Effect of Copper Oxides on the Thermal Oxidative Degradation of the Epoxy Resin

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SYNOPSIS

The effect of copper oxides on the thermal oxidative degradation of a brominated epoxy resin–dicyandiamide system was studied using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The addition of small amounts of Cu_2O or CuO fillers to the epoxy resins affected the relative amounts of highly reacted cyclic species formed during thermal aging and induced catalytic degradation of the epoxy resins. The overall and initial activation energies of the degradation process were found to decrease, and the order in the degradation kinetics of the epoxy resin changed from a near zero order to negative domain (autocatalytic nature) in the presence of copper oxides. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Due to the outstanding heat resistance, adhesive strength, and corrosion resistance of epoxy resins, they have been widely used in building electronic components. For example, in manufacturing multilayer printed circuit boards (PCB), the epoxy laminates are cured against black copper oxides under relatively high temperature and pressure conditions. Generally, the produced PCB have good mechanical strength and durability in hostile environments. However, partial delamination happens in the PCB occasionally due to the removal of the black copper oxide layer by corrosive hole cleaning chemicals used in the production process. In addition, a decay of the bond strength with time at elevated temperature is frequently observed. It is believed that copper oxides accelerate the degradation of the polymer systems in contact and reduce the strength and durability of the epoxy–copper adhesive bonds leading to the failure of lamination in PCB.

The chemical interaction between organic molecules and metal atoms (or ions) often affects the degradation of organic materials on metal surfaces. 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.[1–3]

Allara and co-workers[1] studied the oxidation of a polyethylene–copper laminate by using reflection absorption and internal reflection infrared techniques. They found that copper carboxylate salts, which are catalysts for the oxidative degradation of the polyethylene, can be formed at the polyethylene–copper interface and diffused into the polyethylene matrix for several thousand angstroms. The formation of salts between polyimide and Cu surface was also widely reported.[4–6] Hansen et al.[7] studied the induction periods of thermal oxidation of polypropylene in the presence and also the absence of copper dust by measuring oxygen uptake at different temperatures. It was found that a shorter induction period could be observed in the presence of copper than that in the absence of copper. The thermal oxidation of polypropylene was catalyzed by the addition of copper. A similar result as reported by Meltzer et al.[8]

Comparing with other metals, the epoxy–copper adhesive bonds fail rapidly in oxidizing media. Black

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and Blomquist[9] studied the durabilities of adhesive bonds prepared with an epoxy adhesive on different metal substrates by measuring the shear strength of bonds after high-temperature exposure. They indicated that the bonds prepared with iron substrates had a greater decrease in shear strength than those prepared with aluminum substrates after 100 h exposure at 550°F. The greatest decrease in strength was observed from bonds prepared with copper substrates that lost all of their strength after exposure. It was proposed that iron and copper can cause catalytic degradation of epoxy resins at high temperatures.

Poor durability of epoxy–copper adhesive joints may come from the unique property of the copper oxide. It was pointed out that a mixture of two forms of copper oxides (cuprous and cupric oxide) on copper surface behaved as a defect semiconductor.[10] Electrons can readily move from the metal substrate to the environment and oxidation continues. The cuprous–cupric ion pair can be an effective oxidation–reduction couple that can accelerate the decomposition of polymers.[10,11] In addition, Ishida[12] indicated that the copper surface could induce polymerization of an uncatalyzed diglycidyl ether of bisphenol-A.

The purpose of this work is to study the degradation of a brominated epoxy–dicyandiamide system in the presence of cuprous and cupric oxides. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analyzer (TGA) were used to characterize chemical changes and relative degradation rates of the epoxy resins during thermal exposure.

EXPERIMENTAL

The epoxy system used for manufacturing #7628, #2116, and #1018 laminates for multilayer PCB production was obtained from Asia Chemical Company. The system consisted of the brominated epoxy resin (epoxide equivalent weight = 490, bromine content = 20%), the dicyandiamide (DICY) curing agent (3.8 parts per hundred, phr), and the 2-methyl imidazole accelerator (0.05 phr).

The epoxy system was dissolved in acetone (referred to as a varnish) and coated on a KBr pellet, then the varnish was vacuum dried and cured at 165°C for 90 min. A Perkin-Elmer 1700 Fourier transform infrared spectrophotometer was used to obtain the IR transmission spectra of the epoxy system before and after cure. The IR spectra were taken from 4000 to 450 cm^{-1} at a resolution of 4 cm^{-1} for 100 cycles.

For thermal degradation study, the cured resin was aged in an oven at 165°C for different periods of time, then the specimen was taken out and analyzed by IR periodically. The appearance of new bands and the change in intensities of absorption bands during exposure were observed and calculated. Similar procedures were used to analyze epoxy systems containing 0.1 wt % CuO and Cu_2O fillers. Fillers of 99.9% pure Cu_2O and 99.999% pure CuO were obtained from Strem Chemicals, Inc.

Three different epoxy specimens, the blank epoxy system (referred to as the specimen B-E), the epoxy with 0.1 wt % Cu_2O (referred to as the specimen B-E-Cu_2O), and the epoxy with 0.1 wt % CuO (referred to as the specimen B-E-CuO), were further analyzed with a DuPont 951 TGA instrument. The cured epoxy resin was ground into powders and vacuum dried overnight before TGA analysis. The weight loss behavior of resin powders was measured in a dynamic scanning mode. The temperature was scanned from room temperature to about 400°C at four different heating rates (0.25, 0.5, 1, and 2°C/min). The peak temperatures of derivative weight loss curves, the weight loss percentages, and the initial activation energies were obtained from TGA experiments.

RESULTS AND DISCUSSION

FTIR Analysis

The representative IR spectra of the varnish before and after cure are shown in Figures 1 and 2, respectively. The changes of absorption bands during cure can be easily observed from these two spectra. The large absorption band near 1710 cm^{-1} in Figure 1(A) is characteristic of the carbonyl groups from the residual acetone solvents in the varnish resin (Fig. 1 was taken from the specimen before vacuum dried for comparison purpose). The 1710 cm^{-1} band disappears in Figure 1(B) due to the drying of solvent. The consumptions of cyano (the bands near 2190 cm^{-1}) and epoxide (915 cm^{-1}) groups, accompanied by the formations of new absorbance bands near 1750, 1690, and 1650 cm^{-1} can be clearly identified in Figures 1(A) and 1(B). The tentative IR assignments of the DICY and the epoxy resin are listed in Table I.[13–15]

