems. These would be representative of the compositions that could be created at the interface between these materials during CIRTM processing as a result of diffusion.

IR spectroscopy

A Nicolet Magna IR 860 spectrometer in the transmission mode was used to obtain IR spectra for the resin during different stages of cure. Small quantities of reaction mixture constituents in the required ratio were taken and mixed well. A drop of this mixture was compressed between two transparent NaCl crys-



Figure 7 Formation of dibenzylamine bridges between phenolic groups as a result of reaction of methylol groups with amines.⁶

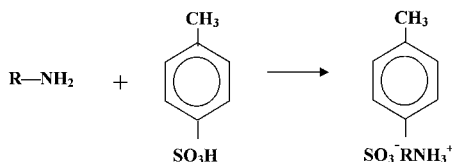


Figure 8 Neutralization of *p*-toluenesulfonic acid (major constituent of phenolic catalyst Phencat 381) with amine.

tal plates supplied by International Crystal Labs (Garfield, NJ). Teflon spacers (0.025 mm thick) were used to regulate the thickness of the sample film. This thickness is recommended for obtaining quantitative spectral information about the bulk cure characteristics, while ensuring that isothermal conditions are maintained by limiting the amount of heat released during the exothermic reaction. This assembly was placed in an aluminum block containing two 100-W cartridge heaters and designed to maintain a constant temperature through regulation by a PID controller and a thermocouple. The cell design allows temperature control to be $\pm 0.5\%$, while allowing the cure process to be monitored in real time.

For experiments conducted in the near IR range, a large amount of material was needed to obtain an acceptable signal-to-noise ratio. This was achieved by using thicker (0.5 mm) lead spacers. The heights of absorption peaks associated with different species in the reaction mixture were recorded for analysis.

Band assignments for vinyl-ester resin

A method developed by Brill and Palmese⁷ can be used to monitor the depletion of carbon-carbon double bonds for vinyl-ester resin systems. For pure vinyl-ester resin polymerization, the depletion in the double bonds of both styrene and vinyl-ester monomers is indicative of polymerization. Band assignments for IR spectra of vinyl-ester resin are available from studies conducted by several researchers.⁸⁻¹⁰ The peak at 945 cm^{-1} corresponds to out-of-plane bending of carbon-hydrogen bonds in the vinyl group of the vinyl-ester monomer, while the peak at 910 cm^{-1} results from wagging of CH₂ in the vinyl group of the styrene monomer. These peaks can be monitored during cure to determine the conversion of each type of monomer separately. The absorption intensities corresponding to bending of aromatic carbon-hydrogen bonds at 830 cm^{-1} in VE and 700 cm^{-1} in styrene can be used to eliminate the effects associated with evaporation or dimensional changes.

Band assignments for epoxy-amine

The assignments of bands for the epoxy and amine in the near IR range have been well documented by

many researchers.¹¹⁻¹⁴ The bands used in this analysis are the epoxy peak at 4530 cm^{-1} , the primary amine peak at 4937 cm^{-1} , and the total amine peak (representing a combination of the secondary and primary amine) at 6500 cm^{-1} . The ratio of absorbance at different times with respect to initial absorbance (at $t = 0$) can be used to determine the conversion profile of the particular group with time as shown below:

$$\alpha_E = 1 - \frac{h(t)_{4530\text{ cm}^{-1}}}{h(t=0)_{4530\text{ cm}^{-1}}} \quad (3)$$

$$\alpha_{A1} = 1 - \frac{h(t)_{4937\text{ cm}^{-1}}}{h(t=0)_{4937\text{ cm}^{-1}}} \quad (4)$$

$$\alpha_{A1A2} = 1 - \frac{h(t)_{6500\text{ cm}^{-1}}}{h(t=0)_{6500\text{ cm}^{-1}}} \quad (5)$$

where α_E , α_{A1} , and α_{A1A2} denote epoxy, primary amine, and total amine conversions, respectively.

Differential scanning calorimetry

A DuPont DSC was used to determine the heat of reaction for vinyl-ester and phenolic cocure. It measures the heat of reaction as a function of time (or temperature, as programmed). Although the individual conversion profiles of the constituent monomers in the resin system cannot be obtained, it is very useful in comparing the reaction kinetics of the system as a whole.

Dynamic mechanical analysis

A Rheometrics solids analyzer RSA II equipped with a temperature-controlled sample chamber was used. The sample dimensions were nominally $48 \times 12 \times 2$ mm. Three-point bend geometry was used, and an oscillatory load was applied to the sample. The instrument interfaces with the RHIOS software, which is used to control experimental parameters and acquire data. The values of storage and loss modulus with respect to time were recorded. The temperature at which the maximum in the loss modulus occurred was taken as the glass transition temperature of the fully cured (postcured at 120°C for 2 h after cure at 60°C) epoxy-amine with varying phenolic resin concentrations.

RESULTS AND DISCUSSION

The results obtained from experiments performed with the two cocure systems, vinyl-ester and phenolic and epoxy-amine and phenolic, are presented in this section.

