

Catalytic Effects of Copper Oxides on the Curing and Degradation Reactions of Cyanate Ester Resin

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ABSTRACT: The catalytic effect of copper oxides on the curing and degradation behaviors of the cyanate ester resin is studied with infrared spectroscopy, attenuated total reflection infrared spectroscopy (ATR), differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA). The result of infrared spectroscopy and DSC analyses indicates that accelerated curing effects from different additives are in the order of zinc octoate > cuprous oxide > cupric oxide. The exothermic characteristics of the cyanate ester resin during cure are drastically affected by the presence of the copper oxides. In addition, it is obtained from TGA analyses that the

thermal stability and degradation mechanism of cyanate ester resins are also significantly affected by the addition of copper oxides whereas the extent of degradation from the cupric oxide is greater than that from the cuprous oxide. These results are attributed to the differences in catalytic effects and surface areas of two copper oxides on the cyanate ester resin in contact during the thermal exposure. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 442–448, 2007

Key words: cyanate ester; cure; degradation; cupric oxide; cuprous oxide

INTRODUCTION

Cyanate ester resins (CEs) have been widely used in the high performance fiber reinforced composites because of their high heat resistance, low water absorption, good dimensional stability, and low dielectric constant.^{1–6} A lot of studies have been performed on investigating the curing and degradation behaviors of CE because of its importance in versatile applications. In general, the CE could be cured with phenols, acids, bases, active hydrogen donors, and metal salt catalyst (e.g., the chlorides, carboxylates, or chelates of tin, iron, titanium, zinc, or copper).^{2–4,7} During cure, the cyanate functional groups in the CE mainly form triazine groups by cyclotrimerization.^{7–15} In some cases, the hydrolyzed carbamate, the self-polymerized cyclic dimmer, and the iminocarbonate intermediates can also be produced.^{5,13–15} Additionally, the carbamate could decompose into isocyanic acid and phenol at a high temperature, the iminocarbonate could subsequently react into triazine compound, and the triazine may also rearrange to create isocyanurate intermediates.^{13–17}

Despite the complex reactions involved, the external environments encountered, for example, metal surfaces (metal oxides) in contact, can also significantly change the curing and the degradation reac-

tions of CE. A lot of studies have been done on investigating the metal surface dependent curing reactions of polymer resins. For example, it is found that the extent of epoxide conversion and ether formation increases in the epoxy coating layer near the steel surface and that high degree of conversion was attributed to a surface related reaction.¹⁸ Various different catalytic curing reactions that occur on the copper surface are reported elsewhere also.^{19–22} It was shown previously that the cuprous oxide attracted more cyanate ester but less bismaleimide resins from the prepreg to its surface than the cupric oxide; the copper surface affected the curing extent of the bismaleimide triazine (BT) resin in contact and the effect of cupric oxide was more significant than that of the cuprous oxide.²²

In addition to the effects on the cure, copper could catalyze the degradation reaction of various polymer resins. Allara et al. found the formation of catalytic copper carboxylate salts at the polyethylene-copper interface.²³ It is the diffusion of these salts into the polymer matrix that causes the oxidative degradation of polyethylene.^{23–25} The formation of salts between polyimide and Cu surface, and the accelerated degradation of polypropylene/Cu and epoxy/Cu systems have also been reported.^{26–30} It is believed that the cuprous/cupric ion pair is an effective oxidation/reduction couple and would accelerate the decomposition or the curing reaction of polymers.^{19,31}

It was shown previously that Cu₂O or CuO affected not only the curing reaction of the epoxy and

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BT systems but also the relative amounts and rates of degraded species formed during thermal aging, henceforth resulting in catalytic degradation of the epoxy and BT resins.^{33,34} The overall and initial activation energies of the degradation process decreased, and the degradation mechanisms (and kinetics) of the resins also changed in the presence of copper oxides.^{33–35}

Although many studies have been done on explaining the curing mechanisms and kinetics of the CE resin, few have been performed on investigating the effect of the copper oxides on the curing and degradation behaviors of the CE despite the wide usage of the modified CE/Cu structures in the high performance electronic circuit substrates. In this article, the influence of the copper oxides on the CE is demonstrated.