The decreases in intensities of bands near 2190 and 915 cm^{-1} can be attributed to the reaction of resin epoxide groups with nitrile groups in DICY.[16] The curing reaction also resulted in the disappearance of the band near 2150 cm^{-1} (no N=C=N
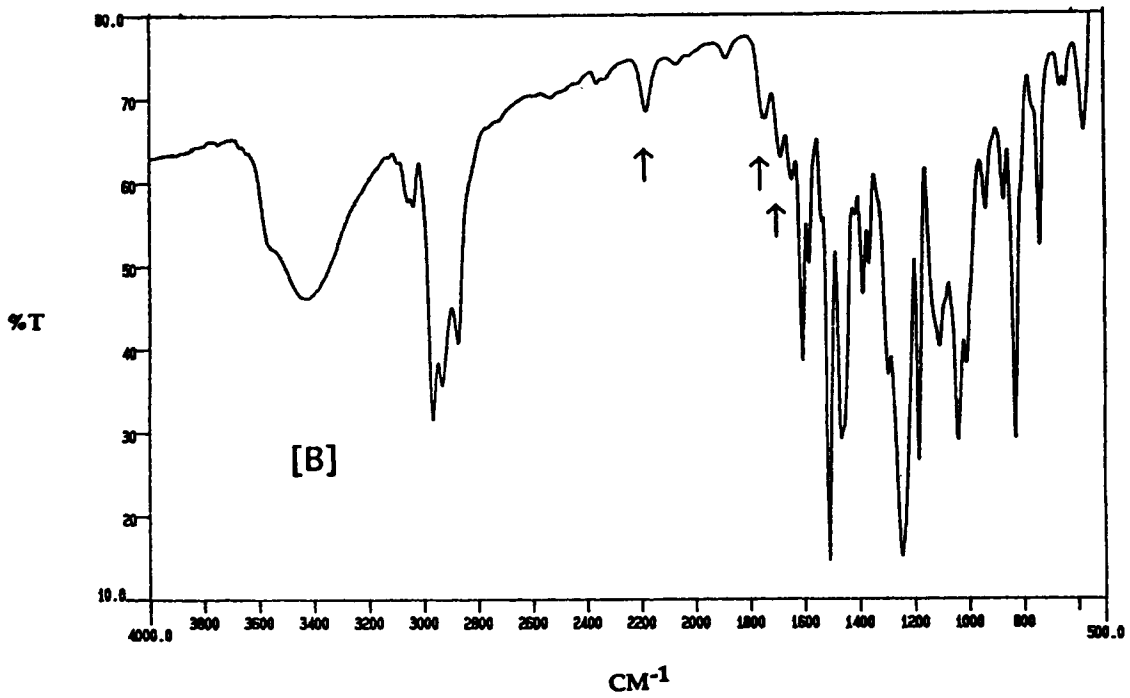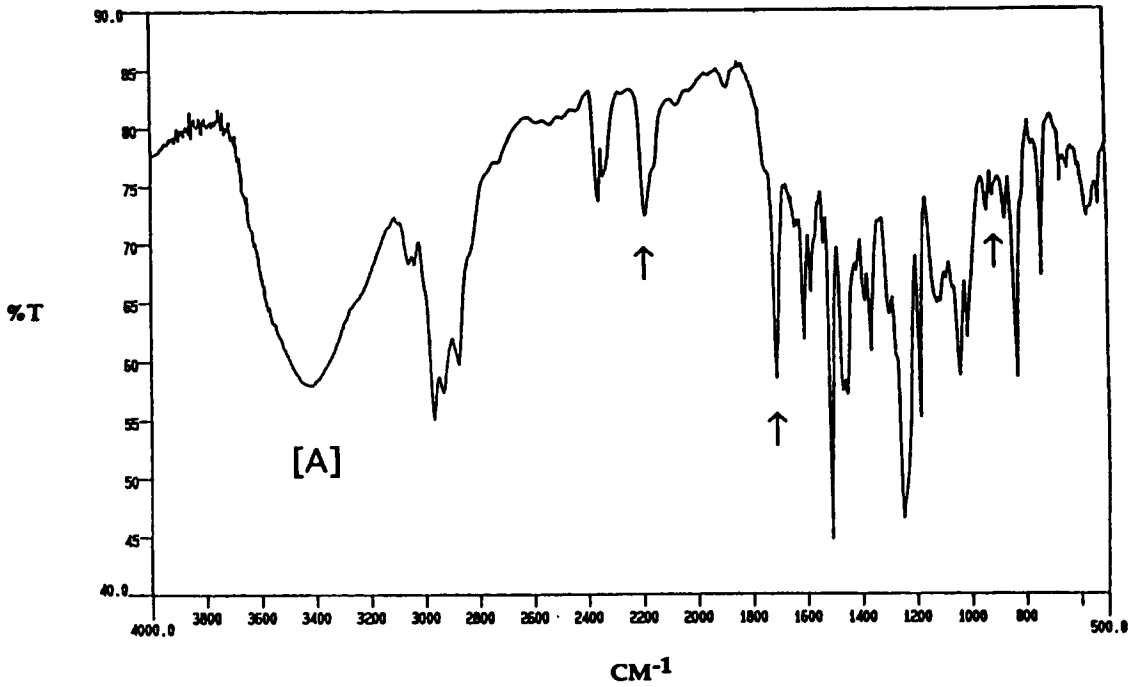
Figure 1 IR spectra of the B-E (A) before cure (before vacuum dried) and (B) after cure.
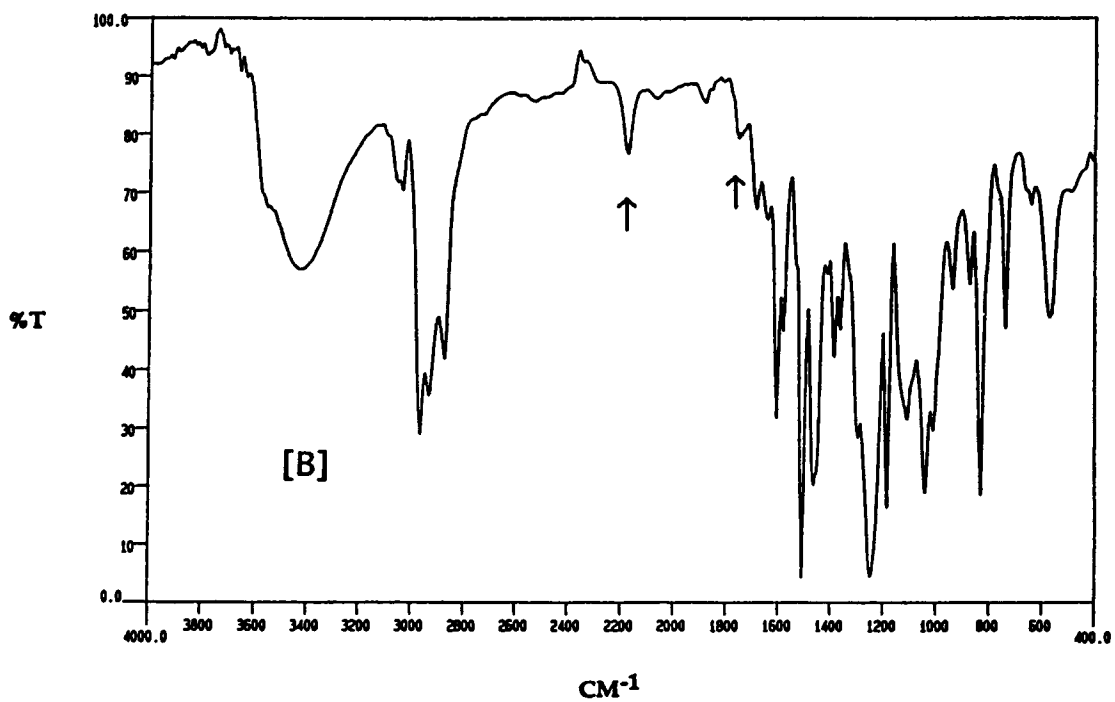
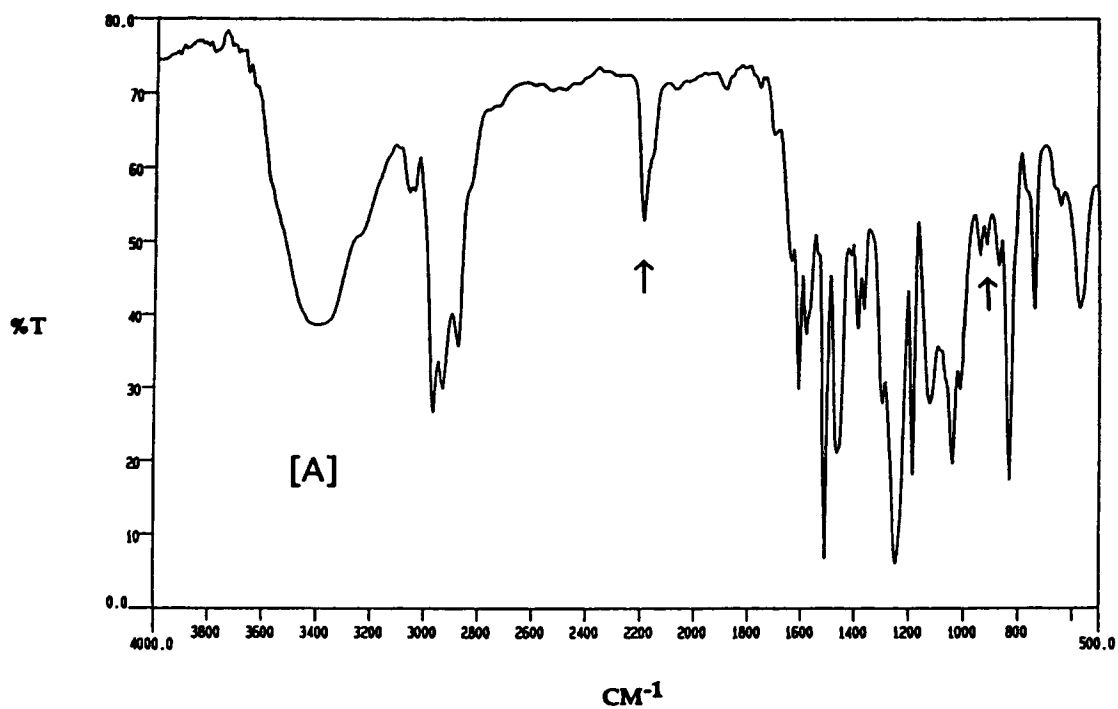**Figure 2**   IR spectra of the B-E-CuO (A) before cure and (B) after cure.