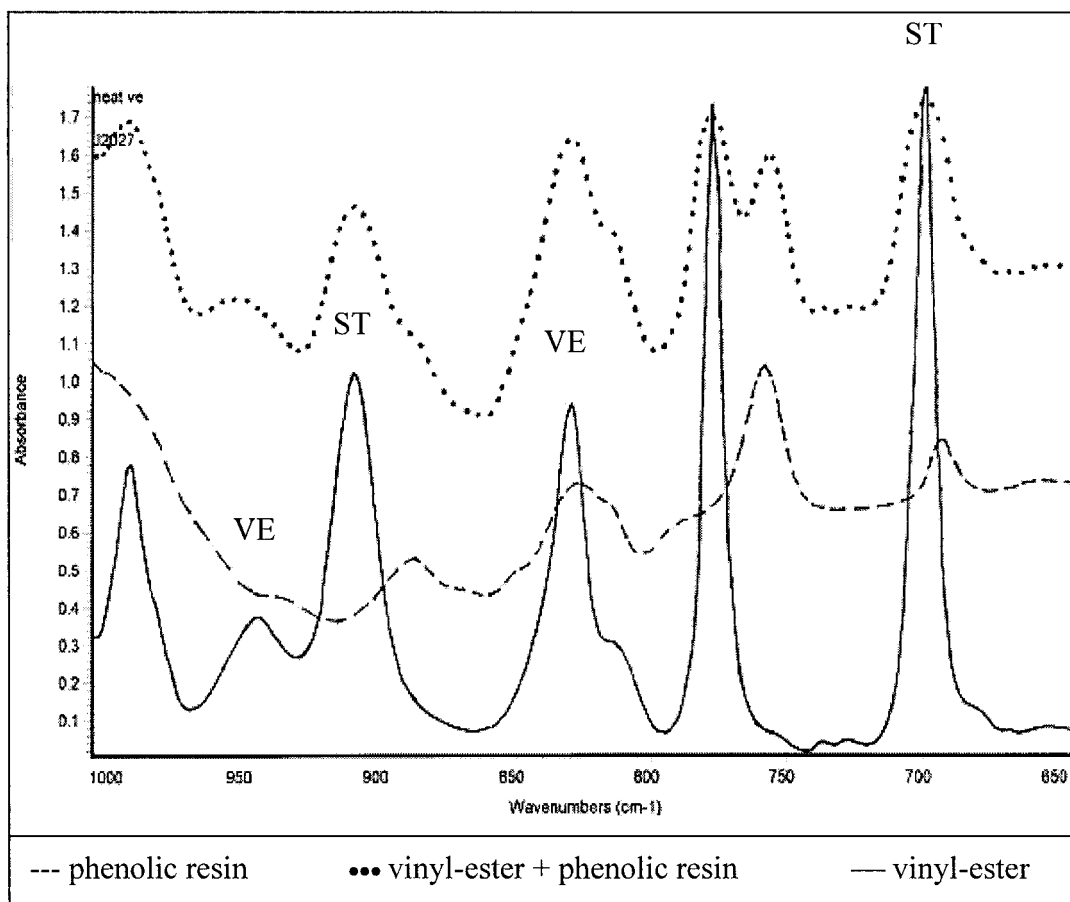


Figure 9 Transmission IR spectra of vinyl ester and phenolic resin and a mixture of equal weights of vinyl-ester and phenolic.

Vinyl-ester and phenolic resin

Figure 9 shows transmission IR spectra of vinyl-ester resin 411-C50 and phenolic resin BPJ2027L and also a mixture of the two. It can be seen from the figure that there is an overlap in the aromatic carbon-hydrogen peaks at 830 and 700 cm^{-1} , and the peaks of phenolic resin. The overlap causes a change in the values of these peaks as reaction proceeds, and therefore, they cannot be used as reference peaks once phenolic resin is introduced into the system, making the quantitative analysis of the spectra obtained from FTIR impossible. However, it can be seen in Figure 10 that there is a small decrease in the height of the peak due to styrene (at 900 cm^{-1}).

To confirm whether there is any polymerization of vinyl-ester resin in the presence of phenolic resin, different concentrations of phenolic resin and pure phenol, respectively, were mixed with the vinyl-ester and maintained at 60°C. The concentration of phenolic resin in these reaction mixtures was 1, 2, 3, 4, and 5 wt % of the vinyl-ester resin. Neither of these mixtures showed any polymerization even after 24 h. This is well in line with the fact that phenol groups act as inhibitor for free-radical polymerization of vinyl

monomers. The concentration of free phenol that can inhibit the reaction is usually of the order of parts per million.² The quantity that was added here is several orders of magnitude higher than that value. DSC experiments conducted to observe the heat of reaction for vinyl-ester polymerization with and without phenolic resin also show that vinyl-ester does not cure in the presence of phenolic resin. The thermograms are presented in Figure 11. The heats of reaction calculated from these traces are 390 and 40 J/g, respectively, for the runs with and without phenolic. The small amount of heat of reaction observed in case of vinyl-ester cocured with phenolic resin (~10% of that without phenolic) is probably due to some amount of styrene homopolymerization, which is also seen from the FTIR spectra in Figure 10, as mentioned before.

It can be concluded that not only are these two resin systems incompatible with each other, any contact between the two would result in an uncured interphase. This is strictly undesirable in any composite application; therefore, it is advisable to use an intermediate layer which completely separates these resin systems.

