

The Effect of Different Metallic Catalysts on the Coreaction of Cyanate/Epoxy

Qi Fang Li,^{1,2} Kun Lu,² QingQuan Yang,² Riguang Jin²

¹Key Laboratory for Nano-Materials, Ministry of Education, Beijing University of Chemical Technology, Beijing, People's Republic of China

²Department of Polymer Science, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing, People's Republic of China

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ABSTRACT: The curing reaction between the diepoxy and dicyanate mixed resins in the presence of three different catalysts Cu(AcAc)₂, manganese octoate, and copper octoate was investigated. The thermal behavior was monitored using differential scanning calorimeter; the transformations of structures during the isothermal and heating process were explored by Fourier transform infrared spectroscopy; the changes of the carbonic-framework of polymer and intermediate products were analyzed by nuclear magnetic resonance. Conclusions can be drawn as follows: Similar to noncatalyzed system, the overall reaction still occurs in two steps: cyclotrimerization of cyanate ester to produce triazine rings, coupled with the formation of some secondary inter-

mediate products, and coreaction of epoxy and triazine rings to form oxazolidinone rings at high temperature. The catalysts can accelerate the curing process and decrease the curing temperature as well as gel time, and manganese octoate presents the best effect on curing rate. But the mechanisms and the structures of intermediate products of metallic-catalyzed epoxy/cyanate are not changed by the addition of catalysts. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2293–2302, 2006

Key words: cyanate ester; epoxy resin; mechanism; metallic catalyst

INTRODUCTION

Epoxy resins are well suited for insulating materials, electric and electronic components, reinforced plastics, and matrix resins for advanced composite materials,^{1,2} because of their high modulus, high strength, excellent chemical resistance, good electrical resistance, low cost, and ease of processing. Unfortunately, their relatively high dielectric loss and poor water absorption properties exclude them from stricter applications such as printed circuit boards requiring high-speed signal propagation and transportation. Cyanate ester resin, a relative newcomer to the composites industry, is an important example of modifiers for epoxy resin. The basic properties of cyanate ester resins, such as low moisture absorption, excellent electrical properties, and good flammability characteristics, make them attractive composite matrices and differentiate them from conventional resins.^{3–5} Consequently, when compared with neat resins, Cyanate ester–epoxy resins exhibit superior performance in both the aerospace and the electronic industry.^{6–10}

The reaction of cyanate esters–epoxy systems caught much attention in the past. Martin reported in 1964 that

copolymerization occurred in the temperature range of 150–250°C, with the formation of oxazole structures.¹¹ In 1987, Gotro *et al.* showed the formation of cyclic isooxazole and postulated that homopolymerization occurred in parallel using infrared absorption spectroscopy.¹² In 1988, Shimp *et al.* then judged that triazine, the product from the trimerization of cyanates, was the intermediate that further reacted on epoxy functions.¹³ Then, Beuer and Bauer proposed a complex mechanism on the basis of the study of 4-chlorophenol cyanate and phenyl glycidyl ether model compounds,¹⁴ after which Shimp and Wentworth undertook a similar study on a monofunctional model closer to dicyanate (cumyl phenyl cyanate) by steric exclusion chromatography (SEC) and Fourier transform infrared (FTIR) spectroscopy in the presence of a cyanate, repeating the same study with nuclear magnetic resonance (NMR) and FTIR.¹⁵ In 1997, Florence *et al.* proposed an epoxy–cyanate coreaction path in the molten state, based on FTIR and ¹³C NMR spectroscopy using model compounds, and showed that the stoichiometry determined the final system.¹⁶ Effects of chemical structure changes on curing reactions were published by Su and Chih-Min Chuang.¹⁷ But a systematic study on the curing behavior in the presence of different catalysts has not yet been reported.

The present study aims at the reaction mechanism of bisphenol-A dicyanate esters-bromic diglycidyl ethers of bisphenol-A systems in the presence of dif-

Correspondence to: Q. F. Li (qflee@mail.buct.edu.cn).