EXPERIMENTAL

The CE (4,4'-dicyanato-2,2'-diphenylpropane, Arocy B-10) is obtained from the Ciba-Geigy Company (Brewster, NY). The electroplated copper foil (0.5 oz/ft²) used is from Mitsui Mining and Smelting Company (Tokyo, Japan). The zinc octoate is 99% pure from Riedel-deHaen. The Cu₂O (99.9% pure) and CuO (99.999% pure) powders are purchased from Strem Chemicals, Inc. Different specimens are prepared to study the curing reaction of the CE resin. Firstly, the reference IR transmission spectra are obtained from the CE resin containing 0.05 phr (part per hundred parts CE) zinc octoate catalyst that cured at 190°C for different periods of time. Then the resins with additional one phr copper oxides (cupric or cuprous oxides) are also cured and analyzed. The CE (with 0.05 phr zinc octoate) and catalytic additives (one phr copper oxide) are mixed in MEK solvent and then vacuum dried overnight to obtain a well-mixed homogeneous mixture. A Perkin-Elmer 1700 Fourier Transform Infrared Spectrophotometer is used to obtain the IR transmission spectra. The IR spectra are taken from 4000 to 450 cm⁻¹ at a resolution of 4 cm⁻¹ for 100 cycles.

The effects of copper oxides on the cure are also obtained by analyzing the surface of CE contacted with the copper substrates after cure with the attenuated total reflection (ATR) infrared spectroscopy. Two copper substrates are used, one is obtained from the copper foil that etched with 8% aqueous H₂SO₄ solution for 5 min, rinsed with distilled water, and blown dry with nitrogen gas (mostly cuprous oxide on the surface as determined by XPS in the previous study). The other is obtained by oxidizing the previously prepared copper substrate at 420°C for 12 min in air to a cupric oxide surface. The CE resins (with 0.05 phr zinc octoate) are vac-

uum dried overnight and cured against both prepared copper substrates separately at 190°C under the pressure of 20 kg/cm² for 2.5 h. Then the copper substrates are peeled off from the specimens to expose the interfacial CE surfaces for analysis. The exposed CE surfaces are pressed against the internal reflection element (IRE) under a constant 32 oz-in torque, which is set by a torque wrench, and placed in an ATR accessory made by Harrick Scientific. Two hundred scans are acquired at a resolution of 4 cm⁻¹ from 4000 cm⁻¹ to 700 cm⁻¹. The KRS-5(60°) parallelepiped multi-reflection IRE is used.

The curing exotherm of four different CE resins (uncatalyzed CE, CE/0.05 phr zinc octoate, CE/1 phr Cu₂O, and CE/1 phr CuO) are obtained from the Perkin-Elmer DSC-7. The dynamic curing exotherm is measured at a scanning rate of 2°C/min under nitrogen environment (with a nitrogen flow rate of 30 mL/min). The specimens prepared from both open (unsealed) and hermetic aluminum pans are used. The cured resins after DSC experiment are also analyzed by infrared spectroscopy.

Different specimens are further analyzed with a Du Pont 951 Thermogravimetric Analyzer (TGA). The CE resins containing (a) 0.05 phr zinc octoate, (b) 0.05 phr zinc octoate and one phr Cu₂O powders, and (c) 0.05 phr zinc octoate and 1 phr CuO powders, are cured at 190°C for 2.5 h first. Then three cured CE specimens are pulverized with a Wig-L-Bug for TGA analysis. The weight loss behavior of the specimen is measured with a dynamic scanning mode. The specimen is scanned from room temperature to about 500°C at a heating rate of 2°C/min with an air flow rate of 42 mL/min. The peak temperatures of derivative weight-loss curves and the weight-loss percentages are obtained from TGA experiments.