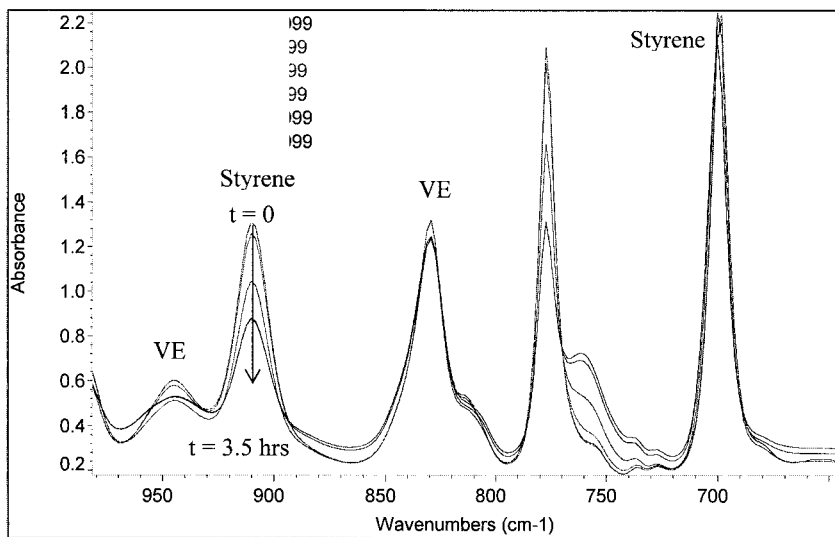


Figure 10 Transmission IR spectra of vinyl-ester 411-C50 (with 2%Trigonox and 0.2% CoNap) mixed with 2% BPJ2027L (with 4% Phencat 381) at different times.

Epoxy-amine and phenolic resin

For the sake of clarity, the analysis of epoxy-amine cure is presented before presenting the analysis of cocure with phenolic resin.

Cure kinetics of epoxy with amine

The conversion profiles of secondary and tertiary amine in the Epon 828-PACM 20 system can be calculated by using simple mass balance equations derived

in the following manner. Applying mass balance over the amines and the epoxy groups in the reaction mixture gives the following relations between the concentration of the various functional groups at any time and the initial concentration:

$$\text{amines: } [A1]_0 = [A1] + [A2] + [A3] \quad (6)$$

$$\text{epoxy: } [E]_0 = [E] + [A2] + 2[A3] \quad (7)$$

where [A1], [A2], [A3], and [E] are the initial concentrations of primary amine, secondary amine, tertiary amine, and epoxy functionalities, respectively, and the subscript 0 indicates initial values. The initial concentrations are known from the composition of the initial mixture. The concentration of epoxy and primary amine with respect to time can be obtained by using the initial values and the conversions of the epoxy and the primary amine, α_E and α_{A1} , as follows:

$$[E] = [E]_0(1 - \alpha_E) \quad (8)$$

$$[A1] = [A1]_0(1 - \alpha_{A1}) \quad (9)$$

where [E] and [A1] are the concentrations of epoxy and primary amine groups at any time t . Because $[A1]_0$, $[E]_0$, [A1], and [E] are all known by direct measurement, eqs. (8) and (9) can be simultaneously solved to obtain the values of [A2] and [A3] with time.

Cure kinetics of epoxy-amine with phenolic

The conversion profiles of epoxy and primary amine with different phenolic resin concentrations at 60°C are shown in Figures 12 and 13, respectively. From the

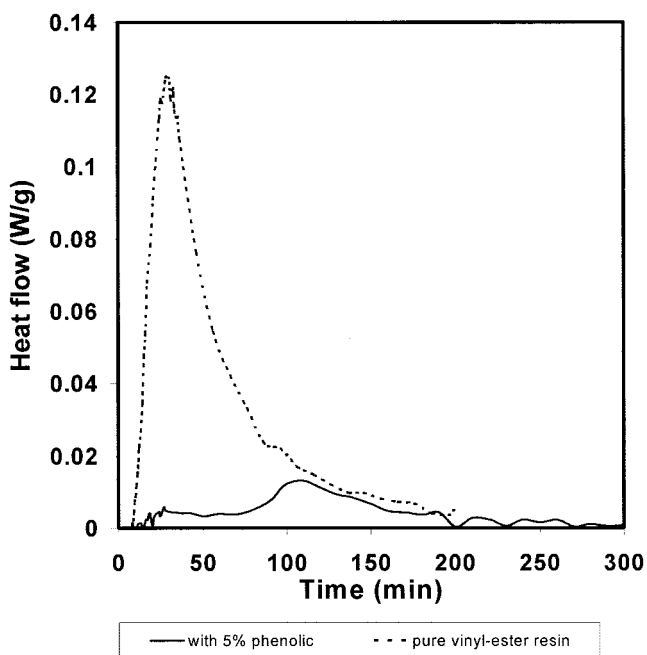


Figure 11 Heat flow versus time curves obtained from DSC for pure vinyl-ester resin and with 5 wt % phenolic resin.