Table I Tentative IR Assignments of the Epoxy/DICY System[13-15]

DICY	IR Assignment	Epoxy	IR Assignment
3385 s	ν_{as} NH$_2$	3450 broad	ν_s OH
3335 s			
3185 s	ν_s NH$_2$	3098 w	ν_s φ—H
3150 s			
2210 m	N≡C—N	3058 w	ν_{as} CH$_2$ epoxy
2165 m	N=C=N	3038 w	ν_s φ—H
1658 s	δ NH$_2$	2998 w	ν_s CH$_2$
1639 s		2968 m	ν_{as} CH$_3$
		2931 m	
1575 m	ν_{as} N—C—N	2874 m	ν_s CH$_3$
		2836 vw	ν_s O—CH$_3$
1506 m	ν_{as} N=C—N	1891 w	φ disubstituted
1254 m	ν_s N≡C—N	1610 s	ν C=C of φ
		1580 m	
		1510 s	
1096 w	NH$_2$ rock	1460 m	ν C=C of φ
			ν_{as} CH$_3$
929 m	ν_s N—C—N	1385 m	δ_s CH$_3$
		1365	
720 w	N=C—N wag	1250 s	ν_s φ—O
669 m	δ N=C—N	1185 s	δ φ—H
		1086 w	in-plane
554 m	NH$_2$ wag	1040 m	ν_s φ—O—C
528 m	N≡C—N twist	1010 m	δ φ—H
			in-plane
500 m	N=C—N rock	948 w	δ φ—H out-of-plane
		915 m	epoxy ring
		835	δ φ—H out-of-plane

ν, Stretching vibration; δ, deformation; φ, aromatic ring; s, strong; m, medium; w, weak; vw, very weak.

group found after cure) and the shift of the band from 2190 to 2180 cm^{-1} (due to the formation of alkylated DICY). The disappearance of the band near 915 cm^{-1} shown in Figure 1(B) indicates complete conversion of the epoxide functional groups during cure, whereas the presence of the band near 2180 cm^{-1} shows the cured resin containing appreciable unreacted nitrile groups.

The 1650 cm^{-1} band was assigned to an imino group formed by the intermolecular addition of hydroxyl to the DICY cyano functionality, and/or by the intramolecular nucleophilic substitution of hydroxyl at the imide functionality.[16,17] The absorption bands near 1750 and 1690 cm^{-1} are characteristic of carbonyls formed by the structural rearrangement of the imino esters into 2-oxazolidones and guanyl ureas, respectively.[15,18] It was reported that the formation of ureas groups (1690 cm^{-1}) can be related

to the formation of highly substituted species contributing substantially to the crosslinking density.[17,19]

Similar observations can be obtained from the spectra of specimens prepared with the CuO and Cu$_2$O added varnishes. Figures 2(A) and 2(B) are IR spectra of the B-E-CuO before and after cure, respectively. The decreases in intensities of the bands near 2186 and 915 cm^{-1}, but the appearances of the new bands near 1750, 1690, and 1650 cm^{-1} are also observed. However, greater relative intensities of bands near 1750, 1690, and 1650 cm^{-1} in spectrum of the cured B-E-CuO than those taken from the B-E are observed [Figs. 1(B) and 2(B)]. The changes in intensities of these bands are indications of different extents of reactions during the cure of resins. As a result, the varnish with CuO had greater extent of cure than the blank varnish. Sim-

ilar results can be obtained from the spectra of the B-E-Cu$_2$O before and after cure shown in Figures 3(A) and 3(B), respectively.