RESULTS AND DISCUSSION

For reference, the FTIR transmission spectra taken from the cyanate ester resin after cured at 190°C for different periods of time are shown in Figure 1. As shown in the spectrum taken before cure [Fig. 1(A)], strong absorption bands from cyanate groups near 2270 and 2236 cm⁻¹ but no characteristic triazine bands at 1564 and 1368 cm⁻¹ are present. After only 5 min at 190°C, the polycyclotrimerization of the cyanate ester resin results in the formation of significant triazine bands near 1564 and 1368 cm⁻¹ and the C—O—C ether band near 1200 cm⁻¹. But a great number of cyanate groups are still unreacted after 5-min cure (based on large residual 2270 and 2236 cm⁻¹ bands). As shown in Figures 1(B)–1(D), after prolonged thermal cure, the residual cyanate groups are gradually consumed and transformed into more

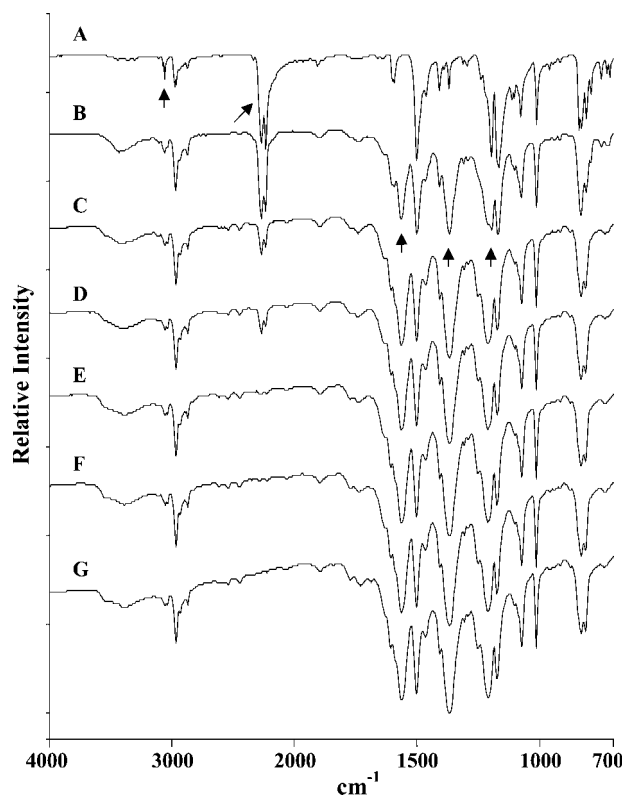


Figure 1 The infrared spectra obtained from the cyanate ester resins treated with different conditions (A: uncured, B: 5 min at 190°C, C: 60 min at 190°C, D: 150 min at 190°C, E: 300 min at 220°C, F: 600 min at 220°C, and G: 2000 min at 220°C).

triazine groups. Nonetheless, it is clear that the cyanate ester resin catalyzed with zinc octoate have substantial amounts of unreacted cyanate groups after 150 min cure at 190°C.

As expected, the formation of triazine is much faster in the beginning of the cure than in the later curing time since few changes in the intensities of the cyanate and triazine bands are obtained during the 60~150-min cure [see Figs. 1(C) and 1(D)]. This is attributed to the decrease of the concentration of reactive functional groups but an increase of the glass transition temperature with the curing extent (or the curing time), which is usually obtained in the isothermally cured resins (become vitrification and change into the diffusion controlled curing stage). Yet, the curing extent of the thermosetting resin at the later stage of the isothermal cure (e.g., in the diffusion controlled region) can usually be promoted by postcuring at a higher temperature. This can be seen in Figures 1(E) and 1(F); the cyanate bands significantly decrease in intensity but are still noticeable after 2000-min cure at 220°C [Fig. 1(G)].

The curing extent of the cyanate resin increases in the presence of copper oxides. Figures 2(A)–2(C) are infrared transmission spectra obtained from the zinc octoate catalyzed cyanate resin with the addition of

0, 1 phr (parts per hundred) cupric oxide, and 1 phr cuprous oxide powders, respectively, after 150 min cured at 190°C. By comparing the relative intensities of cyanate bands near 2270 and 2236 cm^{-1} , it is obvious the amounts of residual cyanate groups decrease significantly and are in the order of Figure 2(A) > Figure 2(B) > Figure 2(C). Consequently, the resins with the copper oxides have a greater curing extent than the resin without. In the case of the resin with the addition of cuprous oxides, it has almost negligible cyanate bands but the largest triazine bands [see Fig. 2(C)]. The catalytic curing effect of the cuprous oxides powders is impressive since there is still a noticeable cyanate band present in the copper-free resin after a long time cure at 220°C [see Fig. 1(G)].