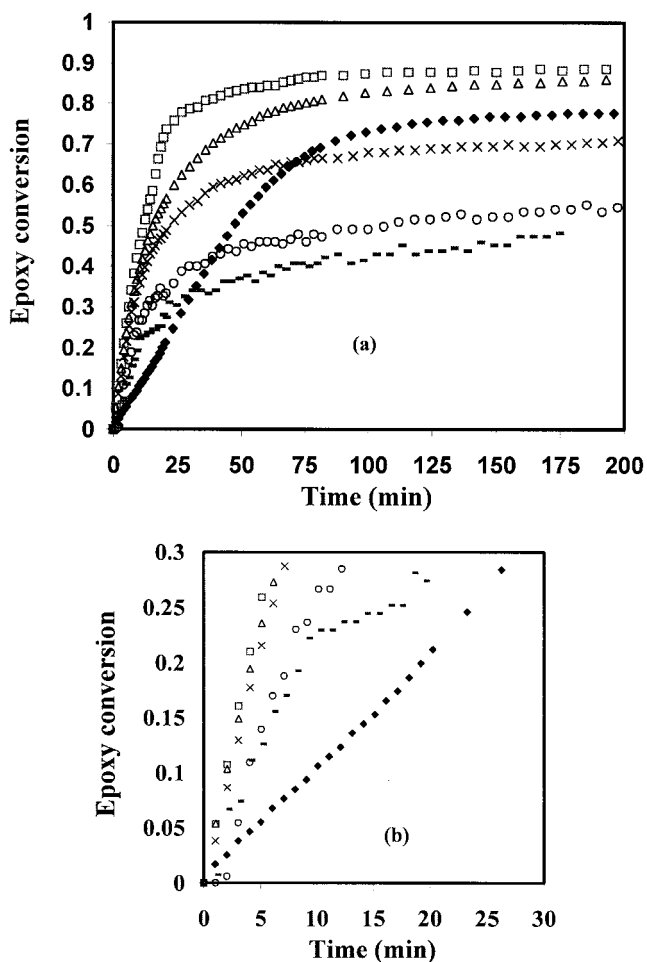


Figure 12 Conversion profiles of epoxy with varying phenolic concentration. (b) Enlarged view of the initial region of the plots shown in (a). \blacklozenge , pure epoxy-amine; \square , with 5% phenolic; \triangle , with 10% phenolic; \times , with 20% phenolic; \circ , with 50% phenolic; $-$, with 60% phenolic.

enlarged views of the initial regions of both figures, it can be seen that the rate of conversion of both epoxy and amine increased significantly upon introduction of phenolic resin into the system. The increase in epoxy conversion rate was clearly a result of the catalytic effect of hydroxyl groups present in the phenolic resin. As mentioned previously, hydroxyl groups accelerate the epoxy ring opening reaction, which leads to an overall increase in the rate of polymerization. The concentration of phenolic resin did not seem to affect the initial rate of epoxy conversion. However, it did have a significant effect on the final conversion of epoxy. The amine conversion rate increased with the addition of phenolic because of the occurrence of the side reaction of the amines with phenolic.

The final conversion of epoxy after cure at 60°C as a function of the phenolic concentration is shown in Figure 14. It increased from 81 to 86% with an increase in phenolic concentration from 0 to 10 wt %. This is perhaps due to a lower crosslink density and hence a

lower diffusion limitation. Further increase of the initial phenolic concentration results in a decrease, rather than an increase, of the epoxy final conversion. It can be argued that there is an interplay of two factors that is producing this particular trend in the cure of epoxy-amine in the presence of phenolic resin. The reasons for these observed trends are discussed later.

As mentioned earlier and illustrated in Figure 14, there is reaction between phenolic resin and amine, which is competitive in nature with the epoxy-amine polymerization reaction. This reaction was observed to be very fast and highly exothermic when experiments were conducted by mixing only the amine with phenolic resin. It is not possible to follow this reaction through IR spectroscopy because it is completed before the collection of spectra can begin. The conversion of primary amine to secondary amine can, however, be observed by using the broad total amine peak at 6500 cm^{-1} . This peak is a combination of the stretching overtones of the primary and secondary amines at 6520 and 6450 cm^{-1} , respectively.¹¹ The spectra pre-

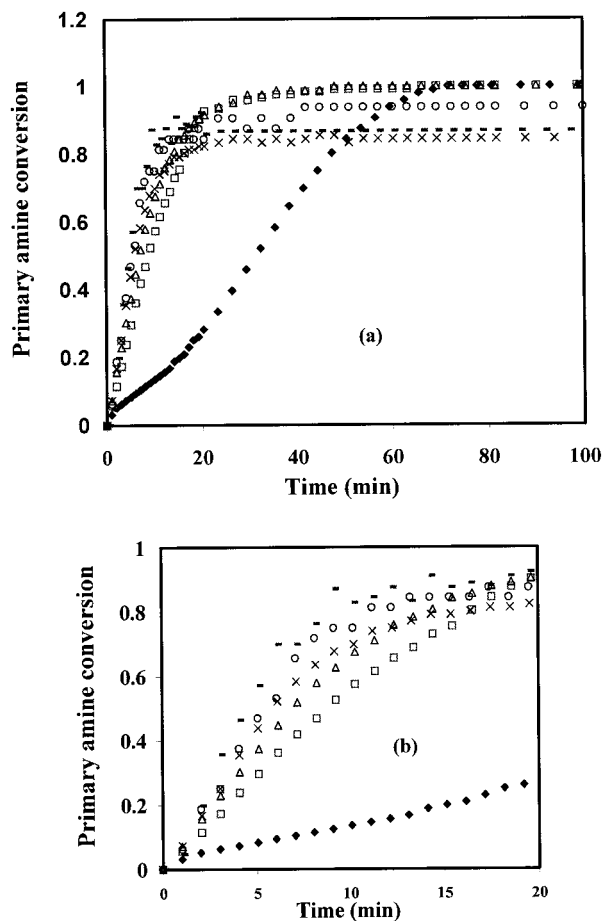


Figure 13 Conversion profiles of primary amine with varying phenolic concentration. (b) Enlarged view of the initial region of the plots shown in (a). \blacklozenge , pure epoxy-amine; \square , with 5% phenolic; \triangle , with 10% phenolic; \times , with 20% phenolic; \circ , with 50% phenolic; $-$, with 60% phenolic.

