Effect of Copper on the Curing and Structure of a DICY-Containing Epoxy Composite System

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ABSTRACT: The curing and structure of an epoxy system containing dicyandiamide (DICY) as hardener were studied as a function of temperature and the presence or absence of copper with the use of differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy in photoacoustic mode (FTIR-PAS). Spectroscopic analysis of specimens taken from the DSC helped to clarify the reaction mechanism in terms of the different schemes that have been proposed. The initial stages, corresponding to the first peak in the DSC exotherm, involve the usual epoxide-amine reactions closely followed by a reaction between DICY nitrile groups and hydroxyl groups to form structures containing iminoether and urea groups. These reactions are slightly retarded in the presence of copper. At higher temperatures, corresponding to the second peak in the exotherm, these structures are transformed into others believed to contain urethane ester groups. This reaction, which may be considered to constitute a form of degradation, is significantly accelerated in the presence of copper. The effect is particularly large around 180°C, a temperature commonly used to cure such systems, so the results have important practical implications, for example, in the lamination of circuit boards. © 2000 Government of Canada. Exclusive worldwide publication rights in the article have been transferred to John Wiley & Sons, Inc. J Appl Polym Sci 75: 1458–1473, 2000

Key words: epoxy; cure; copper; DICY; dicyandiamide

INTRODUCTION

Epoxy systems that make use of dicyandiamide (DICY) as a hardener are widely used as adhesives, matrices for fiber-reinforced composites, and powder coatings. Because DICY is poorly soluble in most epoxy resins at room temperature, it is usually present in the resin in the form of fine particles. Hence it acts as a latent hardener, and reaction with the epoxy resin becomes significant only when the particles begin to dissolve upon raising the temperature.

One important application of DICY-based epoxy systems is in the manufacture of printed circuit boards. In this case, brominated epoxy resins are often used in order to improve the flame retardancy. In circuit boards, the epoxy composite serves as a dielectric layer to separate the layers of copper circuitry, while at the same time providing the necessary structural integrity of the board. For this, the bonding between epoxy and copper is important. Although epoxy resins generally form strong bonds with many metal surfaces, copper presents certain difficulties. In order to assure good bonding, the morphology of the copper surface is usually modified by oxidation. If the copper–epoxy bond is not sufficiently strong, the act of drilling holes in the board can cause delamination, and in subsequent steps in the process, chemicals can penetrate into the cracks and dissolve the copper oxide layer, leading to a phenomenon known as "pink ring." Hence the nature of the interphase between copper and epoxy composite is an important factor in determining the

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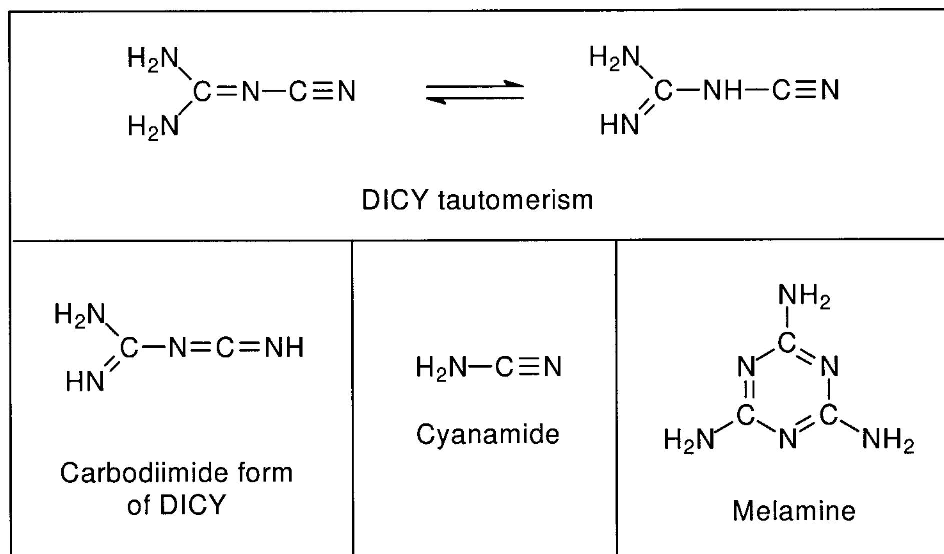

Figure 1 Possible structures of DICY and its rearrangement products.

strength and durability of the adhesive bond and the overall quality of the circuit board.

Although the curing of epoxy–DICY systems has been studied by many investigators,[1–16] it is a very complex process that is still not fully understood because there are many complicating factors. For example, it is well known that DICY exists in two tautomeric forms containing a nitrile group. It can also exist as a carbodiimide tautomer,[14] it can split into two molecules of cyanamide, or it can rearrange into melamine, a cyclic trimer of cyanamide.[3] The different structures are illustrated in Figure 1. There is also the question of the dissolution of the DICY, in which the particle size will obviously play a role.[5] Furthermore, in commercial products, tertiary amine or dimethyl urea compounds are usually added to accelerate the reaction and lower the cure temperature. It is generally acknowledged that the first stages of curing proceed according to well established mechanisms for amine curing agents.[17] The N–H bonds react with epoxide rings to form linkages containing secondary hydroxyl groups, which can then further react with epoxide rings to form ether linkages. These reactions are shown in Figure 2(a). Etherification can also result from homopolymerization of epoxide rings, initiated by tertiary amine catalysts or by hydroxyl groups initially present in the resin. However, in the specific case of DICY, the usual curing reactions are known to be accompanied by others not normally observed in simple amine-epoxy systems. For instance, infrared (IR) spectroscopy shows that the nitrile peak near 2180 cm^{-1} disappears, while a strong carbonyl peak appears near 1740 cm^{-1}. Different mechanisms have been proposed to explain these changes, and the main features of some of them are shown in Figure 2. [For simplicity, the free DICY molecule is used in these reaction schemes, but in actual fact some of the DICY N–H bonds will have already reacted with epoxy groups as shown in Fig. 2(a)]. Saunders et al.[1] suggested that a hydroxyl group adds across the nitrile group to form an iminoether that then rearranges to form a substituted guanyl urea, thus explaining the appearance of carbonyl groups. This reaction can be either intermolecular, forming a crosslink, as shown in Figure 2(b), or intramolecular, forming a cyclic structure. According to Saunders, the first possibility is more likely. However, Zahir[4] suggested that the reaction is intramolecular and involves the loss of cyanamide to form tautomeric 2-iminooxazolidine and 2-aminooxazoline rings, as shown in Figure 2(c). The C═N bonds present in these rings give rise to an IR peak at 1660 cm^{-1}. Another peak at 1700 cm^{-1} was attributed to urea groups formed either by rearrangement of the ring structures just mentioned or by the intermolecular reaction proposed by Saunders. The carbonyl peak at 1736 cm^{-1}, which appears at higher temperatures, was explained in terms of urethane linkages formed by opening of the rings through reaction with hydroxyl groups.[4] Zeppenfeld et al.[11] agreed with Zahir in assigning the IR peak at 1683 cm^{-1} to urea groups and the one at 1738 cm^{-1} to another carbonyl structure. However, Gilbert et al.[13] subsequently proposed a somewhat different mecha-