The accelerated curing of the copper oxides added cyanate systems can be confirmed by the dynamic DSC analyses. Figure 3 shows DSC dynamic scanning thermograms obtained from different cyanate ester systems. A sharp melting endotherm near 80°C and a broad curing exotherm but with different characteristics are obtained from all four cyanate resins. As shown, the change in curing behaviors can be obtained from the difference in exothermic peaks. Firstly, the onset of the curing exotherm starts about 210°C for the uncatalyzed cyanate resin but decreases with the addition of copper oxides. The cure begins at 160 and 170°C from the cyanate resins containing 1 phr cuprous and cupric oxide powders, respectively. Although these onsets are higher than that from the 0.05 phr zinc octoate catalyzed system (onset starts at 130°C), they are significantly lower than the uncatalyzed resin. This result indicates that the accelerated curing effects from different fillers are in the order of zinc octoate > cuprous oxide > cupric oxide.

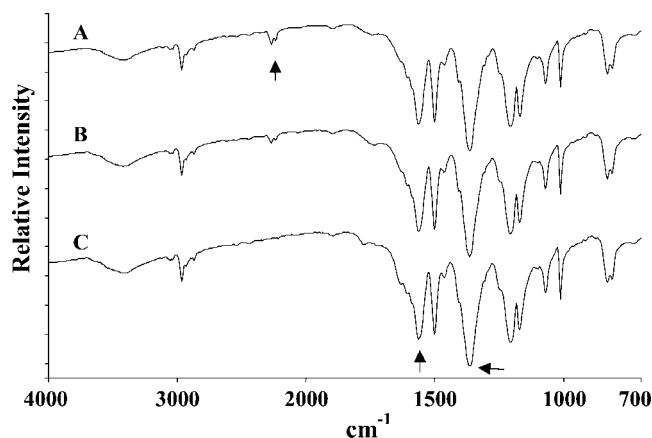


Figure 2 The infrared spectra of the cyanate ester resins cured in the presence of A: 0.05 phr zinc octoate, B: 0.05 phr zinc octoate and 1 phr CuO , and C: 0.05 phr zinc octoate and 1 phr Cu_2O .

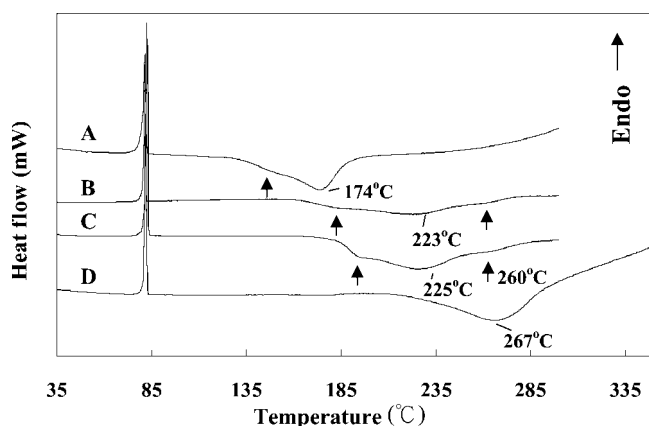


Figure 3 The DSC thermograms of the cyanate ester resins cured with A: 0.05 phr zinc octonate, B: 1 phr Cu_2O , C: 1 phr CuO , and D: uncatalyzed.

Also shown in Figure 3, the peak temperatures (T_p) of curing exotherms are 174, 223, 225, and 267°C for zinc octoate, cuprous oxide, cupric oxide added systems, and the uncatalyzed resin, respectively; since a lower peak temperature of the curing exotherm is usually indication of a higher reaction rate and sometimes a smaller activation energy of cure which are obtained in many metal salt catalyzed cyanate systems.^{36,37} The difference obtained in T_p also confirms the significant catalytic effects of two copper oxides during the cure.