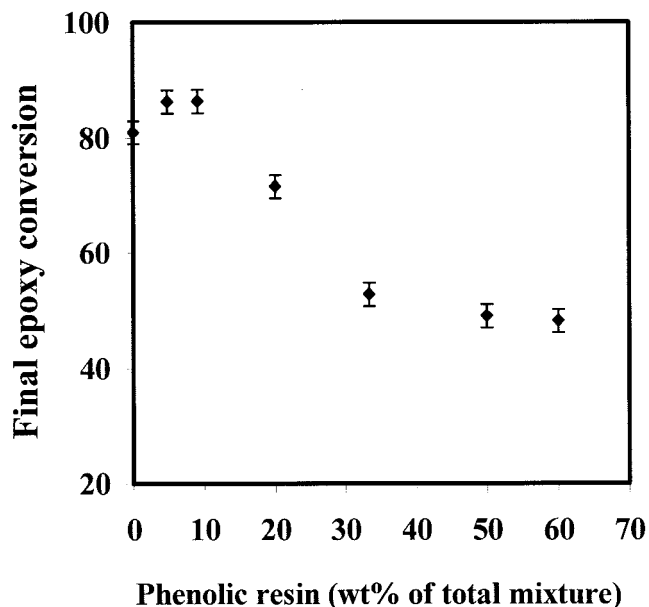


Figure 14 Conversion of epoxy after cure at 60°C with varying phenolic concentrations.

sented in Figure 15 show the broad peak at 6500 cm⁻¹ for the pure amine sample and amine mixed with different concentrations of phenolic resin (one-half of

the weight of amine and equal to the weight of amine). It can be seen that as the concentration of phenolic was increased in the amine, the secondary amine peak increased in relation to the primary amine peak. In Figure 16, this peak has been deconvoluted to separate the stretching overtones of the primary and secondary amines at 6520 and 6450 cm⁻¹, respectively. It can be seen that the secondary amine peak is higher relative to the primary amine peak in the case where equal weight of phenolic resin is mixed with the amine, indicating that primary amine is converting to secondary amine through reaction with phenolic resin.

Consumption of amine by phenolic resin from a stoichiometric mixture of epoxy and amine would render the mixture deficient in amine groups. This probably explains the decrease observed in epoxy conversion with higher phenolic concentrations. Assuming excess epoxy, the final conversion of primary amine is not expected to change upon addition of phenolic resin. This is observed in the systems with 5 and 10 wt % phenolic. However, in the mixtures with higher concentrations of phenolic resin, the final value of primary amine conversion drops. No particular trend was observed in the decrease in conversion, which was between 95 and 85% instead of the expected 100%. The possible reason for this decrease could be that the epoxy is also reacting with secondary

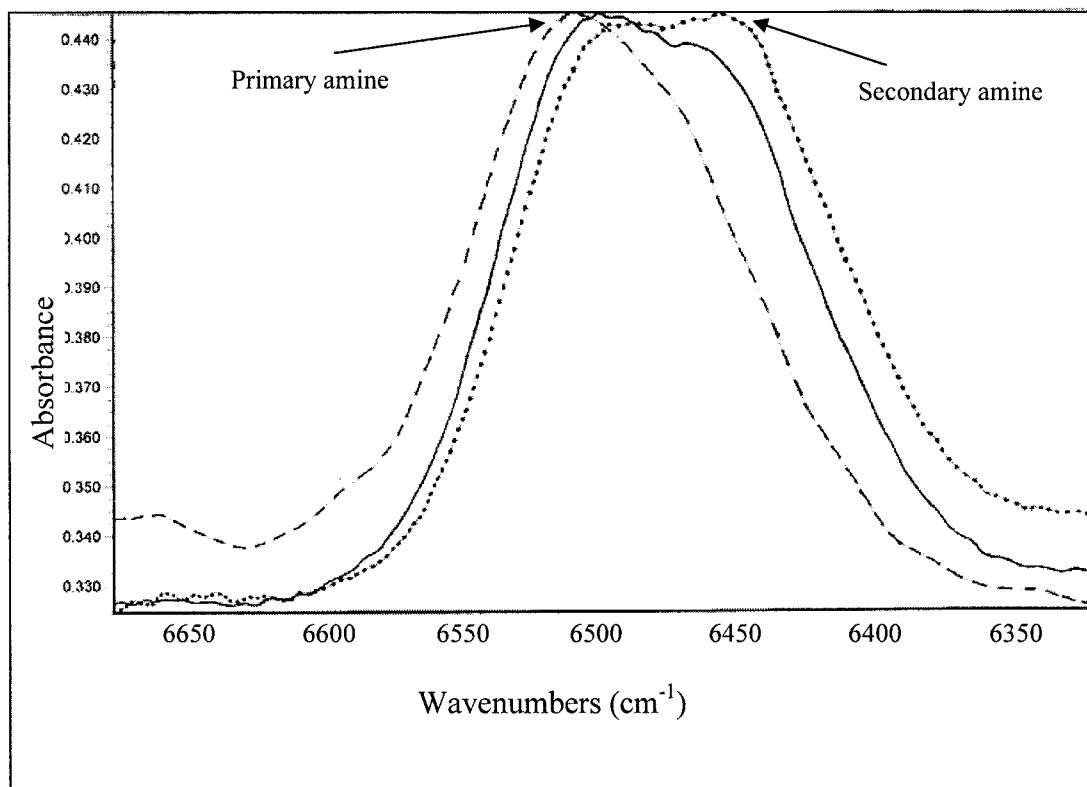


Figure 15 Transmission near IR spectra of amine with phenolic resin showing the conversion of primary amine to secondary amine. ---, pure amine; —, amine + 47 wt % phenolic; ···, amine + equal weight of phenolic.