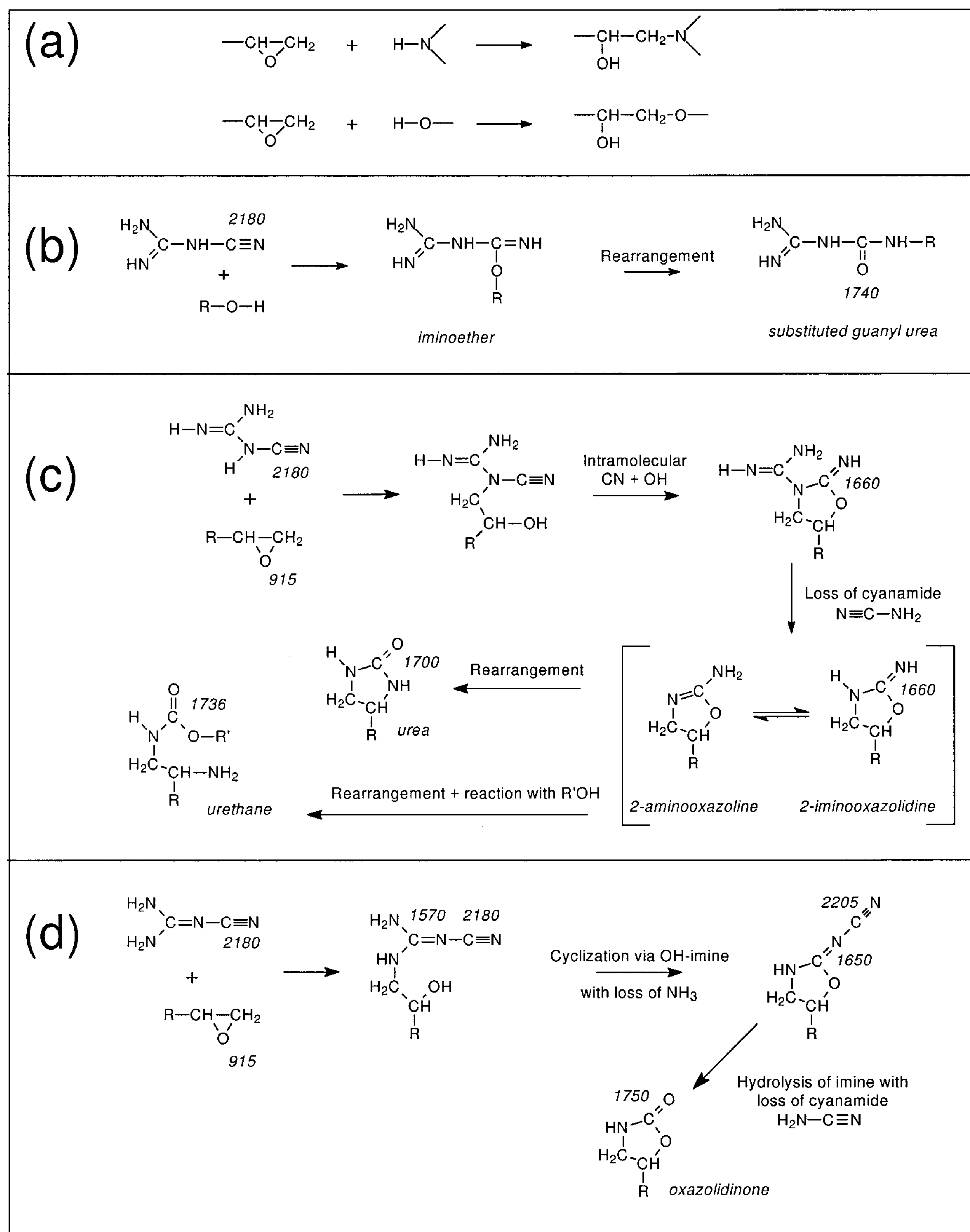

Figure 2 Main features of some of the proposed mechanisms for epoxy cure with DICY. (a) General reactions for amine cure; (b) mechanism of Saunders et al.[1]; (c) mechanism of Zahir[4]; (d) mechanism of Gilbert et al.[13] Numbers in italics represent IR absorption frequencies in cm^{-1}.

nism [Fig. 2(d)] in which a hydroxyl group adds across the C═N bond of the DICY moiety with loss of ammonia to form a five-membered iminooxazolidine ring. The imino group is then hydrolyzed by water present in the system to produce a five-membered cyclic urethane (2-oxazolidinone) ring that gives rise to the IR peak at 1740–1760 cm^{-1}. The disappearance of C═N groups was also explained in terms of hydrolysis. The mechanism proposed by Pfitzmann and coworkers[14,15] combines aspects of the Zahir and Gilbert mechanisms. Like Zahir, they postulated the formation of tautomeric oxazoline and oxazolidine rings, but suggested that they are formed by direct reaction of epoxide rings with one of the C═N bonds in the carbodiimide tautomer of DICY. Like Gilbert, they explained the 1740 cm^{-1} IR peak by hydrolysis of the oxazolidine to form oxazolidinone. Finally, Grenier-Loustalot et al.,[16] like Saunders, attributed this peak to ureas formed by reaction between nitrile and hydroxyl groups. However, both Grenier-Loustalot[16] and Pfitzmann[15] also provided evidence that at high temperatures nitrile groups disappear through rearrangement to form a melamine ring structure. The variety of mechanisms proposed confirms the complexity of the reaction and the need for further work in order to elucidate the details. The situation is not helped by the fact that unequivocal assignment of carbonyl peaks in the IR spectrum is difficult because the frequency is sensitive to both hydrogen bonding and ring strain.

The presence of copper and its oxides in the system makes the situation even more complicated, and recently Hong and Wang[18,19] studied the influence of copper on the curing mechanism of epoxy–DICY mixtures. The chemical interaction between organic molecules and metal atoms (or ions) often accelerates the degradation of organic materials on metal surfaces. Among the metals, copper is known to be one of the most powerful oxidation catalysts.[20] It was reported that the oxidative degradation of hydrocarbon-like organic polymers on the copper surface often produces carboxylic acids, which appear to have adverse effects on the stabilities of metal-organic systems. The carboxylic acids formed can further react with the metal surface to produce soluble metal salts. The diffusion of these salts into the polymer matrix is the main cause of polymer degradation.[21] The oxidative influence of copper has been observed at the interface with polyethylene,[21] polypropylene,[22] polyimide,[23] and epoxy resin.[24] According to Vaughan, there is another mechanism of epoxy-copper interface damage.[25] Undissolved DICY in contact with the copper surface will break down into ammonia gas, some of which, being more free to move than solid DICY, aids in curing the epoxy resin. The balance can react with the copper oxide to produce nitrogen gas and water. Voids in the laminate and a number of other failures have been attributed to these byproducts.

The object of the present work was to achieve a better understanding of the nature of the curing of an epoxy–DICY system, particularly in systems involving copper, because of their importance in the electronics field. To do this, the curing of epoxy powder separated from a typical commercial glass-epoxy prepreg was studied by differential scanning calorimetry (DSC) in both dynamic and isothermal modes, with and without incorporation of copper powder. Specimens cured in the DSC instrument under different conditions were subsequently analyzed by photoacoustic Fourier transform IR spectroscopy (FTIR-PAS) in order to characterize the chemical changes resulting from the thermal treatment.

EXPERIMENTAL

Materials

The epoxy powder was obtained by flaking off resin from a common commercial prepreg material (Polyclad 7628). The composition of this material is proprietary, but the IR spectrum confirmed that the major components are typical of the systems used for printed circuit boards, namely a brominated DGEBA epoxy resin (diglycidyl ether of bisphenol A) cured with DICY hardener. Since it is a commercial product, the resin would be B-staged (i.e., partially polymerized) as a result of the manufacturing process. The copper powder was Grade 102 from Alcan Powders and Pigments. The presence of a thin natural oxide coating was confirmed by energy-dispersive X-ray analysis. Mixtures of epoxy powder and copper containing from 0% to 50% by weight copper were prepared by mixing in a blade mixer.

Differential Scanning Calorimetry

Two sets of DSC experiments were performed, in dynamic and isothermal modes. In dynamic mode, the curing exotherm was measured on a Perkin Elmer DSC 7 instrument. The specimen (typically 20 mg) was placed in an aluminum pan and inserted into the DSC at room temperature.

Scans were done over the range 30 to 280°C at scan rates of 5 and 20°C/min. Scanning was stopped at 280°C, shortly after the end of the exotherm, in order to minimize any thermal degradation. After each scan the specimen was rapidly cooled and then rescanned from 80 to 160°C at 20°C/min in order to determine the glass transition temperature T_g of the cured material. All measurements were performed under nitrogen atmosphere. In the isothermal mode, heat flow curves were measured at different temperatures with a Setaram Model CDP111 calorimeter on samples weighing about 100 mg. These were also rescanned in dynamic mode to determine the T_g of the cured material. However, in order to obtain specimens with a shape more suitable for IR spectroscopic analysis, the isothermal experiments were repeated under the same conditions (without the second scan) in the Perkin-Elmer instrument (Norwalk, CT).

IR Spectroscopy

IR spectra of the epoxy system with and without copper were measured on a Nicolet 170SX FTIR instrument (Madison, WI). Because of the difficulty of measuring the epoxy-copper mixtures by means of conventional techniques, the photoacoustic technique was used (Model 200 cell, resolution 8 cm^{-1}, 100 scans; MTEC Photoacoustics, Ames, IA). This made it possible to transfer specimens directly from the DSC to the photoacoustic cell for analysis, after removal of the container lid. The irregular surface and the presence of copper particles do not present a serious problem for the PAS technique, as they would for transmission or reflection measurements.

For the dynamic DSC measurements, the specimens for IR investigation were obtained by quenching samples of both the epoxy resin alone and a 50 : 50 epoxy-copper mixture at different stages of the scan. For example, samples were cured at 20°C/min from 30°C to 160, 180, 210, 220, 240, 260, 280, and 290°C, cooled at a rate of 50°C/min down to 50°C, and then removed from the DSC. In the case of the isothermal scans, specimens were cured at different temperatures (ranging from 160°C to 210°C) until no further heat evolution was detected.