Additionally, the shapes of exotherms are different among various analyzed specimens. A broad peak is obtained in uncatalyzed cyanate resin while the main exothermic peak accompanied with a preceding shoulder is observed in all catalyzed systems (see Fig. 3). The shouldering exothermic peak is usually obtained in many metal salt catalyzed cyanate ester systems, which is attributed to the multiple/parallel reaction mechanisms during the cure and the possible formation of active catalytic species or imidocarbonate intermediate.³⁷⁻⁴¹ As indicated, the width between the shoulder and the maximal peak is different among three catalyzed resins and increases in the order of zinc octoate < cupric oxide < cuprous oxide. This implies that a difference in the catalytic effect would affect the succeeding catalytic reaction (represented by T_p of the main peak) and the zinc octoate has a much better overall accelerating effect than two copper oxides. In addition, although the cuprous oxide results in a lower onset curing temperature than the cupric oxide, it has a T_p similar to that of the cupric oxide. The main catalytic reaction seems to be not affected by the different catalytic power of two copper oxides. The result would be due to the insufficient catalytic capability of the copper oxides and which leads to a slower succeeding catalytic reaction. This can also be confirmed from the result that the DSC of two copper oxides

catalyzed resins have small shoulders near 260°C, which is close to that of the T_p (267°C) of uncatalyzed resin. The high temperature exothermic shoulder is usually observed and attributed to the competing autocatalytic reaction in uncatalyzed CE resins.^{37,39,41} The results here confirm the presence of small amounts of not catalyzed resins in the copper oxides catalyzed specimens.

It is interesting to note that the reaction heats calculated from the DSC exotherms of four DSC specimens are significantly different. The reaction heats obtained from the uncatalyzed CE, CE/0.05 phr zinc octoate, CE/1 phr Cu_2O , and CE/1 phr CuO are 243.1, 179.2, 190.9, and 319.3 J/g (with the standard deviation <6.0 J/g), respectively. The zinc octoate catalyzed CE has the greatest extent of cure (see below) but the lowest reaction heat than the other three specimens. This is different from the past experience that a greater reaction heat is usually obtained from the curable-resin system (e.g., epoxy or unsaturated polyester resins) with a greater extent of cure. Regardless of the uncertainties involved in the calculations, the results obtained indicate that the presence of the foreign catalyst can not only accelerate the cure (as described previously) but can also possibly change the reaction routes of the CE during the thermal exposure, henceforth, affect the reaction heats. It have been demonstrated in other studies that the formation of intermediate by-products during cyclotrimerization could be promoted and the reaction order of the CE be changed by adding the catalysts.^{37,39,42,43} A further study on explaining these differences would be needed.

The difference in curing reactions obtained from the DSC analyses is confirmed from the IR spectra taken from the cured specimens after DSC experiments. As shown in Figure 4, small bands near 2217 and 1640 cm^{-1} are present in the spectra of cured

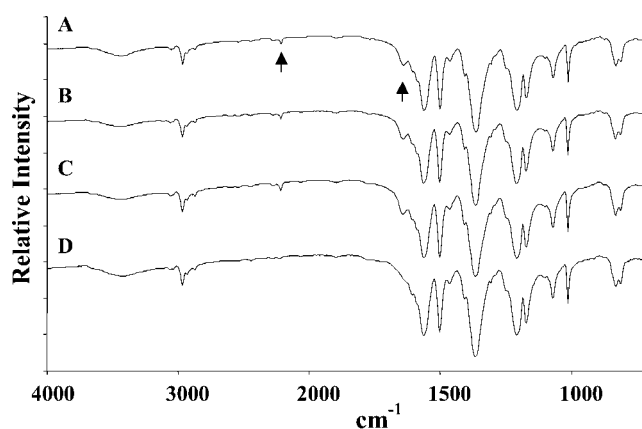


Figure 4 The infrared spectra obtained from the tested DSC specimens of cyanate ester resins cured with A: 1 phr Cu_2O (hermetic cell), B: 1 phr Cu_2O (open cell), C: 1 phr CuO (hermetic cell), and D: 0.05 phr zinc octoate (hermetic cell).