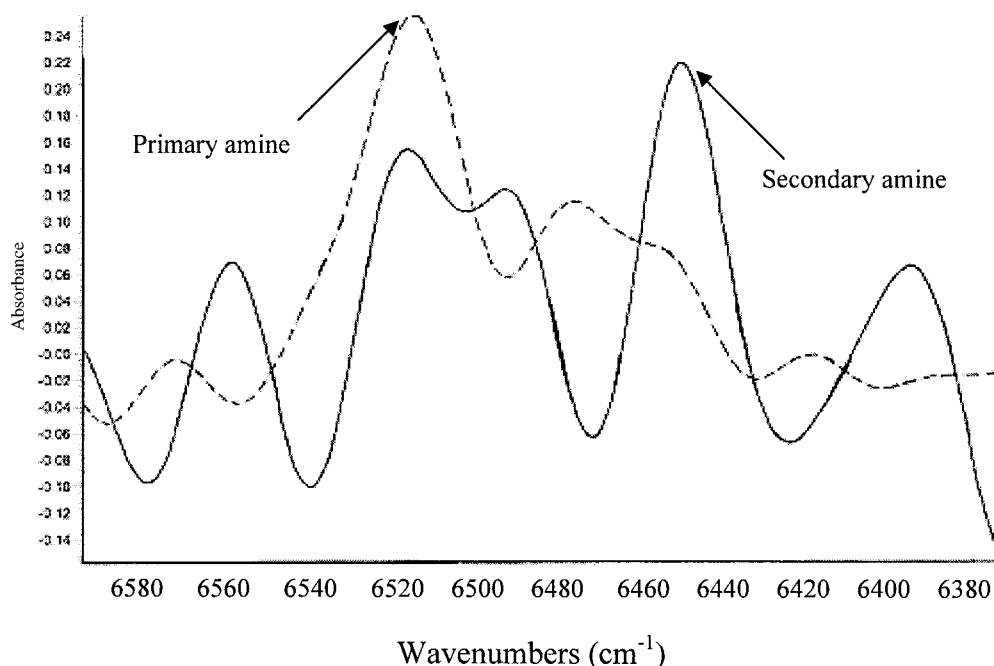


Figure 16 Deconvoluted transmission near IR spectra of pure amine and amine with equal weight of phenolic. ---, pure amine; —, amine + equal weight of phenolic resin.

amines, and because the epoxy conversion is only about 50%, primary amines could still remain unreacted. There is also a possibility that a peak of the phenolic system interfered with the peak at 4937 cm^{-1} , but it cannot be confirmed because of a lack of information about the behavior of the near IR spectra of phenolic during reaction.

The major reaction of phenolic resin with the epoxy-amine resin is with the amine through benzylamine bridge formation. As a result of their mutual interactions, a reaction mixture containing epoxy-amine and phenolic resin can be expected to have an interpenetrating network of phenolic-amine and epoxy-amine chains. As the phenolic resin is mostly composed of disubstituted phenols, its reaction with amine would primarily result in straight chains. These would tend to reduce the crosslink density of the system, which in turn would reduce the diffusion limitation to reaction of secondary amines and epoxy, thereby increasing epoxy conversion as observed at low concentrations of phenolic resin (the curves for 5 and 10 wt % phenolic resin in Fig. 11). The effect of reduction in diffusion limitation was, however, canceled out at higher concentrations of phenolic resin, which rendered the mixture highly nonstoichiometric because of consumption of amines by phenolics. It can be seen that increasing the phenolic concentration ceases to have any effect on the epoxy conversion after the concentration of phenolic reached 33 wt %.

The glass transition temperature (T_g) values obtained for cured samples correspond well with the above results. Figure 17 shows T_g as a function of

phenolic concentration in the fully cured epoxy-amine/phenolic cocure samples. The T_g of pure epoxy-amine samples was found to be 153°C , which decreased with the increasing phenolic resin concentration in the material. It was found that the decrease in T_g , up to 33 wt % phenolic, was almost linear and then it asymptotically approached a value close to 60°C . This result is well in line with the trend in the

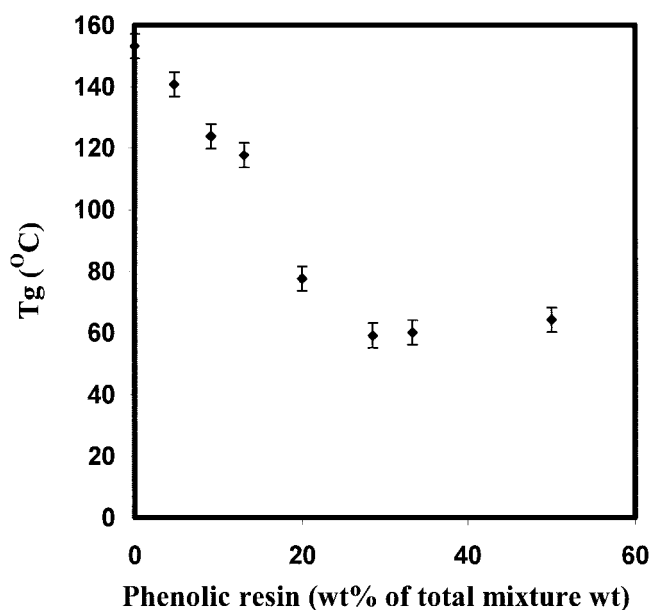


Figure 17 Influence of phenolic concentration on the glass transition temperature of epoxy-amine.