The effects of addition of CuO and Cu$_2$O on the

chemical reactions of the epoxy–DICY system can be observed more clearly from the IR analyses of thermal aged resins. Figures 4(A), 4(B), and 4(C) are IR spectra of the B-E, the B-E-CuO, and the B-
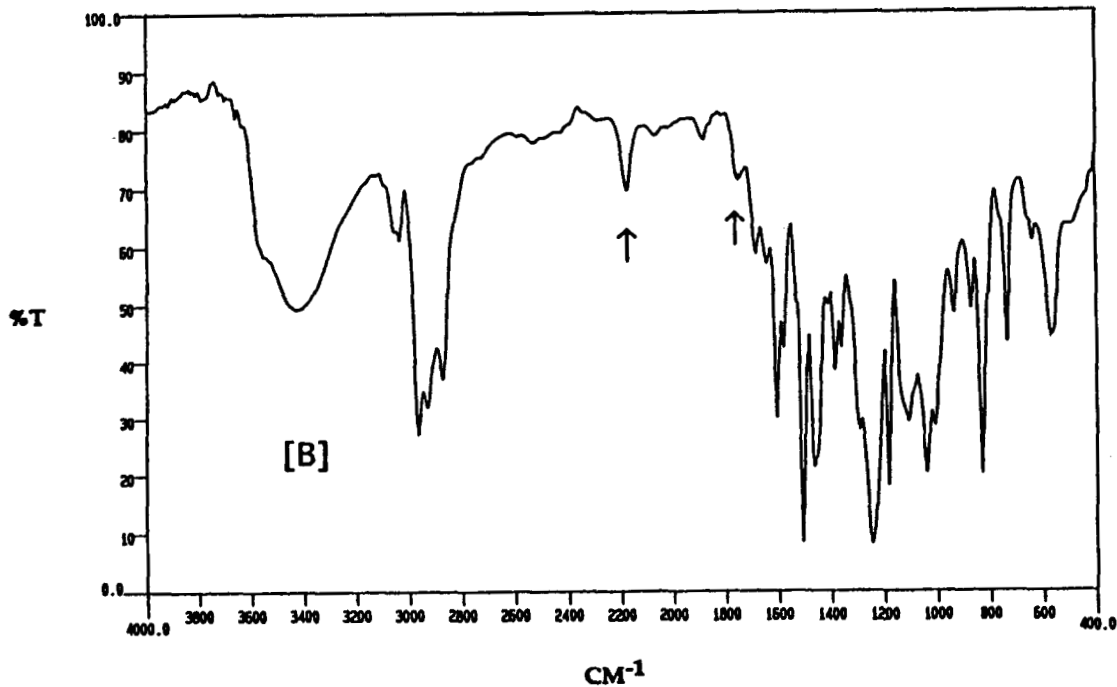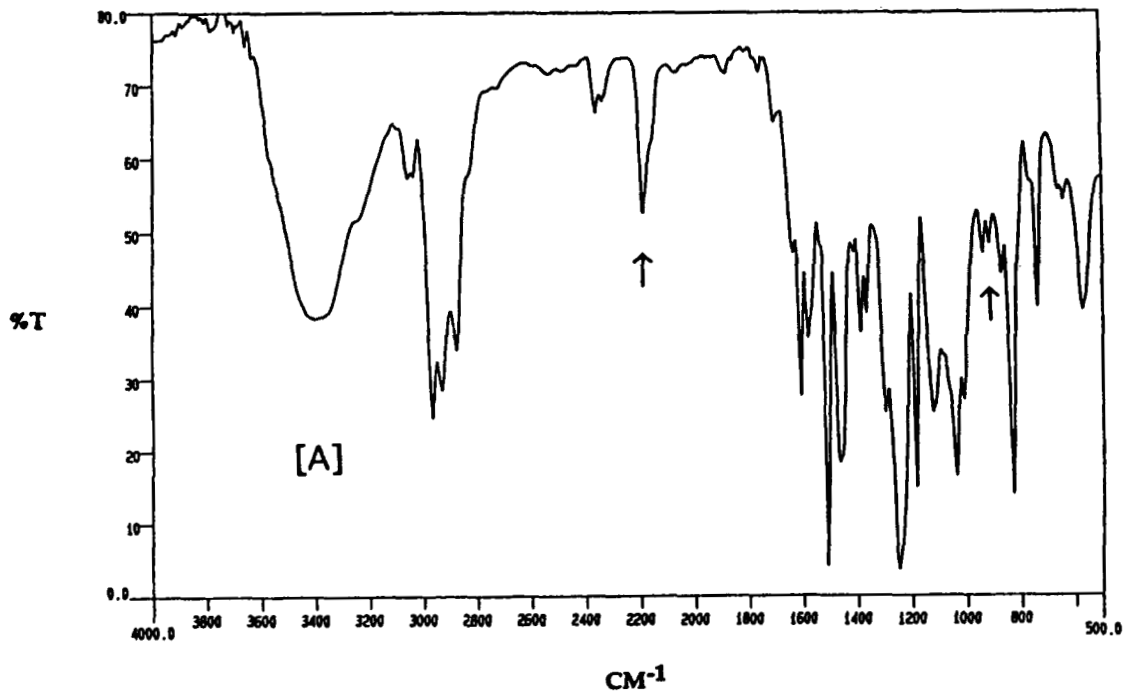