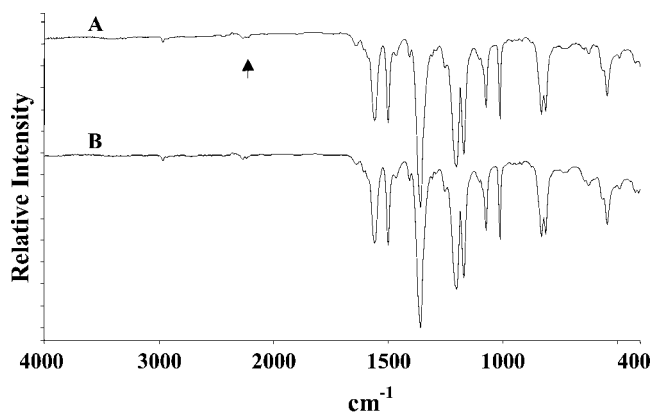


Figure 5 The KRS-5(60°) ATR spectra obtained from the surfaces of the hot-pressed cyanate ester resins in contact with A: Cu₂O and B: CuO.

copper-catalyzed resins. The 2217 and 1640 cm⁻¹ bands are attributed to the characteristic bands of isocyanurate and dimer formed during the cure which are absent in the cured resin that catalyzed by zinc octoate [Fig. 4(D)]. These two functional groups are also detected in the semicured cyanate resins in this study. For example, a small shoulder near 1640 cm⁻¹ is also present in Figures 1(B)–1(D) taken from partially cured zinc octoate catalyzed system, and which is diminished after prolonged cure [Figs. 1(F) and 1(G)]. Due to the limited catalytic power, the copper catalyzed resins have more dimer groups formed than the zinc octoate catalyzed system (Fig. 4). As a result, both isocyanurate and dimer functional groups are detected in copper added specimens even after DSC temperature scanning up to 300°C because of the incomplete cure.

Additionally, as expected and shown in Figure 4, the cuprous oxide catalyzed resins (from both hermetic and open DSC pans) have smaller 2217 and 1640 cm⁻¹ bands than the cupric oxide catalyzed specimen which also indicates that the catalytic curing effect of the cuprous oxide is better than that of the cupric oxide. However, the cuprous oxides used have an average particle size about 15 μ and the surface area about 1.9 m²/g, while the cupric oxides added have an average particle size of 55 μ and the surface area about 0.6 m²/g, and which can lead to a difference in the catalytic curing behaviors obtained.

To objectively compare the catalytic effect of two copper oxides, the ATR infrared analyses are performed directly from the resin surfaces cured against two different copper surfaces used in industry. The ATR spectra obtained from the cyanate ester resin surfaces contacted with the acid etched cuprous oxide surface and the black cupric oxide surface after cured at 190°C for 150 min are shown in Figures 5(A) and 5(B), respectively. As obtained, two spec-

tra show few differences and have similar small cyanate bands left and large triazine bands formed in the cured resins. Both two surfaces analyzed have a similar surface area in contact with the copper substrates, henceforth, the result indicates that both cuprous and cupric oxides could have a similar catalytic curing effect on the cyanate ester system. Nonetheless, since the penetration depth of the ATR spectra is in the order of micrometer for the absorption bands discussed and the KRS-5 (60°) IRE used in this study, the difference in cure between two surfaces obtained may still have a chance to be masked by the limited sensitivity of the ATR technique.

The presence of the copper oxides can not only affect the curing reaction but also can influence the thermal stability of the cyanate ester resin. As shown in Figure 6, the TGA thermograms from the resins with copper oxides are clearly different than that from the resin without copper oxides. The onset temperatures of the weight loss obtained from Figure 6 are 280.4, 261.1, and 239.7°C for the cyanate ester resin containing no copper oxides, 1 phr cuprous oxide, and 1 phr cupric oxide, respectively. As obtained, the thermal stability of three cyanate ester resins are in the order of the copper-free cyanate ester resin > the resin with cuprous oxide > the resin with cupric oxide, and the addition of copper oxides would significantly promote the degradation process.