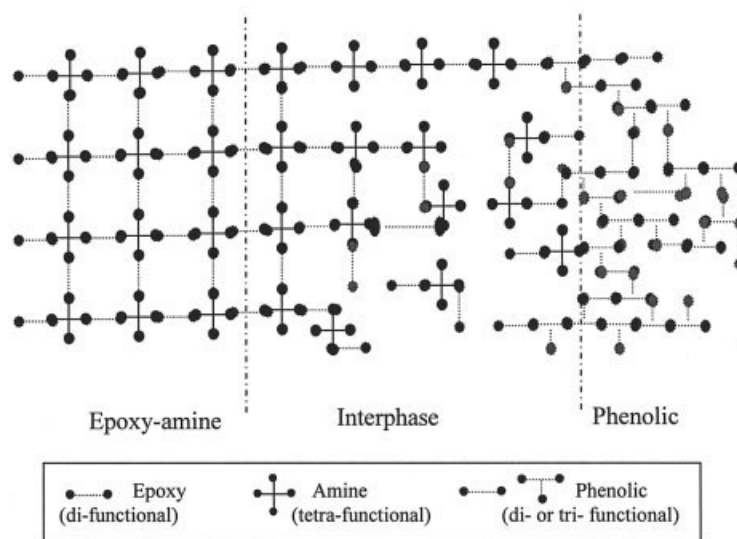


Figure 18 Proposed network structure of the cocured epoxy-amine and phenolic resin systems.

final epoxy conversions. It is known that the T_g of a material strongly depends on its network structure. A decrease in T_g can, therefore, be interpreted as a decrease in the crosslink density of the material. This would mean that the network containing phenolic resin was less tightly crosslinked compared to the pure epoxy-amine network, as has been proposed in the discussion of conversion profiles. A schematic diagram of network structure of the cocured epoxy-amine and phenolic resin based on the above discussion is presented in Figure 18. A model to quantify the effect of phenolic resin-amine reaction on the cure of epoxy-amine system is discussed in the next section.

Analysis of epoxy-amine/phenolic cocure

The mass balance eqs. (6) and (7) are valid for pure epoxy-amine system only. When phenolic resin is introduced into this system, significant changes in the final epoxy conversions, as discussed before, lead us to believe that there is another reaction taking place, and therefore, this analysis must be modified. The reaction between primary amine and phenolic illustrated in Figure 7 has been found to occur very rapidly, making it difficult to follow by IR spectroscopy or DSC. In the analysis described here, it is thus assumed that there is an instantaneous reaction between the methylol components of phenolic resin and primary amine.

The fraction of primary amine consumed by phenolic is denoted by ϕ . The initial concentrations used in the mass balance expressions have been modified to account for this as follows.

The initial primary amine concentration $[A1]_0$ is reduced by a factor of ϕ , and the initial secondary amine concentration is increased by the same amount.

The relation for calculating the concentration profile of epoxy is not affected by this assumption.

Thus, concentration profiles of amines and epoxy can be calculated as using the following modified mass balance expressions:

$$[E] = [E]_0(1 - \alpha_E) \quad (10)$$

$$[A1] = [A1]_0(1 - \phi)(1 - \alpha_{A1}) \quad (11)$$

$$[A2] = [A2]_0 + 2\{[A1]_0(1 - \phi) - [A1]\} - [E]_0(\alpha_E) \quad (12)$$

The value of ϕ is difficult to determine experimentally because the reaction appears to be practically instantaneous. The following method was developed to determine this value. It involves the use of the broad band at 6500 cm^{-1} in the near IR spectrum that corresponds to a combination of primary and secondary amine absorbances. The decrease in height of this peak can be represented as follows:

$$\alpha_{A1A2} = 1 - \frac{h(t)_{6500 \text{ cm}^{-1}}}{h(t=0)_{6500 \text{ cm}^{-1}}} \quad (13)$$

The combined conversion of primary and secondary amine can also be calculated by using the values of $[A1]$ and $[A2]$ from eqs. (11) and (12) according to the relation:

$$\alpha_{A1A2} = \{[A1] + [A2]\}/[A1]_0 \quad (14)$$

Henceforth, the combined conversion of amine calculated from eq. (14) will be referred to as the calculated value, whereas the one obtained through eq. (13) will be referred to as the measured value. The calculated

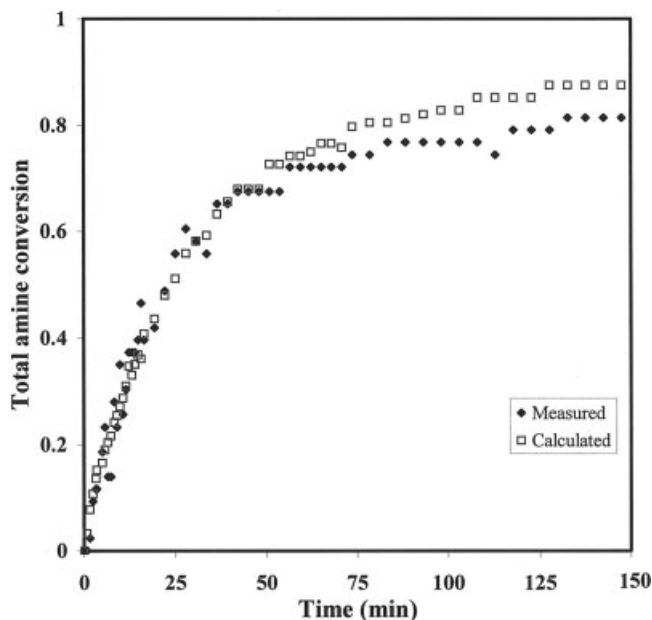


Figure 19 Measured and calculated total amine conversion for epoxy-amine with 20 wt % phenolic resin ($\phi = 0.40$ for calculated values).

value requires that ϕ be known. A graphical method was used to find the best fit for calculated values of α_{A1A2} by substituting different values of ϕ . The value of ϕ that gave the closest match between the calculated and measured α_{A1A2} was chosen. A typical plot of the measured and calculated values of total amine conversion with respect to time is presented in Figure 19 as an example of how close a match was obtained. The values of ϕ obtained from the graphical method discussed here are plotted in Figure 20.