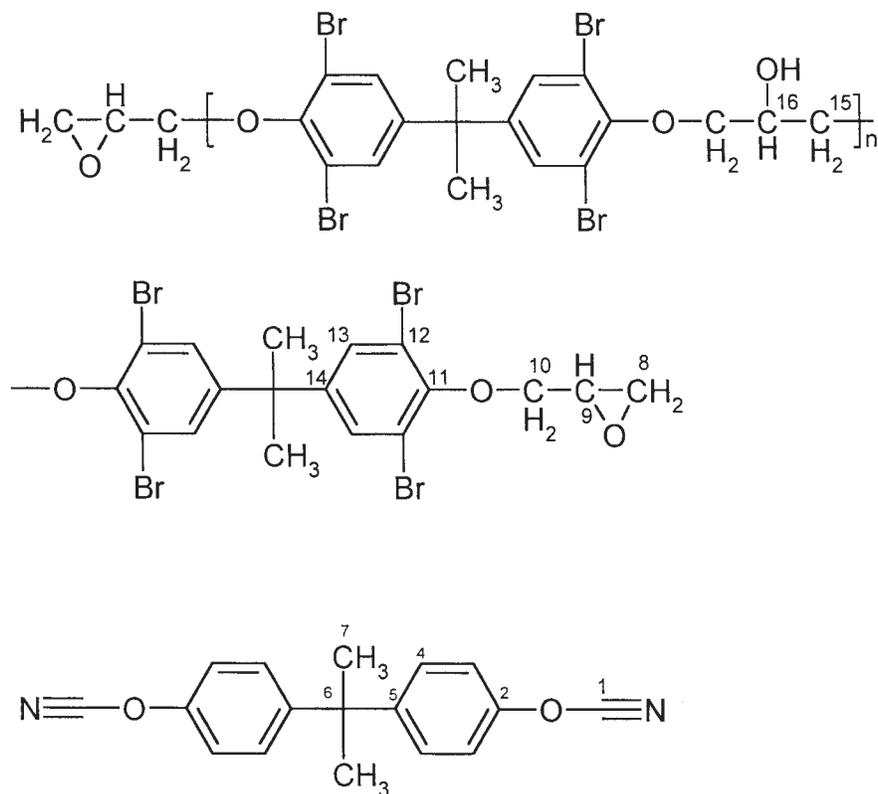


Figure 1 The structural formula of materials in the present study (Prepolymer of Bromic diglycidyl ether of bisphenol; Bisphenol-A dicyanate).

ferent metallic catalysts such as $\text{Cu}(\text{AcAc})_2$, manganese octoate, and copper octoate. Simultaneously, the transformations of chemical species were explored during the isothermal and heating up process. All intermediate structures were determined employing FTIR and ^{13}C NMR.

EXPERIMENTAL

Materials

Bisphenol-A dicyanates (BADCy) were received from 637 Institute in Jinan, China. Purity was more than 95% (determined by HPLC). Prepolymer of Bromic diglycidyl ethers of bisphenol-A (Br-DGEBE) were received from Ciba-Geigy. The epoxy resin prepolymer and cyanate resin used in the study are shown in Figure 1. $\text{Cu}(\text{AcAc})_2$ was provided by 637 Insstitute in Jinan, China. Manganese octoate and copper octoate were both synthesized in this laboratory.

Sample preparation

Catalyst preparation

First, 0.5 mol NaOH was dropped into 1 mol octanoic acid. After a 3-h reaction, 1 mol MnCl_2 was dropped into the solution mentioned earlier. Then, after an-

other 2-h reaction, the mixture was filtered in vacuum. The filtration was done three times to purify manganese octoate. The preparation of copper octoate is similar to that of manganese octoate.

Sample for NMR and FTIR

Cyanate ester and epoxy were added into a solvent of *N,N*-dimethyl methylamide (DMF/DMM) according to the 40 : 60 (by weight). In a catalyzed system, the weight of the catalyst is 0.1% of that of the mixture resulting from epoxy and cyanate. The resultant solutions were dropped onto the heater. After 90, 120, 150, 180, 210, 240, 1800, 4500, and 7200 s of heat treatment, the samples were removed for FTIR test. And those solutions heated for 60 and 120 s were used for NMR test to detect various intermediate structures.