RESULTS AND DISCUSSION

Dynamic DSC Studies

Some dynamic DSC curves obtained for different epoxy-copper mixtures at scan rates of 20°C/min and 5°C/min are shown in Figures 3 and 4, respectively, and the data obtained from all the DSC curves (including the repeat scans to determine the final glass transition temperature T_g) are summarized in Table I.

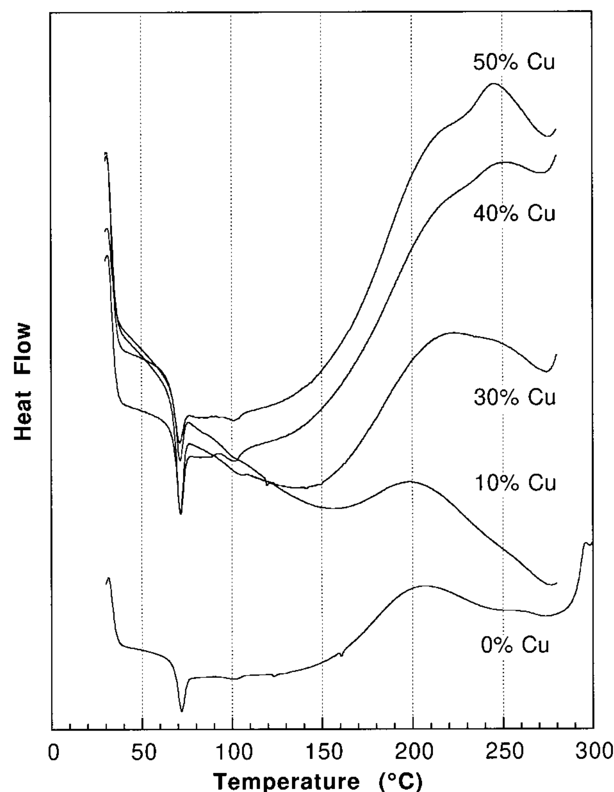

Figure 3 Dynamic DSC curves obtained at a scan rate of 20°C/min for epoxy–copper mixtures containing different amounts of copper.

The peak observed near 70°C corresponds to the glass transition of the B-staged resin. The curing exotherm is observed above 100°C and consists of two overlapping peaks whose position and size depend on both scan rate and copper content. The temperature at which the first maximum in the exotherm peak occurs is shown as T_{m1} in Table I. Because the peaks are broad and overlapping, it is difficult to determine this value precisely. However, it is clear that for both scan rates the maximum of the first peak occurs at higher temperature in samples containing 30–50 wt % copper than it does in those containing 20% or less. The peak onset temperature as determined from analysis of the DSC curve also shows a similar trend. The second exotherm peak, on the other hand, shows the opposite behavior. As the copper content increases, its maximum shifts to lower temperature and it also appears to become more prominent compared to the first peak.

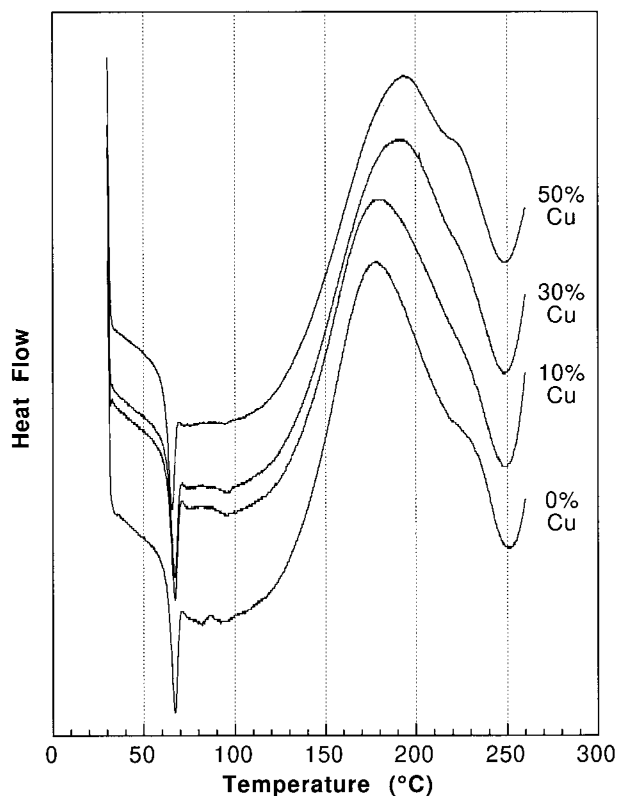

Figure 4 Dynamic DSC curves obtained at a scan rate of 5°C/min for epoxy–copper mixtures containing different amounts of copper.

The heat of reaction values ΔH were determined by integrating the area under the exotherm peak and dividing by the weight of resin in the sample. It can be seen in Table I that the heat of reaction is constant at 110 J/g when the samples are heated slowly (5°C/min). At 20°C/min, the values are significantly lower than at 5°C/min and show some variation with the copper content. A small (5 wt %) copper addition appears to decrease the ΔH by 25–30%, but a further increase of copper slightly increases the ΔH. There may be two factors contributing to the variations in ΔH: a general lowering at high scan rates as a result of a change in reaction path (possibly related to the rate of dissolution of the DICY) and a second effect specifically related to the presence of copper. The glass transition temperature T_g of the cured resin is also affected by both copper content and scan rate. At a given scan rate it is lower when the copper content is high, and for a given copper content it is lower for samples cured at the higher scan rate. The results obtained at a scan rate of 5°C/min are probably more meaningful, because they would be closer to those obtained under normal cure conditions.

It is well known that the glass transition temperature of a thermosetting resin is related to the crosslinking density after cure.[19] This suggests that the slight increase in ΔH for higher copper concentrations at a 20°C/min cure rate is not due to additional crosslinking, but rather to a higher ΔH value for the polymer reactions specifically affected by the copper. The variation in ΔH with copper content is negligible at a scan rate of 5°C/min. It appears that a slow rate of curing decreases the effect of copper on the curing kinetics.

As already mentioned, the exotherm shows two peaks, the second of which becomes more pronounced with increasing copper content. The most interesting phenomenon is the shift of the first and the second peaks of the curing exotherms. It is well known that copper adsorbs DICY molecules and inhibits its dissolution,[26] and this may explain why copper retards the appearance of the first peak. At the same time, it accelerates the appearance of the second one. Considering that the T_g of the epoxy decreases with copper concentration, one can conclude that there is a connection between the intensity of the second peak and the degree of crosslinking.

Table I Data Obtained from Dynamic DSC Scans of Epoxy–Copper Mixtures

Cu (wt %)	ΔH (J/g)		T_{m1} (°C)		T_g (°C)	
	20°C/min	5°C/min	20°C/min	5°C/min	20°C/min	5°C/min
0	72	110	202	176	133	139
5	53	109	203	176	131	137
10	57	109	204	176	125	136
20	58	—	206	—	118	—
30	58	110	214	189	117	133
40	63	—	215	—	116	—
50	80	110	215	190	116	132