It follows from the above discussion that it would be advisable to add amine in excess of the stoichiometric amount in the cocure of epoxy-amine and phenolic. This approach was tested on the mixture with 20 wt % phenolic. A DMA sample was made in which the initial concentration of amine was 1.4 times the stoichiometric amount. The T_g of this material increased from 77 to 117°C. The conversion profiles for a mixture with the same composition are given in Figure 21. It can be seen that there was an increase in the epoxy conversion while the amine conversion did not change.

CONCLUSION

The effect of cocure of phenolic resin with vinyl-ester and epoxy-amine resins was investigated through the use of FTIR, DSC, and DMA. A thorough understanding of the interactions of these systems at the molecular level has been developed, which will aid in the design of resins, adhesives, and separation layer combinations for CIRTM.

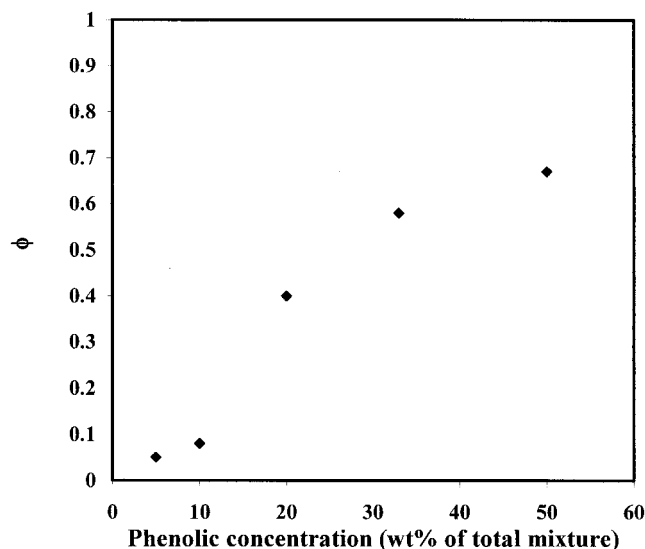


Figure 20 Fraction of primary amine consumed by phenolic resin as a function of the concentration of phenolic resin during the cocure of epoxy-amine and phenolic resin.

It was found that the cure of vinyl-ester is strongly inhibited in the presence of phenolic resins. Therefore, it is advisable to have an impermeable separation layer in between these two systems if they are to be used in parts manufactured by CIRTM.

It is commonly believed that amine-cured epoxies are compatible with phenolic resins. Our investigations, however, revealed that the reaction between phenolics and amines results in incomplete epoxy conversion during cure and also a decrease in the

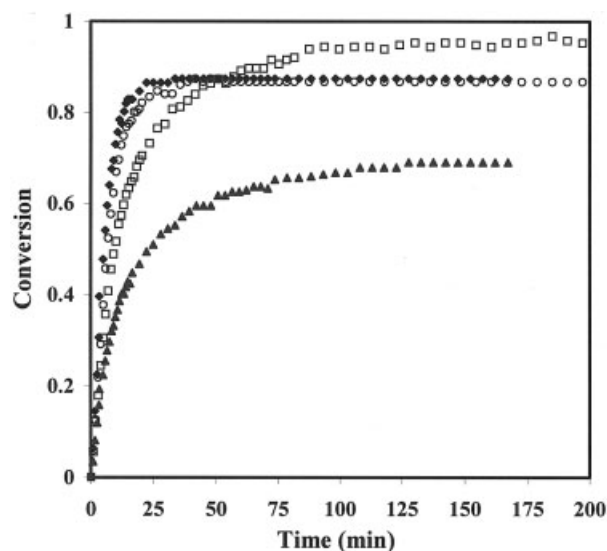


Figure 21 Comparison of epoxy and amine conversions for epoxy resin with initial amine concentrations of 28 and 40 wt %. Phenolic concentration in each of the mixtures is 20% of the total mixture weight. \blacklozenge , amine original; \circ , amine modified; \blacktriangle , epoxy original; \square , epoxy modified.

crosslink density, significantly lowering the T_g of the material. A model to quantify the effect of phenolic resin on the cure of epoxy-amines has been proposed. By using this model, the fraction of primary amine consumed by the phenolic can be estimated. It was found that increasing the initial amine concentration in the cocure reaction mixture leads to an increase in the epoxy conversion as well as the T_g of the material. Therefore, it is recommended that in cocure of epoxy-amine and phenolic resins, the initial concentration of amine must be greater than the stoichiometric amount to compensate for the amine consumed by the phenolic resin.

This work is part of a joint project among UD-CCM, Tuskegee University, the University of California, San Diego, North Carolina A&T State University, Prairie View A&M University, and industry to develop intelligent RTM for Integral Armor Applications funded by U.S. Army Research Labs.

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