Experimental techniques

Differential scanning calorimetry

The differential scanning calorimeter (DSC) (PerkinElmer Pyris-1 DSC) was used for examining the heat of the reaction of the cyanate esters–epoxy system. Approximately 3–8 mg of sample was placed on an aluminum pan, weighed, and sealed in a press. The sealed pan was

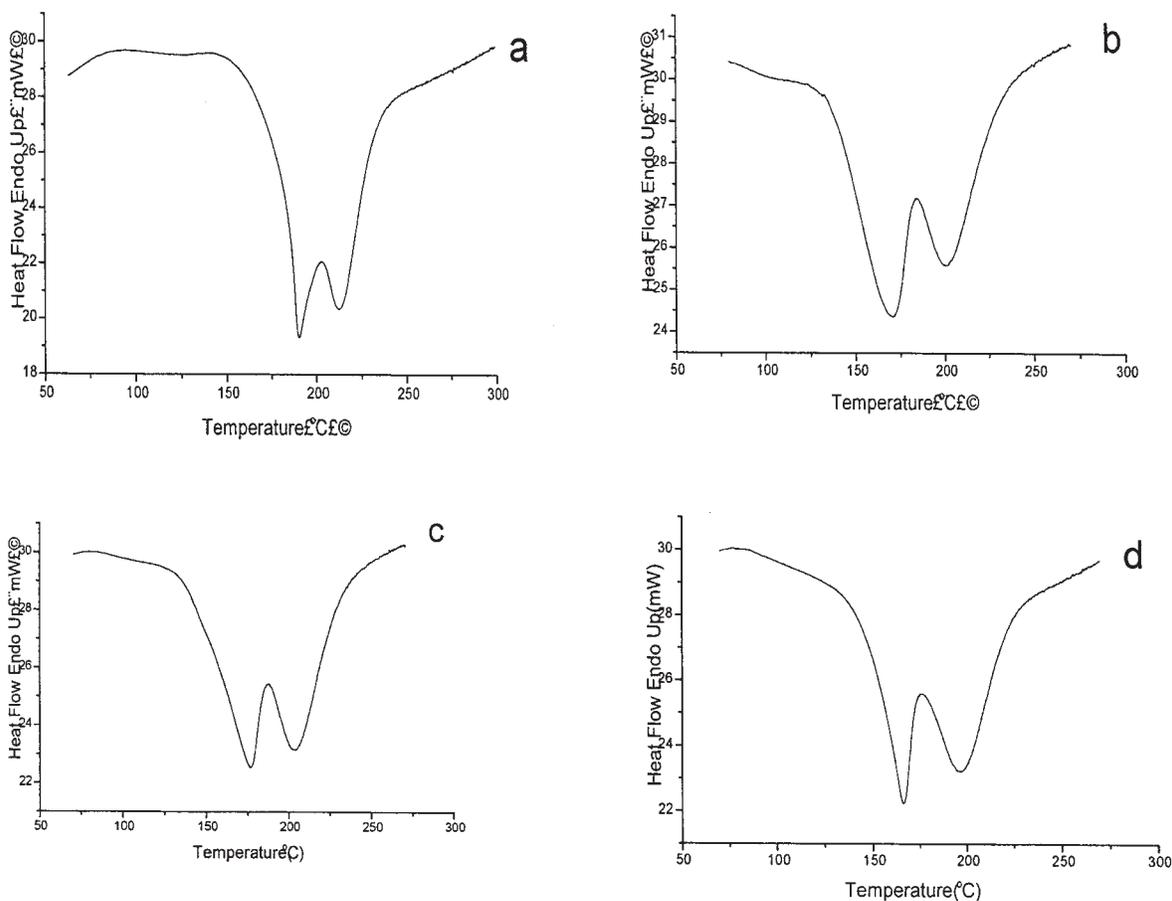


Figure 2 DSC curves for noncatalyzed and catalyzed Br-DGEBA/BADCy systems (BADCy at 40 phr, heated at 10°C/min under nitrogen). (a) Noncatalyzed, (b) $\text{Cu}(\text{AcAc})_2$, (c) copper octoate, and (d) manganese octoate.