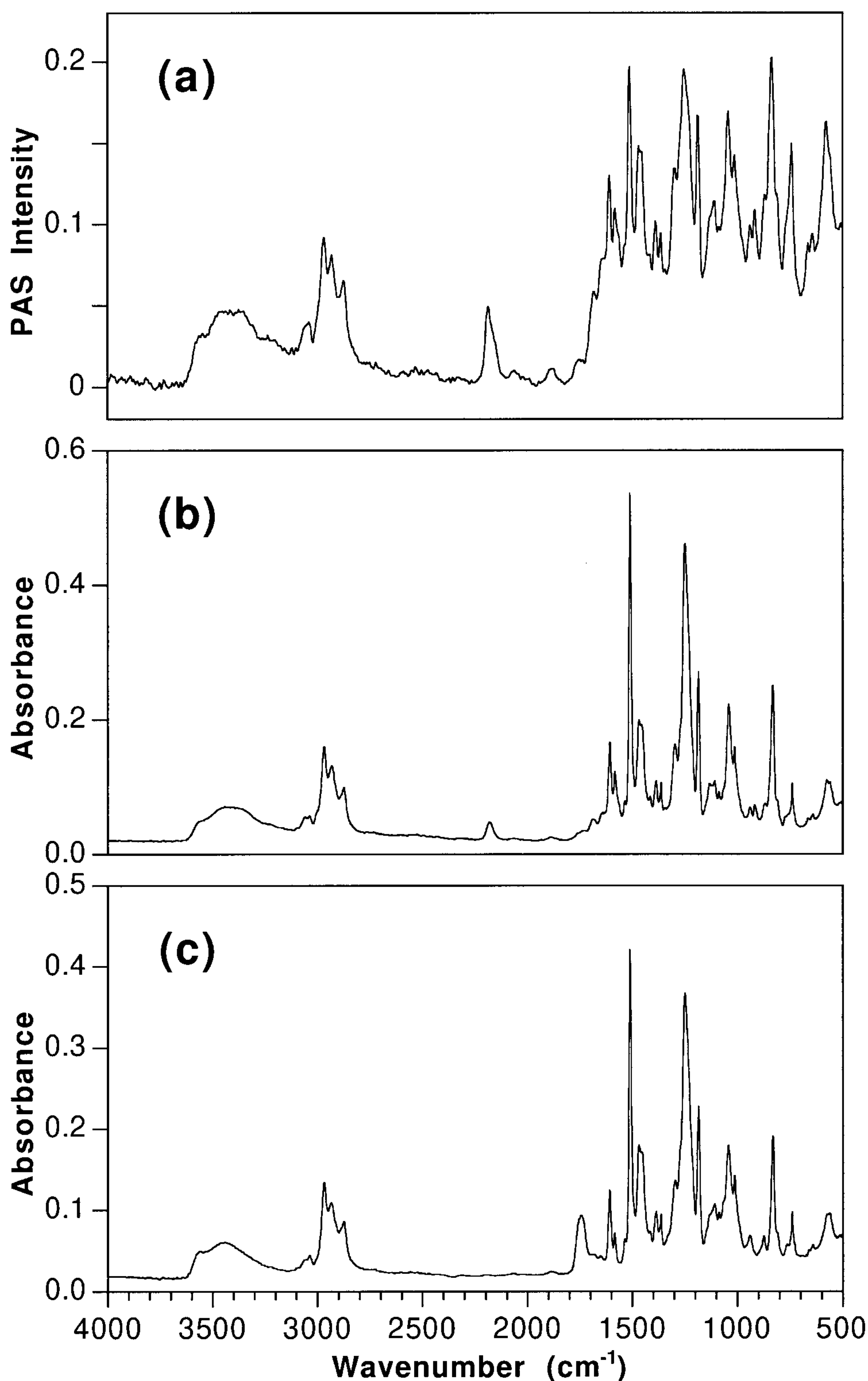

Figure 5 Comparison of IR spectra of the epoxy system. (a) Photoacoustic spectrum of resin powder, before cure; (b) transmission spectrum of thin solvent-cast film, before cure; (c) transmission spectrum of same film, after cure.

It was with the aim of explaining these observations that FTIR analysis of partially reacted specimens was performed as described previously. Figure 5(a) shows the photoacoustic FTIR spectrum of the initial (B-staged) epoxy powder. For comparison purposes, the transmission spec-

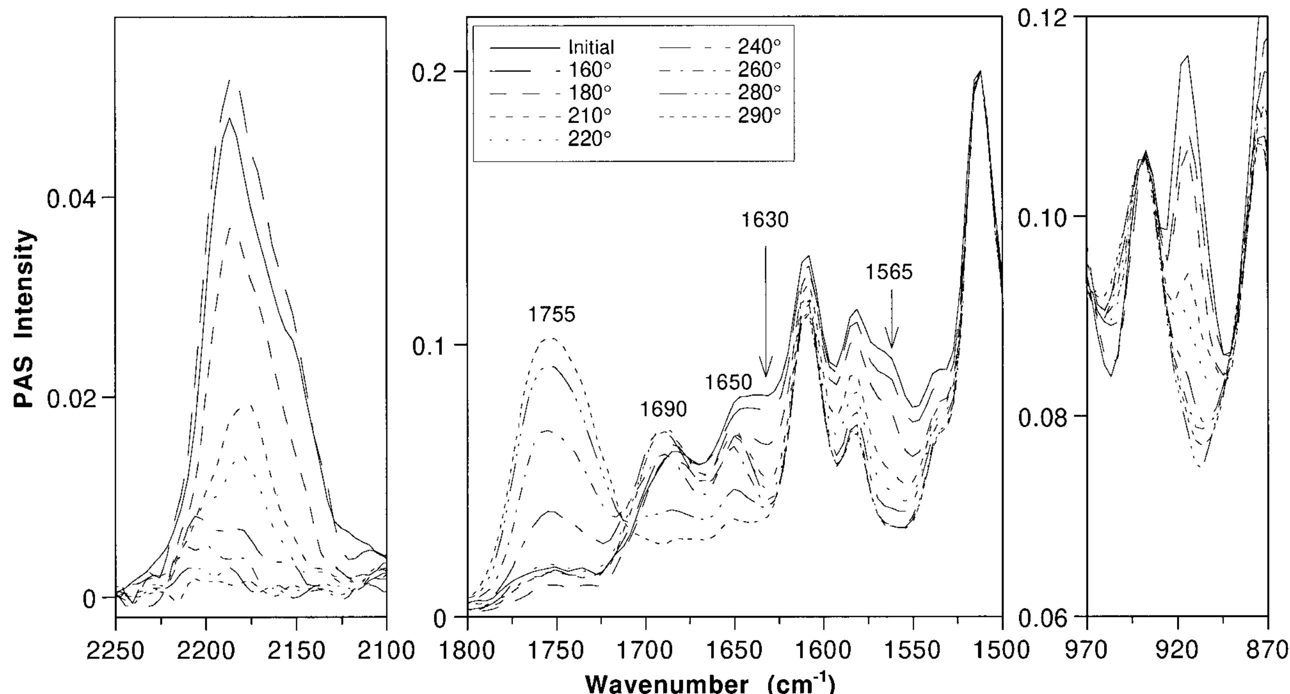

Figure 6 Photoacoustic FTIR spectra of neat epoxy resin specimens quenched at different temperatures (°C) in the DSC scan at 20°C/min.

trum of a thin solvent-cast film of the same material is shown in Figure 5(b). It can be seen that the agreement is very good, although the relative peak intensities are different in the PAS spectrum. Figure 5(c) shows the spectrum of the same film after curing for 100 min at 177°C. The main changes brought about by the curing occur in three specific regions. Figure 6 shows these regions in more detail for a set of photoacoustic spectra of neat epoxy resin specimens scanned in the DSC at 20°C/min and quenched at different temperatures in the scan. The spectra have been normalized with respect to the aromatic ring peak at 1515 cm^{-1} and baseline-adjusted where necessary. Figure 7 shows the spectra obtained in a similar manner for a 50 : 50 epoxy-copper mixture. Two easily interpretable changes involve the disappearance of the nitrile peak at 2180 cm^{-1} and the epoxide ring peak at 915 cm^{-1}. The changes occurring in the 1800–1500 cm^{-1} region are more complex, as several bands change in intensity. The major ones and their usual assignments are as follows: (a) 1755 cm^{-1} (ester C=O stretch); (b) 1690 cm^{-1} (urea C=O stretch); (c) 1650 cm^{-1} (imine C=N stretch); (d) 1630 cm^{-1} (amine N–H bend); and (e) 1565 cm^{-1} (amine N–H bend). The peaks at 1610, 1580, and 1515 cm^{-1} are associated with aromatic ring vibrations and change little during the cure.

Although photoacoustic spectroscopy has the advantage of being applicable to samples that are not amenable to transmission or reflection measurements, it also has certain disadvantages. The noise level is higher and the stronger peaks of the spectrum tend to be saturated; hence quantitative analysis is difficult. Nevertheless certain trends are evident, and it was possible to measure the peak intensities at different frequencies in Figures 6 and 7 in order to follow at least semiquantitatively the evolution of specific groups as a function of advancement through the DSC scan. The results are depicted in Figure 8. At the first temperature studied, 160°C, the reaction had just begun. Already there can be seen ([Fig. 8(a,b)] a decrease in epoxide rings and amine N–H groups, in keeping with the fact that the epoxide-amine reaction is well known to be the first to occur. At the same time Figure 8(c) shows a slight increase in the nitrile absorption at 2186 cm^{-1}; this behavior could be caused by the diffusion of DICY molecules and their reacted species in the epoxy prepolymer.[8] The other peaks show little change from the initial B-staged state. The temperature range between 160°C and about 230°C corresponds approximately to the first peak in the DSC exotherm. In this range, the epoxide and amine peaks continue to decrease. (The amine absorption at 1630 cm^{-1} is difficult to measure accu-