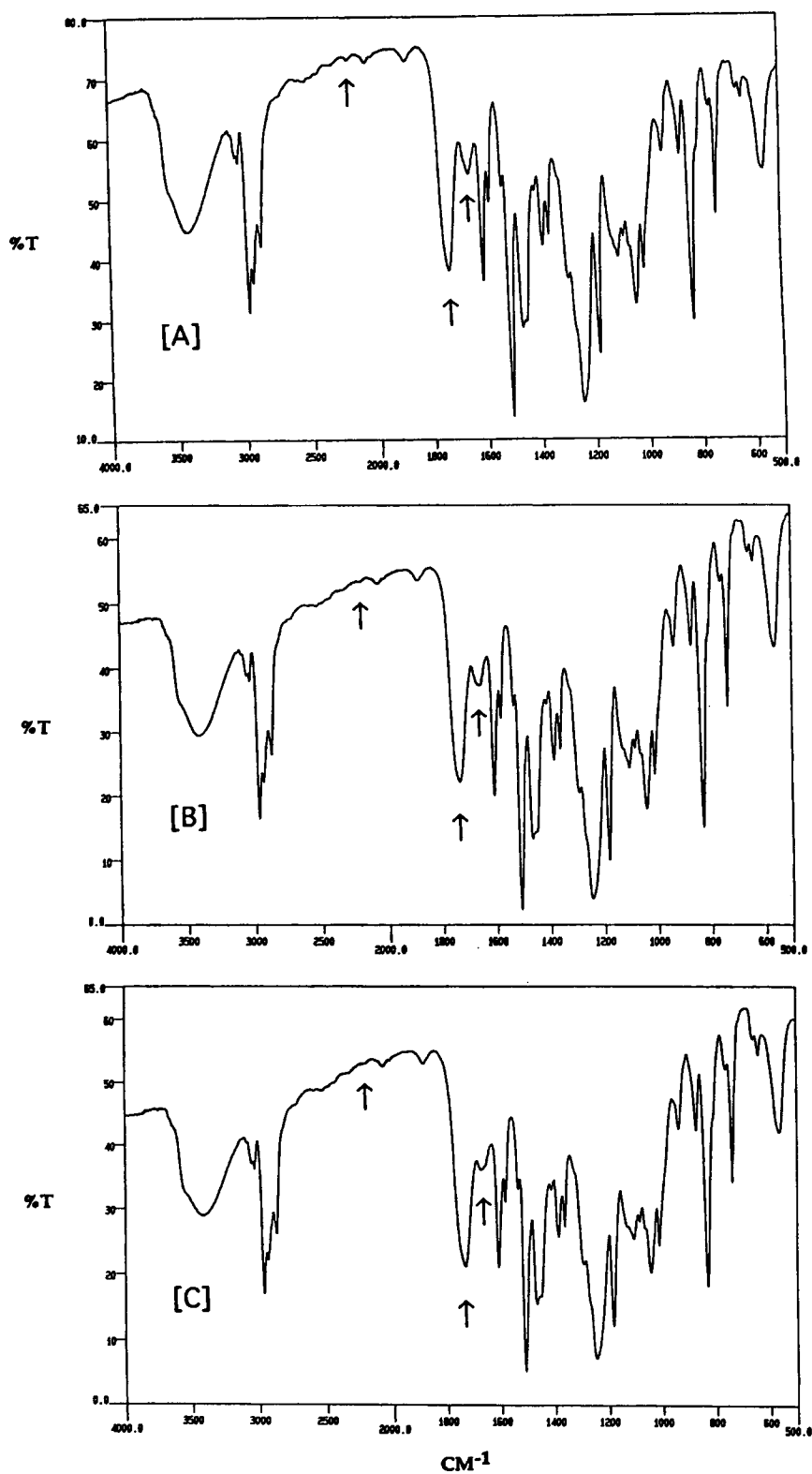Figure 3   IR spectra of the B-E-Cu$_2$O (A) before cure and (B) after cure.

Figure 4   IR spectra of (A) the B-E, (B) the B-E-CuO, and (C) the B-E-Cu₂O after 930 min exposure at 165°C.

E-Cu$_2$O after thermal aging at 165°C for 930 mins, respectively. The accompanying changes in intensities of IR bands during thermal aging are shown in Figures 5, 6, and 7. The band near 835 cm^{-1}, a characteristic band of benzene ring deformation, was chosen as an internal standard. It is shown in Figure 5 that the intensities of bands near 1750 and 1650 cm^{-1} increase, while the intensities of bands near 2180 and 1690 cm^{-1} decrease with increasing aging time.

From previous characterizations of these bands, it was found that more cyclic products were formed during aging. The increase in intensities of 1650 cm^{-1} bands was from the intermolecular reaction of hydroxyl with the DICY cyano functionality and by the intramolecular nucleophilic substitution of hydroxyl at the imide functionality.[16,17] Henceforth, the accompanied reduction in intensity of the cyano band (2180 cm^{-1}) was also observed. After long time exposure the guanyl ureas (or ureas) could decompose into 2-oxazolidones, bringing forth the decrease and the increase in intensities of the 1690 and 1750 cm^{-1} bands, respectively.[17]

It was shown that the cyclization of highly substituted DICY is the cause for the liberation of ammonia and alkyl amines,[17] all of which can react rapidly with epoxide to produce tertiary amine adducts at the temperatures required for DICY–epoxide reaction. The nitrile functional groups are consumed during the formation of these degraded products. However, a small IR band near 2180 cm^{-1} is shown in Figure 4(A) indicating that the cyano groups are not totally consumed after 930 min aging.

Similar behaviors are also observed in Figures 6 and 7, which are obtained from the IR analyses of the B-E-CuO, and the B-E-Cu$_2$O, respectively. However, greater changes in intensities of bands near 1750 cm^{-1} are observed in Figures 6 and 7 than in Figure 5. Furthermore, the almost disappearance of cyano bands (2180 cm^{-1}) in Figures 4(B) and 4(C) indicates that the degradation reactions proceed to a greater extent for resins with the addition of CuO or Cu$_2$O. This can also be confirmed from the trend of decrease in intensities of 1650 cm^{-1} bands at the later stage of aging [Figs. 6 and 7). This intensity reduction indicates consumption of imido groups to produce oxazolidone-like species without forming new imido groups. In addition, the band near 2180 cm^{-1} also decreases in intensity due to the formation of oxazolidone products.