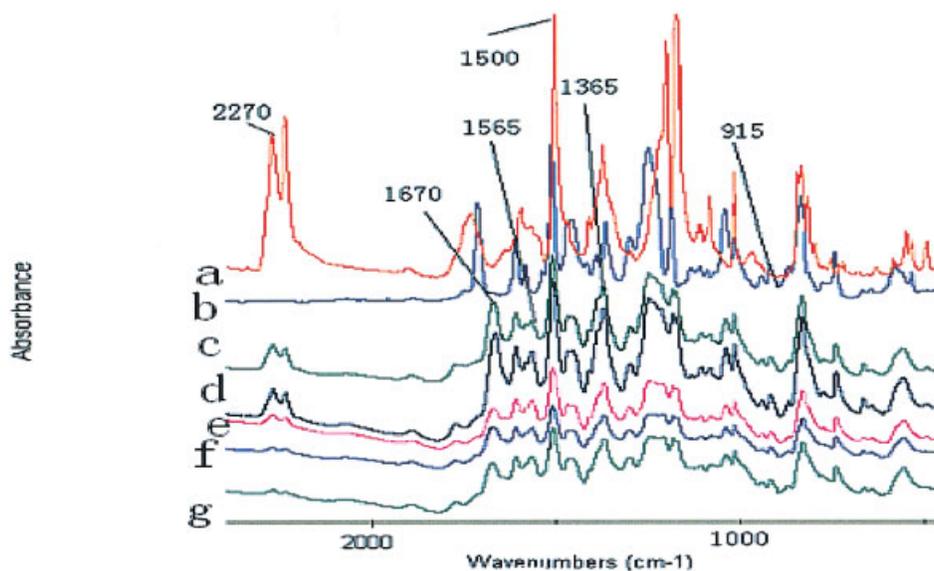


Figure 3 FTIR spectra of Br-DGEBA/BADCy system (BADCy at 30 phr, heat treated at 170°C for various time durations). (a) BADCy, (b) Br-DGEBA, (c) 120 s, (d) 150 s, (e) 180 s, (f) 210 s, and (g) 240 s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
The Change of Characteristic Absorbance of Epoxy/Cyanate in the Presence of $\text{Cu}(\text{AcAc})_2$

Sample	Heating time (s)	A_{1367}/A_{1508}	A_{1565}/A_{1508}	A_{1667}/A_{1508}
Epoxy		0	0	0
Cyanate		0	0	0
Epoxy/cyanate	120	0.823823	0.631954	0.736091
Epoxy/cyanate	150	0.864038	0.66804	0.753973
Epoxy/cyanate	180	0.883679	0.762849	0.704238
Epoxy/cyanate	210	0.910843	0.800002	0.798795
Epoxy/cyanate	240	0.920765	0.802368	0.748634

then placed inside the DSC and the sample was heated at the rate of $10^\circ\text{C}/\text{min}$ from 75 to 250°C .

Fourier transform infrared spectroscopy

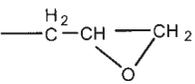
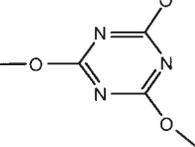
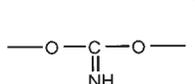
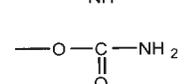
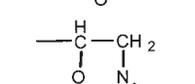
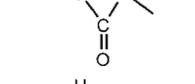
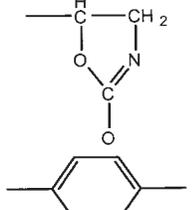
The FTIR (PerkinElmer 1760X spectrometer) was used to monitor the extent of reaction and investigate the cure chemistry. The condition is listed as follows: spectral width, $4000\text{--}400\text{ cm}^{-1}$; 32 accumulations; resolution, 4 cm^{-1} triangular apodization signal processing. Depending on their physical state, samples were

analyzed in the form of a film between two NaCl faces or mixed into a potassium bromide disk. These bands were monitored to determine the extent of cure for all of the samples.