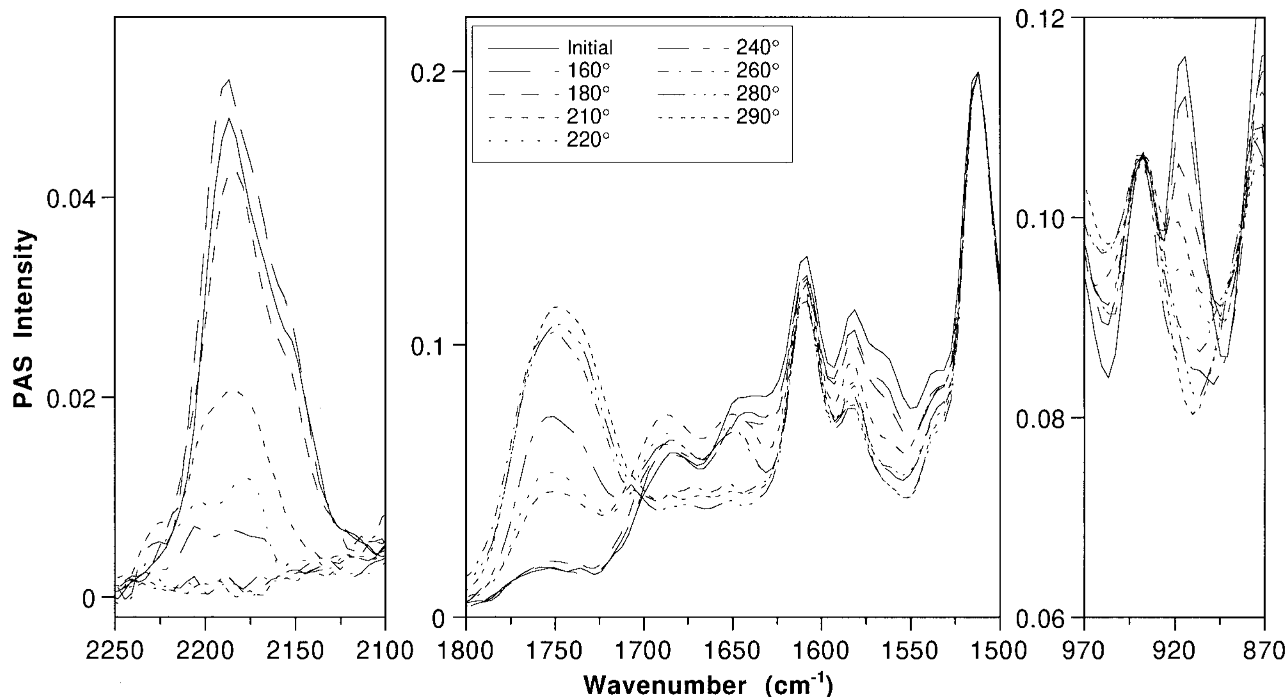

Figure 7 Photoacoustic FTIR spectra of 50 : 50 epoxy–copper mixture quenched at different temperatures (°C) in the DSC scan at 20°C/min.

rately because it does not appear as a distinct peak.) However, the drop in epoxides and amine is now accompanied by a significant decrease in the nitrile peak [Fig. 8(c)] and an increase in the urea peak [Fig. 8(d)]. At the same time, the imine peak [Fig. 8(e)] shows little change. It appears that nitrile groups are being converted into urea groups, either by direct reaction with hydroxyl groups or by passage through an intermediate state involving cyclic iminooxazolidine or aminooxazoline structures. Possible mechanisms for this were described in the Introduction. An interesting observation is the fact that copper seems to accelerate somewhat the formation of urea groups in this temperature range.

The temperature range above about 230°C corresponds to the second peak in the DSC exotherm. As the temperature rises beyond 230°C, epoxide, amine, and nitrile groups continue to decrease and by 290°C are completely consumed. (The epoxide and amine peaks disappear, as can be seen in Figures 6 and 7, but the measured absorbance does not fall to zero because they lie in valleys between two adjacent peaks.) There is also now a substantial decrease in both urea and imine groups [Figs. 8(d,e)], accompanied by a strong increase in ester carbonyl groups [Fig. 8(f)]. The decrease in the absorbance at 1650 cm^{-1} at advanced stages of curing was attributed by Lin et al.[10] to intermolecular rearrangements. Copper has an accelerating effect on these reactions. In fact, it can be seen from Figure 8(f) that the onset of rapid ester formation occurs at about 220°C when there is no copper present, but at 180°C when the mixture contains 50 wt % copper. Since these systems are often cured around 180°C (for example, in circuit board lamination), the effect of the copper can be very significant. In the present case, at the end of the DSC scan both the samples with and without copper show practically no epoxide, nitrile, or amine groups. However, the copper-containing sample shows a higher ester content. This confirms that the chemical structure of the network is different and may explain why the copper-containing samples have a lower T_g (Table I). The second peak in the DSC exotherm appears to be clearly associated with the reaction that produces the ester peak at 1755 cm^{-1}.

Isothermal DSC Studies

The results just presented help to explain the two peaks in the dynamic DSC curve. However, most curing of DICY systems is done at temperatures under about 180°C, where the reaction that produces ester groups appears to be less important.

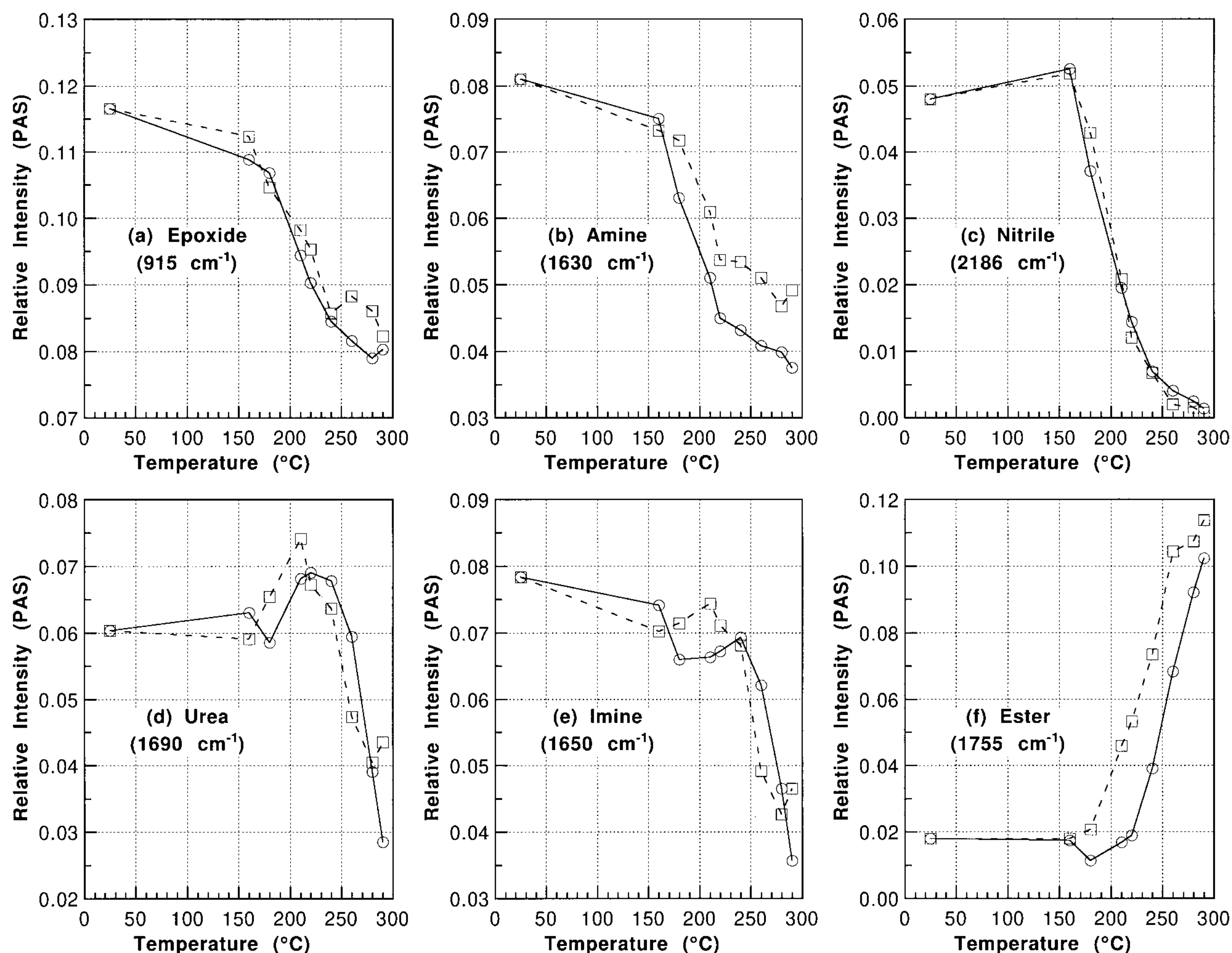

Figure 8 Variation in intensity of different peaks in the IR spectrum as a function of temperature in the dynamic DSC scan, for neat epoxy resin (○) and a 50 : 50 epoxy–copper mixture (□).