It is interesting to notice that a shoulder near 2205 cm^{-1} gradually appeared as the band near 2180
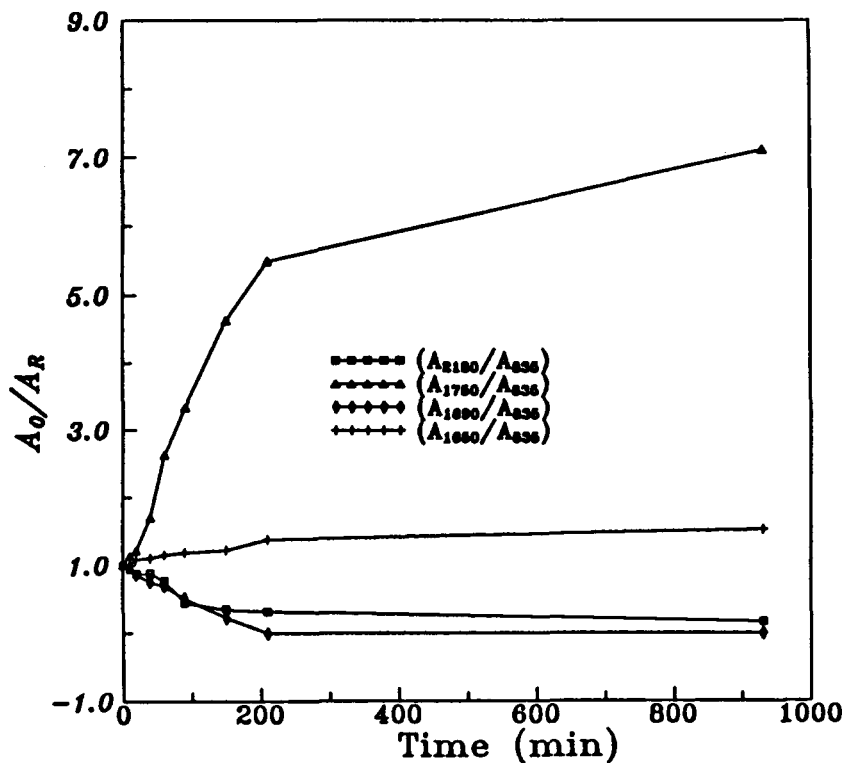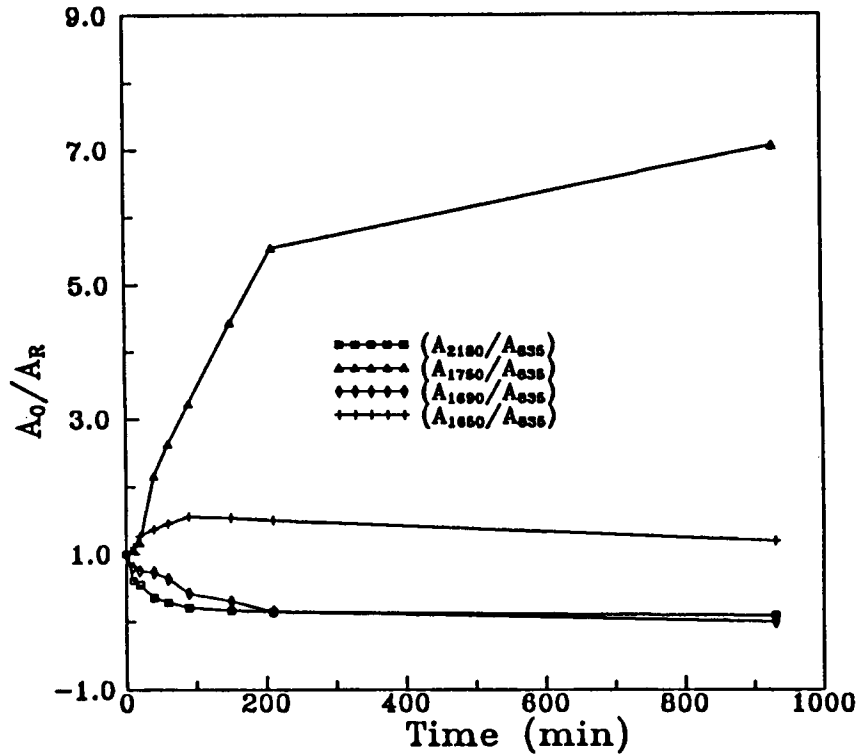

Figure 5   Changes of relative IR absorbances in the B-E during thermal aging.

Figure 6   Changes of relative IR absorbances in the B-E-CuO during thermal aging.
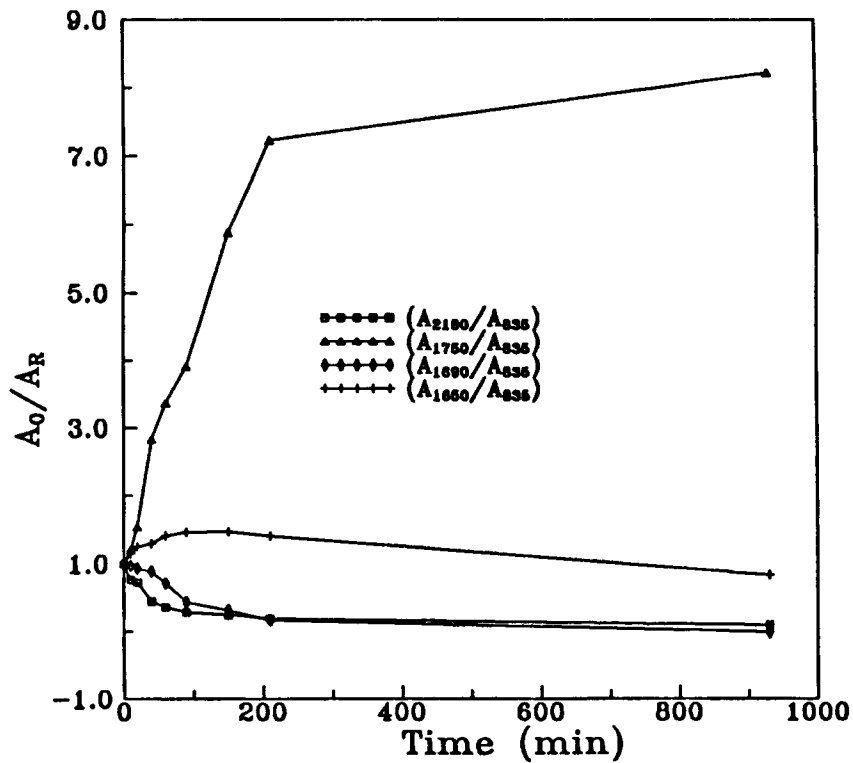

Figure 7   Changes of relative IR absorbances in the B-E-Cu$_2$O during thermal aging.

cm^{-1} decreased in intensity. The formation of cyclic products from the alkylated DICY was considered to cause the appearance of the 2205 cm^{-1} band.[17] This band appeared in spectra of the B-E-CuO, and in the B-E-Cu$_2$O only after 40 min aging, which was earlier than in the spectrum of the blank resin. However, the intensity of the 2205 cm^{-1} band decreased after long time exposure indicating the formation of oxazolidone-like products and the loss of materials.

From the shifts of absorption bands of concern it is possible to observe the difference in degradation rates of three specimens. The bands near 1750 cm^{-1} from spectra of the B-E, the B-E-CuO, and the B-E-Cu$_2$O shift to 1742, 1736, and 1733 cm^{-1} after 930 min aging, respectively. These shifts are from the formation of new absorption bands at lower wavenumber, which is characteristic of degraded products like aldehyde, or acid groups.[20,21] Much greater increases of ratios of A(1750)/A(835) than ratios from other bands shown in Figures 5, 6, and 7 are attributed to the formation of these new products because the formation of 2-oxazolidones alone was unable to cause the great change observed. The extent of band shifts shown also indicates the faster degradation of resins in the presence of CuO or Cu$_2$O.