Dynamic FTIR spectroscopy

The solutions of epoxy/cyanate for dynamic FTIR were the same as those for NMR and FTIR, but this solution was tested directly without preheating, unlike those for FTIR and NMR. FTIR (Nicolet 60SXB) worked at a heating rate of $10^\circ\text{C}/\text{min}$. And the spectrum was recorded every minute. The initial temperature was 60°C and the end temperature was 280°C .

TABLE II
Characteristic Frequencies of Main Functional Groups During Coreaction of Epoxy/Cyanate

Functional groups	Frequency (cm^{-1})
$\text{—O—C}\equiv\text{N}$	2270–2235(C \equiv N)
	915 (915 (C—C))
	1565(N—C \equiv N)
	
	1365(N—C—N) 3330(NH)
	1670(C—N) 1700(C=O)
	1750(C=O)
	1695(C=N)
	1508(pheny rings)

Nuclear magnetic resonance

The NMR (Bruker AV-600 spectrometer), which is much easier for group-judgement than FTIR, was used to record high resolution ^{13}C NMR in liquid under the following condition: Chemical shifts were given on the basis of tetramethylsilane as internal standard. To attribute carbon classes (CH, CH_2 , CH_3 , quaternary), distortionless enhanced polarization transfer was adopted.

RESULTS AND DISCUSSION

Analysis of DSC

The heat of reaction was monitored by DSC. Figure 2(a) displays the DSC curve for Br-DGEBA/BADCy system without catalysts. Obviously, there are two large exothermal peaks obtained from each of sample, which indicate that two reactions occurred during the curing of Br-DGEBA/BADCy system.

Similar to the case of noncatalyzed system, the DSC curves of metallic-catalyzed systems also have two large exothermal peaks, suggesting that the addition of catalyst does not change two-step successive reaction mechanism. However, the addition of catalysts can decrease the temperature of the reaction. And, the thermal reactivity zones are different in different systems: the lowest temperature of the reaction occurred in the system catalyzed by manganese octoate (166

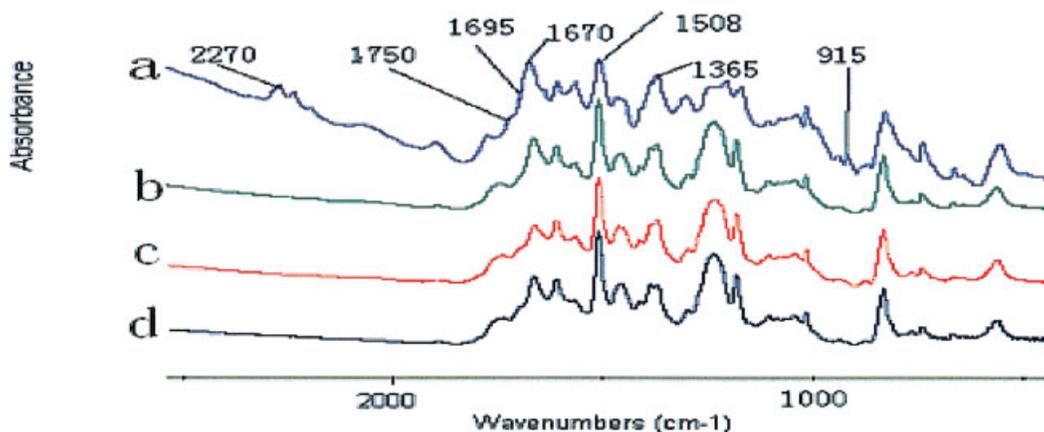


Figure 4 FTIR spectra of manganese octoate-catalyzed Br-DGEBA/BADCy at different heating time durations: (a) 90 s, (b) 180 s, (c) 450 s, and (d) 720 s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and 195°C), followed by the $\text{Cu}(\text{AcAc})_2$ (170 and 201°C), copper octoate (177 and 205°C), and noncatalyzed (190 and 210°C). Hence, the influence of manganese octoate on reaction temperature is the most distinct. At the same time, the peaks of polymerization exotherms broaden after the introduction of catalysts, showing that the catalysts can slow the exothermic rate that contributes to the control of the process condition.