In order to further elucidate the behavior under such conditions, isothermal DSC experiments on both neat epoxy resin and a 50 : 50 copper–epoxy mixture were performed in the Setaram calorimeter at temperatures ranging from 100°C to 220°C. In all cases, the sample was held at the reaction temperature until after the end of detectable heat evolution. It was then cooled and rescanned to determine the glass transition temperature. The times t_1 and t_2 given in Table II correspond to the time at which heat evolution was no longer detected and the time at which the heating was stopped, respectively. Some typical isothermal DSC curves are given in Figure 9. The reaction rate becomes significant within a minute or two after the sample is inserted into the calorimeter, before thermal equilibrium has been attained, so it is difficult to calculate accurate values of the heat of curing ΔH. A second set of samples was prepared under similar conditions in the Perkin-Elmer DSC, but instead of a second scan these were subjected to FTIR-PAS.

Table II Duration of Isothermal DSC Experiments

Cure Temp. (°C)	Epoxy Only		50 wt % Copper	
	t_1 (min)	t_2 (min)	t_1 (min)	t_2 (min)
100	200	230	200	230
120	190	230	188	225
140	120	170	118	180
160	85	100	82	130
180	80	100	78	100
200	60	75	57	70
210	55	75	54	60
220	45	75	45	50
240	25	40	25	40

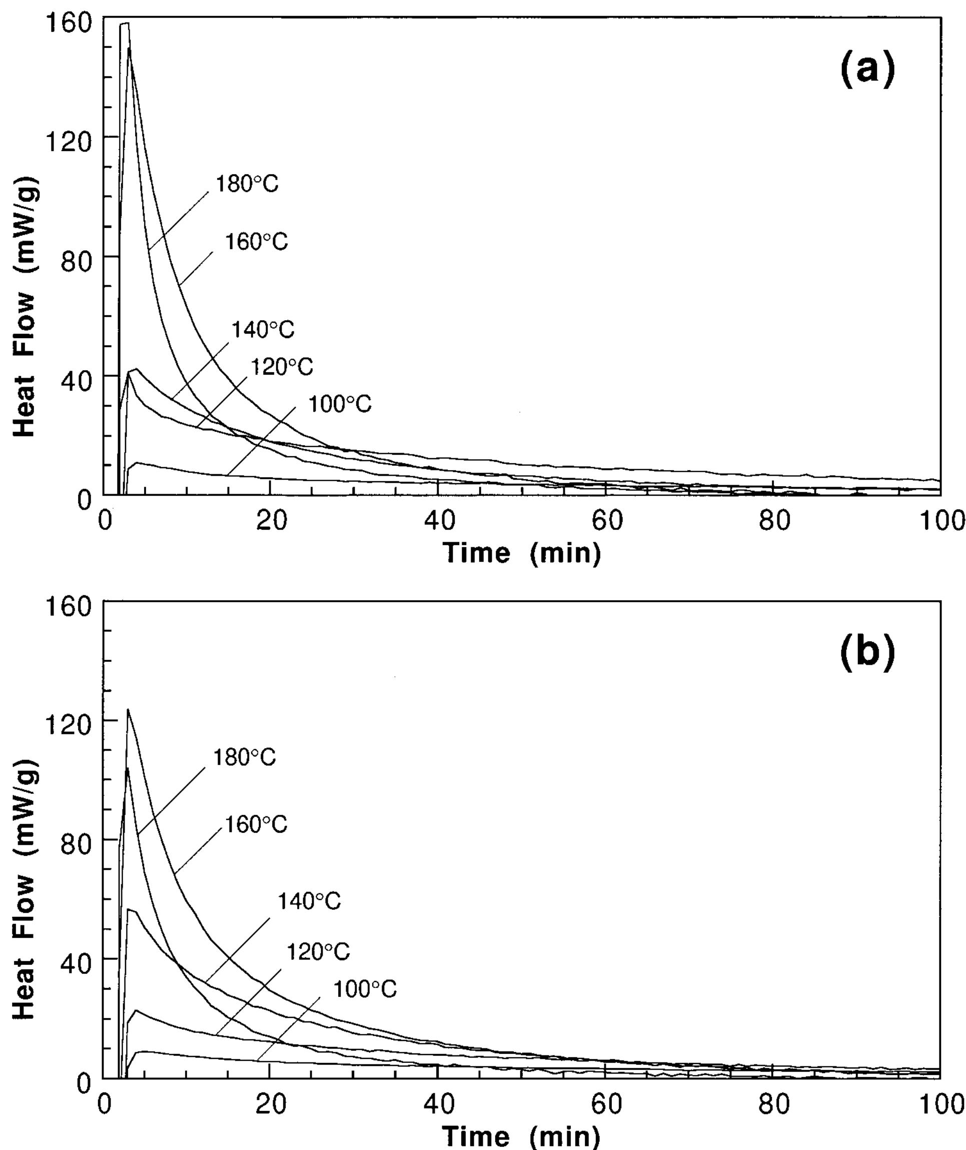

Figure 9 Heat flow curves observed for isothermal DSC cure at different temperatures of (a) neat epoxy resin and (b) epoxy–copper mixture, 50:50 by weight.

The results for the samples cured at different temperatures are shown in the following figures: glass transition temperatures in Figure 10; normalized photoacoustic FTIR spectra for the neat epoxy and the 50 : 50 mixture in Figures 11 and 12, respectively; and the variation of peak intensities in Figure 13.

For the sample cured at 100°C, the extent of reaction is rather low. The epoxide peak at 915 cm^1 is less intense than in the unreacted resin, but is still quite significant (Figs. 11 and 12); only about half of the epoxide groups have reacted. The nitrile peak at 2186 cm^{-1} is almost as intense as in the unreacted resin. At this temperature the only significant reaction appears to be that involving epoxide and amine groups. The low extent of reaction explains the weakness of the DSC exotherms at 100°C in Figure 9. At 120°C and 140°C the extent of reaction is higher, but still low, regardless of whether or not copper is present. The epoxide peak is now weak, indicating that most of the epoxide groups have reacted at these temperatures. There is also a significant drop in the number of nitrile groups present [Figs. 11, 12, 13(c)]. However the glass transition temperature (Fig. 10) is in the range of only 100–110°C, much lower than the ultimate value of about 135°C.

One reason for the low extent of cure at 100–140°C is the limited solubility of the DICY at

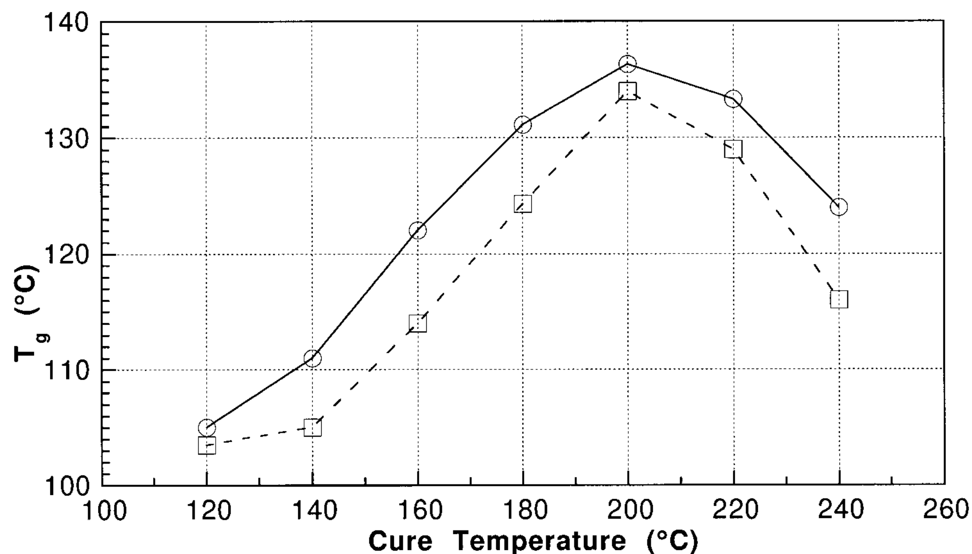

Figure 10 Glass transition temperature of samples cured isothermally at different temperatures: neat epoxy resin (○) and a 50 : 50 epoxy–copper mixture (□).

these temperatures. As pointed out by Amdouni et al.,[12] at low temperatures the epoxide groups react mainly through etherification because the DICY is not available for reaction. A second reason is that as the resin crosslinks, its T_g rises from the initial value of about 70°C. When the T_g approaches the cure temperature, the resin vitrifies and the crosslinking reaction becomes very slow as a result of diffusion control of the kinetics. However, when the cure temperature is well above the ultimate T_g of about 135°C, the reaction can proceed to its full extent, the DSC exotherms become much stronger (Fig. 9), and the glass transition temperature increases significantly (Fig.