In addition, the bands near 1650 cm^{-1} from spectra taken from the B-E, the B-E-CuO, and the B-E-Cu$_2$O were found shifted to 1657, 1663, and 1671 cm^{-1} after aging, respectively. It was indicated that the degradation of amine-cured epoxy resins could result in NH and NH$_2$ groups having absorption band in the 1640–1680 cm^{-1} region.[20] Lin[21] also found that the degradation of DGEBA-type epoxy resins could form phenoxy group with absorption band near 1665 cm^{-1}. The generation of these degraded products could also happen in our system. The broadening of the band near 1660–1670 cm^{-1} region is observed in Figures 4(B) and 4(C) but not in Figure 4(A), which also shows faster degradation of the B-E-CuO and B-E-Cu$_2$O systems. The catalytic degradation of epoxy resins in the presence of CuO and Cu$_2$O are also confirmed by TGA shown as follows.

TGA

The representative TGA weight loss derivative curves of the B-E, the B-E-CuO, and the B-E-Cu$_2$O specimens taken at a heating rate of 1°C/min are shown in Figure 8. The weight loss before 150°C is believed to be the release of absorbed moisture (or residual solvents) and volatile compounds (like
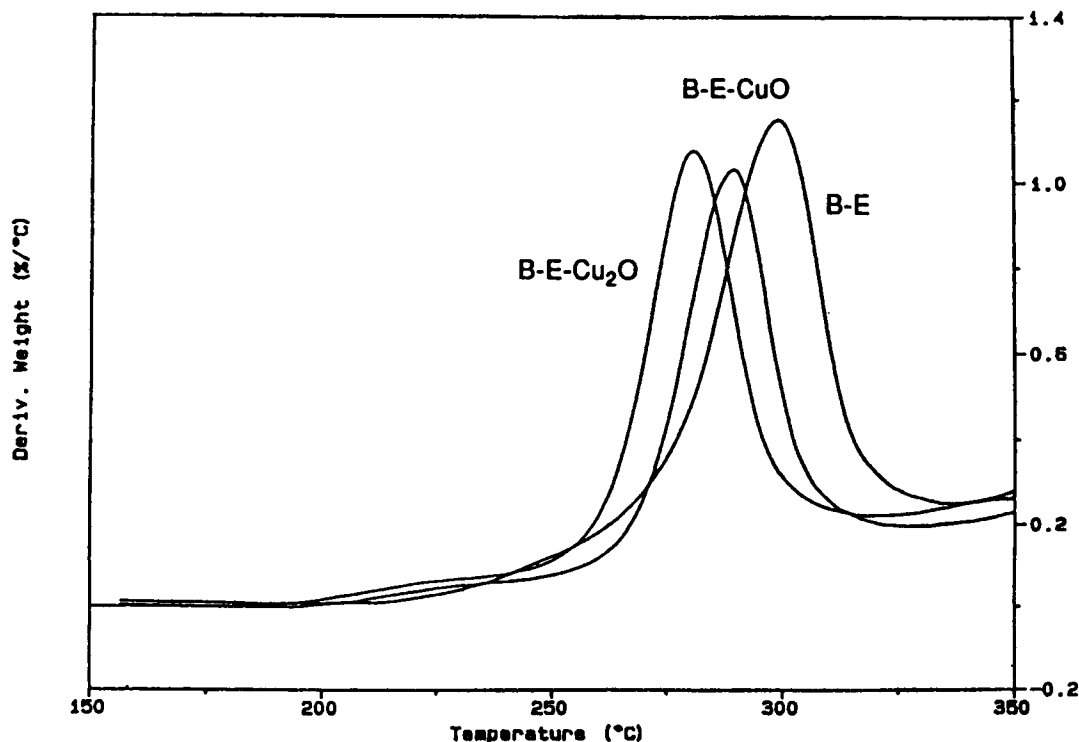

Figure 8   TGA derivative curves of different specimens taken at 1°C/min heating rate.

NH_3) from the postcuring effect of the TGA scanning process.[19] The major weight loss process results from the main chain scissions in the epoxy resin. About 40% weight loss is observed in this process.

It is shown in Figure 8 that the peak temperatures corresponding to maximal weight loss rate of the TGA spectra of three specimens are different. The peak temperatures are 298.0, 284.6, and 278.3°C from TGA curves of the B-E, the B-E-CuO, and the B-E-Cu_2O specimens, respectively (Table II). The difference in peak temperatures is related to the difference in the kinetic parameters.[22] In general, the specimen with a lower peak temperature has a smaller activation energy of the degradation process (for specimens from the same materials). As a result, it was established that the resins with 0.1 wt % Cu_2O or CuO had a lower activation energy of degradation than the blank resin. This fact confirms the catalytic degradation behavior of Cu_2O or CuO in the epoxy–DICY system.

When a polymer film on the copper substrate undergoes oxidation at high temperature, diffusion of cuprous and cupric ions into the polymer matrix takes place. These ions cause the decomposition of hydroperoxides formed during degradation, and then accelerate the deterioration of the polymer.[23] The catalytic effect of copper oxides is started from the abstraction of tertiary hydrogen atoms generating radicals and reducing copper oxides during the reaction. The Cu^+ ions decompose ROOH groups and convert into Cu^{2+} ions in the polymer film. The Cu^{2+} ions then decompose more ROOH groups and change back to Cu^+. The RO and ROO radicals generated during these reactions accelerate the oxidation of polymer molecules.[23]

By comparing the peak temperatures, it reveals that the catalytic degradation effect of Cu_2O is greater than that of CuO on the epoxy–DICY system. This can also be observed from the TGA curves taken at other heating rates. The shift of peak temperatures of three specimens taken at 2, 0.5, and

0.25 are following the same trend as that of TGA curves taken at 1°C/min heating rate. Although the peak temperatures of TGA curves decrease with decreasing heating rates,[22] the peak temperature taken from the B-E-Cu_2O specimen is still the lowest, indicating that the activation energy of which is probably the smallest.[24]

From the method described by Flynn,[25] the initial activation energy of a degradation process is obtained from the following equation:

$$\frac{E}{R} = \frac{d}{d\alpha}\left[T^2 \frac{d\alpha}{dT}\right] - 2T \qquad (1)$$

where α is the fraction of conversion given by $\alpha = (W_0 - W)/(W_0 - W_f)$ (W is the weight of sample and the subscripts, 0 and f, refer to weights at the beginning and the end of the measurement), T is the absolute temperature, R is the gas constant, and E is the activation energy. This equation holds for all values of α for zero-order reactions, and is quite accurate for all reactions when $0 < \alpha < 0.05$.[25]

According to Eq. (1) the representative initial activation energies of three specimens were calculated from the TGA data taken at 1°C/min heating rate (see Fig. 9). The data greater than 4% weight loss were rejected in order to improve the accuracy of Eq. (1).[25] The initial activation energies calculated were 32.0, 29.2, and 12.7 kcal/mol for the B-E, the B-E-CuO, and the B-E-Cu_2O, respectively (see also Table II). Hence, the addition of Cu_2O or CuO decreases the initial activation energy of the thermal degradation process of the epoxy–DICY system.