As previously described, the catalytic effects of the copper surface on the degradation reaction of polymeric materials have been demonstrated by many investigators.^{44,45-50} The significant catalytic effect of copper oxides is attributed to the oxidation–reduction nature between cuprous and cupric oxides. In the previous study, it is demonstrated that the copper oxides enhanced the degradation of the bismaleimide triazine resin and also affected the reaction

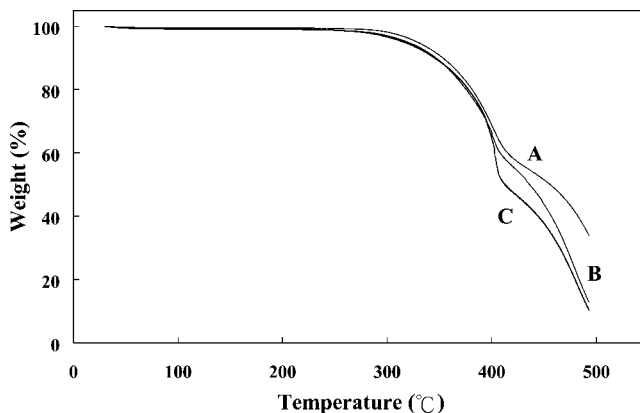


Figure 6 The TGA thermograms of the cyanate ester resins cured by 0.05 phr zinc octonate and with A: no copper oxides, B: 1 phr Cu₂O, and C: 1 phr CuO.

mechanism. Other studies also proved that the degradation of the cyanate ester resin would be accelerated by the copper naphthenate.^{51,52}

In this study, the degradation mechanism of the cyanate ester resin could also be changed by the presence of the copper oxides since the extent and the rate of the weight loss shown in Figure 6 are significantly different among three specimens. It is clear that there are two main weight loss processes in the TGA thermograms, the first from the onset to about 400°C and the second from 400 to 500°C (the end of the TGA experiment). The weight loss at the lower temperature could be related to part of the unstable structures formed in the specimens for the curing condition used [see previous results obtained from Fig. 1(D)].³⁷ The main loss at the higher temperature is from the decyclization of the triazine ring which is observed in many fully cured different cyanate ester resins.^{37,53} In both two stages, the extent and the rate of weight loss of three resins are in the order of the copper-free cyanate ester resin < the resin with cuprous oxide < the resin with cupric oxide. The percentages of the residual weight of three specimens at 500°C are 33.6, 12.5, and 10.2% for the cyanate ester resin containing no copper oxides, 1 phr cuprous oxide, and 1 phr cupric oxide, respectively. These results imply that the degradation mechanisms of the cyanate ester resin are changed and accelerated by the addition of the copper oxides. Although the detail of this catalytic degradation is unknown at this stage, the TGA results obtained here indicate that the thermal durability of the cyanate ester resin/copper system used in the electronic circuit substrate would be significantly deteriorated because of the catalytic nature of copper oxides in contact.

CONCLUSIONS

The effect of copper oxides on the curing and degradation behaviors of the cyanate ester (CT) resin is demonstrated. It is confirmed by infrared spectroscopy and DSC analyses that the cure of cyanate ester resin in the presence of different additives are in the order of zinc octoate > cuprous oxide > cupric oxide > no additive. DSC results also indicate that the onset temperature and the exothermic heat of the cyanate ester resin during cure are all significantly affected by the addition of the copper oxides. Moreover, the thermal degradation of cyanate ester resins are significantly promoted by the presence of copper oxides and the catalytic degradation effect of the cupric oxide is greater than that of the cuprous oxide. The thermal degradation mechanism could also be changed in the resin containing copper oxides. It is believed that the differences in catalytic effects and surface areas of two copper oxides on the cyanate

ester resin in contact result in the difference obtained during thermal exposure.

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