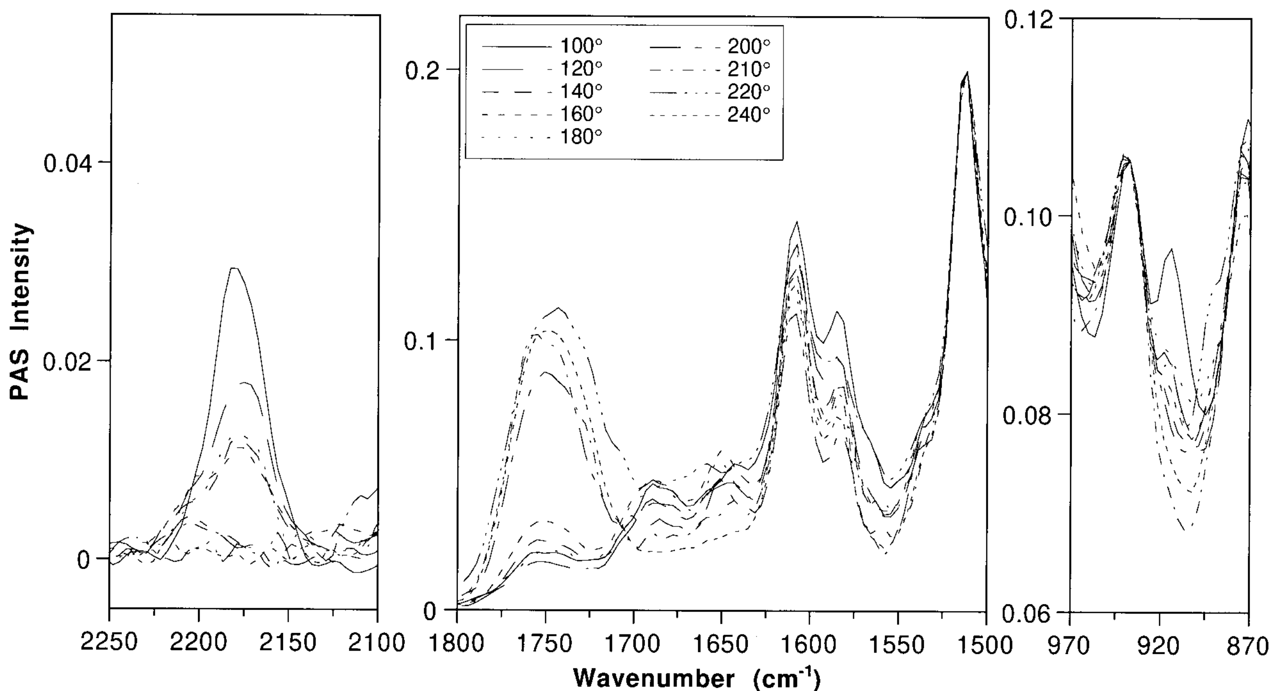

Figure 11 Photoacoustic FTIR spectra of neat epoxy samples cured isothermally at different temperatures as indicated (°C).

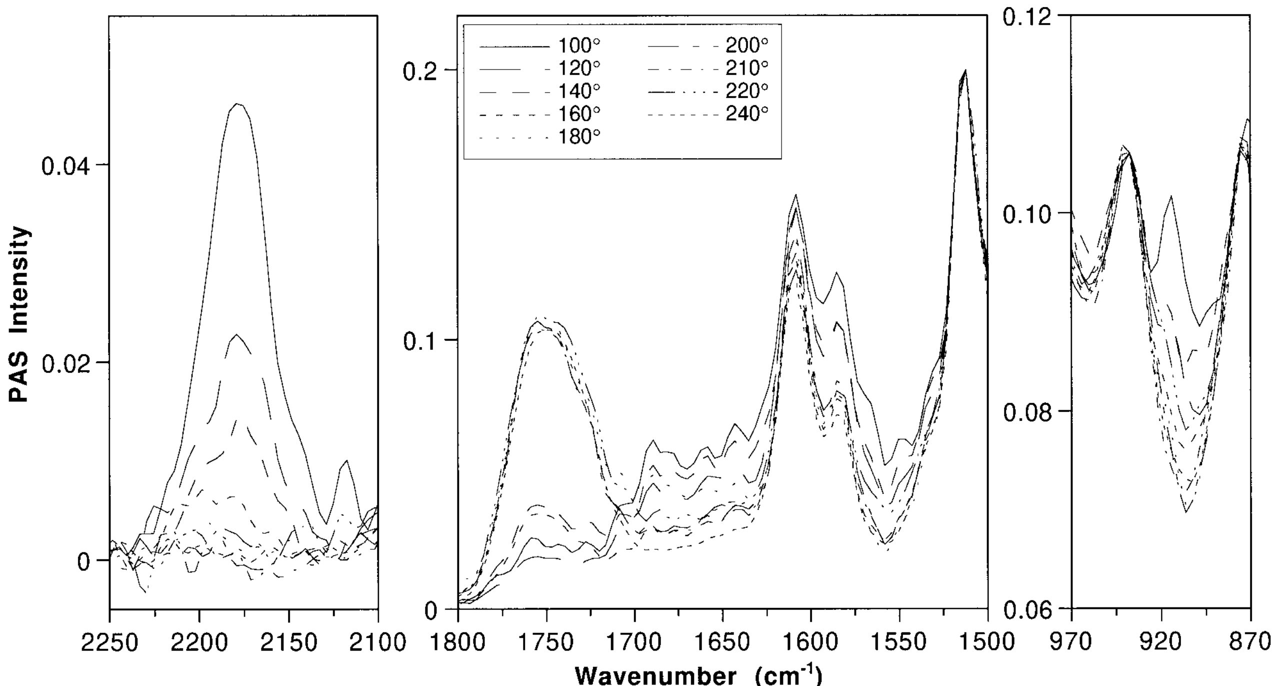

Figure 12 Photoacoustic FTIR spectra of a 50 : 50 epoxy–copper mixture cured isothermally at different temperatures as indicated (°C).

10). The highest T_g value and therefore the highest degree of crosslinking is achieved at a cure temperature of 200°C. Above this the T_g drops somewhat, presumably as a result of degradation of the crosslinked network.

The presence of copper does not appear to have a large effect on the DSC exotherms. However, the samples containing copper consistently show a T_g value that is about 5°C lower than that of the equivalent sample without copper (Fig. 10), so the copper does have some effect on network formation. (The somewhat smaller difference observed at 200°C is probably not significant, given the experimental error.) Figure 13(c) suggests that at low cure temperatures the copper inhibits the reaction of the nitrile groups. The effect is small but is probably real. The urea and imine peaks occur in a rather complex region of the spectrum and as a result they show considerable scatter [Figs. 13(d,e)]. However both show a decreasing trend with cure temperature, whether or not copper is present. The ester peak at 1755 cm^{-1} is more clearly defined, and shows particularly interesting behavior [Fig. 13(f)]. At 160°C it is rather weak, regardless of whether or not copper is present. At 180°C, however, it is much stronger when copper is present. By 200°C it is strong in both cases. This result was confirmed by repeating the experiments. Thus, the copper catalyzes the reaction that produces the carbonyl peak at 1755 cm^{-1} and lowers the temperature at which this reaction becomes important. The effect of the copper is most significant around 180°C, the usual recommended cure temperature for such systems. It is interesting to note that in the same temperature range the imine content appears to be lower when copper is present [Fig. 13(e)].