Moreover, it seems that the B-E-Cu_2O degrades faster than the B-E-CuO. In spite of the different surface chemistries between Cu_2O and CuO fillers, great differences in particle sizes and surface areas were found between Cu_2O and CuO used. It was measured that Cu_2O had a solid structure with a

Table II   Information Obtained from TGA Weight Loss Curves

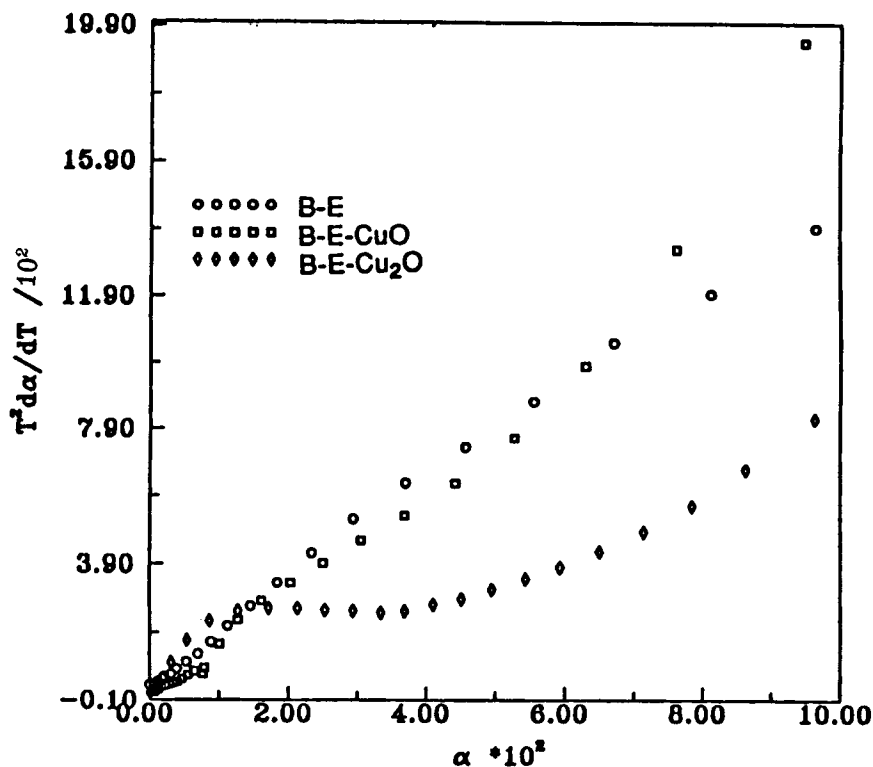| Sample Ramp Rate (°C/min)	B—E			B—E—CuO			B—E—Cu_2O		
	E (kcal/mol)	T_i (°C)	T_p (°C)	E (kcal/mol)	T_i (°C)	T_p (°C)	E (kcal/mol)	T_i (°C)	T_p (°C)
2	34.2	211	303.4	32	194	296.0	15.1	168	290.7
1	32	195	298.0	29.2	182	284.6	12.7	160	278.3
0.5	27.2	179	283.8	24.8	172	270.1	10.3	152	262.6
0.25	26.4	170	273.7	24	165	259.2	8.74	148	256.2

Figure 9 Plot of $T^2(d\alpha/dT)$ vs. α from TGA curves of different specimens taken at 1°C/min heating rate.

diameter about 15 μm (based on scanning electron microscopy) and the surface area about 1.9 m^2/g (from surface area analyzer ASAP 2000 of Micrometrics Instrument Co., using the BET equation), but CuO had a porous structure with a diameter about 55 μm and the surface area about 0.6 m^2/g. It is inappropriate at current stage to conclude that Cu$_2$O can degrade the epoxy–DICY system faster than CuO. More work is in progress in order to differentiate the effects of Cu$_2$O and CuO.

The degradation reaction starts at a lower temperature as the activation energy of the degradation process decreases. This is shown in Table II. The degradation starts at 195, 182, and 160°C for the B-E, the B-E-CuO, and the B-E-Cu$_2$O (1°C/min heating rate), respectively. Thus, the presence of copper oxides in the epoxy–DICY system reduces the thermal stability of the resin. Similar results can be obtained from TGA data taken at other heating rates (see Table II).

The initial weight loss data are useful for aging prediction of polymeric materials because the properties that are related to natural aging deteriorated in the early stage of the degradation.[22] Regarding

the strength of adhesion, adhesive bonds between epoxy–copper laminates would lose their desirable strength and durability when the degradation begins.[26] The results from initial activation energies calculations confirmed the easy deterioration of adhesion strength between the epoxy system and the copper substrate.

It is also shown in Figure 9 that the slopes of the curves plotted $T^2(d\alpha/dT)$ versus α increase with α from specimens containing copper oxides, whereas the plot of $T^2(d\alpha/dT)$ versus α is nearly a straight line for the blank epoxy resin (regardless of the different heating rates used). This indicates that the degradation of the blank epoxy–DICY system studied follows a near zero-order kinetics.[27,28] However, the degradation kinetics changes to the negative order with autocatalytic character when small amounts of copper oxides are added to the resin. The presence of copper oxides not only lowers the activation energy for degradation but also affects the degradation mechanism of the epoxy–DICY system. The preferential adsorption of labile DICY molecules on the copper oxides is thought to be responsible for the observed accelerated degradation.[26]

CONCLUSIONS

1. From IR analyses it was ascertained that the curing of the epoxy–DICY system formed cyclic products and the presence of Cu_2O and CuO in the epoxy resins affected the contents of these highly reacted cyclic species.
2. From the relative changes of intensities of IR bands during thermal aging, the epoxy resins were catalytically degraded with the additions of CuO and Cu_2O.
3. The catalytic degradation of epoxy resins in the presence of CuO and Cu_2O were also confirmed by the TGA measurement. The activation energies of the thermal oxidative degradation decreased when either CuO or Cu_2O was added to the epoxy system.
4. The degradation kinetics of the epoxy–DICY system followed a near zero-order reaction, and changed to the negative order (autocatalytic) in the presence of copper oxides.

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