According to Figure 10, for the isothermally cured samples thermal degradation becomes significant above 200°C and results in a decrease in T_g. Even without copper, the sample cured at 240°C had a T_g of only 124°C. However, Table I shows that samples without copper cured dynamically had T_g values of 133°C and 139°C, even though they were heated to a final temperature of 280°C. The apparent discrepancy may be explained in terms of chemical kinetics and the different time scale of the two experiments. The samples cured by isothermal DSC at 240°C were cured for 40 min, all at 240°C, whereas the samples cured by dynamic DSC, even at the slower rate of 5°C/min, spent only 16 min in the temperature range 200–280°C. Thus, the latter samples underwent less degradation. The same argument applies to the FTIR results. For the isothermally cured samples, Figure 13 shows that ester formation becomes important at 180°C when no copper is present and 160°C with 50% copper. For the

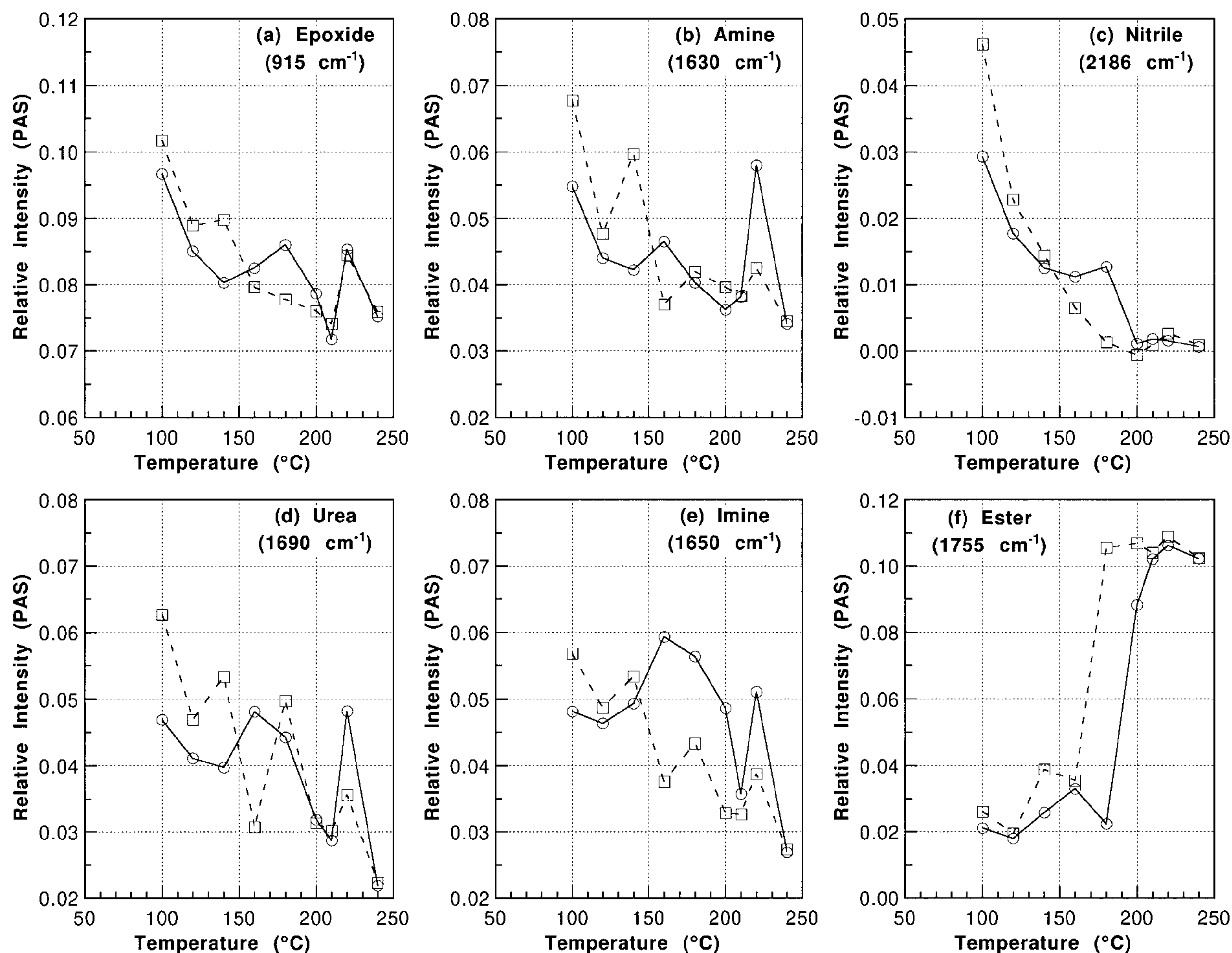

Figure 13 Variation in intensity of different peaks in the IR spectrum as a function of the isothermal cure temperature, for neat epoxy resin (○) and a 50 : 50 epoxy–copper mixture (□).

dynamically cured samples of Figure 8, the different time–temperature relationship means that ester formation becomes detectable only when the temperature reaches 220°C without copper and 180°C with copper. In the corresponding DSC curves of Figure 3, the temperature is even higher (over 230°C) before the second peak (attributed to the ester-producing reaction) becomes obvious, but in fact it starts before that and is partly hidden by the first exotherm peak.

GENERAL DISCUSSION AND CONCLUSIONS

The isothermal DSC results corroborate the dynamic DSC results, which together with the FTIR data help to elucidate the curing behavior, although the details are still not completely clear because of the complexity. Based on the above results for the particular system studied, we propose the following explanation, which combines elements of previously suggested mechanisms. The first (and main) stage of the cure mechanism, corresponding to the first exotherm peak in the dynamic DSC curve, involves several reactions. These include, first of all, the usual well-known epoxide-amine and epoxide-hydroxyl reactions.[17] These are closely followed by a reaction involving conversion of nitrile groups into urea groups, probably through reaction with hydroxyl groups to give an iminoether structure that undergoes rearrangement. The nitrile-hydroxyl reaction may be intermolecular, as suggested by Saunders et al.,[1] or intramolecular to give a five-membered ring, as suggested by Zahir.[4] The imine C═N

bonds in this structure contribute to the IR peak at 1650 cm^{-1}, while the urea carbonyl bond is responsible for the peak at 1690 cm^{-1}.

The second stage of the curing process, which occurs at higher temperature and gives rise to the second exotherm peak in the dynamic DSC curve, corresponds to the growth of the strong carbonyl peak near 1750 cm^{-1}. Some workers[1,16] have assigned this peak to urea carbonyl groups. However, we feel that the frequency is rather high for urea groups, even in a cyclic structure.[27,28] Instead, we prefer the suggestion that it arises from urethane ester groups. These could be present either in an open form, as proposed by Zahir,[4] or in a five-membered oxazolidinone ring, as proposed by Davidson,[6] Gilbert et al.,[13] and Pfitzmann et al.[14,15] The latter is more likely. The carbonyl band has been reported to absorb at 1730 cm^{-1} in oxazolidone,[28,29] at 1750 cm^{-1} in 3-methyl-2-oxazolidinone,[28] at 1760 cm^{-1} in oxazolidinones formed by isocyanate-epoxy reactions,[30] and almost always around 1750 cm^{-1} in a series of alkyl oxazolones (like oxazolidinones but with a C═C double bond in the ring).[31] Open-chain alkyl urethanes, on the other hand, generally absorb around 1700 cm^{-1} in the solid or neat liquid state, where hydrogen bonding occurs,[28,29,32] although the position shifts to around 1730 cm^{-1} when hydrogen bonding is negligible, as in very dilute solution.[27,29,32] Furthermore, the lower imine content observed here in association with the growth of the peak at 1750 cm^{-1} provides support for Gilbert's mechanism involving hydrolysis of imine bonds to form oxazolidinone rings. In actual fact, two types of ester group may be present, because close examination of the band near 1750 cm^{-1} in Figures 5(c), 6, 7, 11, and 12 shows that it is asymmetric and appears to comprise two peaks, one near 1760 cm^{-1} and one near 1740 cm^{-1}. Whatever the exact mechanism of the cure, it is clear that copper has an effect. The first stage of the cure appears to be slightly retarded by the copper, probably because of association between DICY and the surface of the copper. On the other hand, copper significantly accelerates and increases the importance of the second stage of the curing, which gives rise to the IR ester band at 1755 cm^{-1}. This reaction does not form new crosslinks, and in fact may break some of them through hydrolysis of imine bonds. This amounts to alteration of the polymer network and results in a change of physical properties, such as the lowering of the glass transition temperature that was observed here.

Hong and Wang[18,19] have demonstrated that copper oxide particles also have a significant effect on the curing of DICY-containing epoxy systems. They found that adding cupric and cuprous oxide to the resin led to an increase in unreacted DICY, and this was attributed to adsorption of DICY on the oxide surface.[18] They also found that both oxides accelerate the degradation of the resin, as measured by means of IR spectroscopy (including the peak at 1750 cm^{-1}) and by thermogravimetric analysis. Furthermore, Hong[24] recently has studied the degradation of thin epoxy films on metal surfaces and found that the degradation is significantly faster on copper than on aluminum or steel.

We have shown in this work that for the system studied, the effect of the copper is particularly significant around 180°C, which is often the temperature used for circuit board lamination. This means that the copper–epoxy interphase may differ from the bulk of the matrix, and this has important implications related to the practical questions of bond strength, residual stresses, and overall mechanical performance. The effect of the copper is not necessarily bad, however, because a lower degree of crosslinking at the interphase may result in a less brittle resin and reduce the risk of delamination at the copper–epoxy interface.

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