Analysis of FTIR

The band appearing at 1500 cm^{-1} in cyanate ester is the characteristic adsorption peak of phenyl rings.^{16,18}

But this band shifts to 1508 cm^{-1} because of the Br substitute on the phenyl rings.

As shown by Figure 3, during the first 4 min of the curing reaction, the characteristic adsorption band at 2270 cm^{-1} attributed to cyanate decreases gradually and disappears eventually, but the change of epoxide band at 915 cm^{-1} was very small. It could be concluded that the cyanate reacted at first and the epoxy did not take part in the reaction. Accompanying the reduction of cyanate band, three obvious adsorption bands emerge at 1565, 1369, and 1670 cm^{-1} . These three bands are assigned to the vibration of $\text{N}-\text{C}=\text{N}$ in triazine rings, vibration of $\text{N}-\text{C}-\text{O}$ in triazine rings, and vibration of $\text{C}=\text{N}$ in iminocarbonate re-

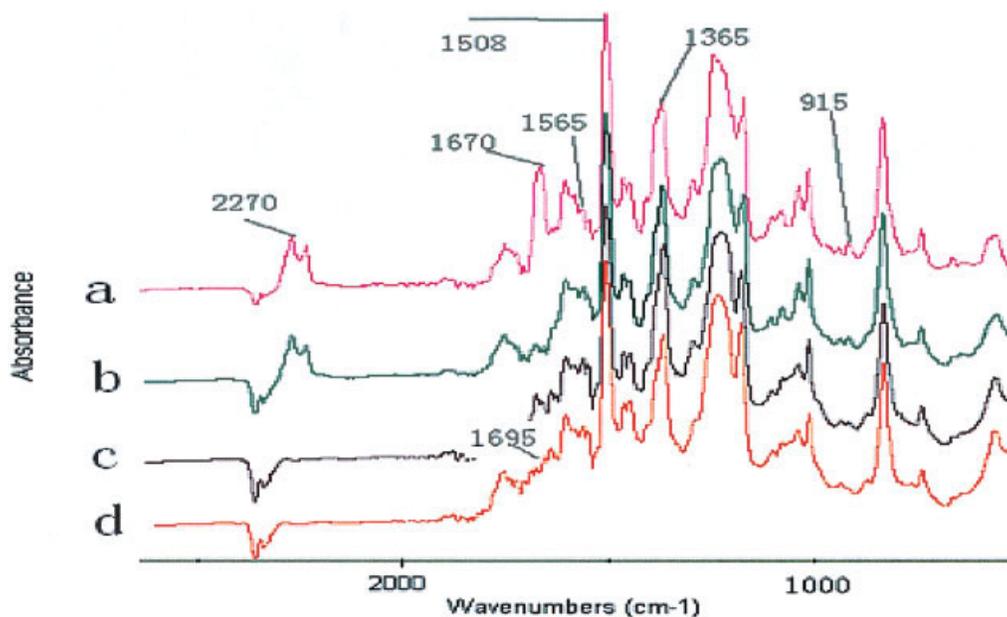


Figure 5 Dynamic heating FTIR spectra of Br-DGEBA/BADCy systems. (a) 60°C, (b) 130°C, (c) 180°C, and (d) 210°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
The Change of Main Characteristic Absorbance in Dynamic FTIR

Temperature (°C)	A_{915}/A_{1508}	A_{2270}/A_{1508}	A_{1565}/A_{1508}	A_{1695}/A_{1508}	A_{1666}/A_{1508}
60	3.221371	3.118486	0	0	2.202769
70	3.246133	3.128884	0	0	2.414846
80	3.251125	3.136891	0	0	2.519449
90	3.269906	3.162572	0	0	2.661319
100	3.255742	3.149646	0	0	2.790288
110	3.246454	3.150253	0	0	3.043402
120	3.197578	3.112217	0	0	3.152278
130	3.148825	3.131143	2.420733	0	3.26116
140	3.075625	3.140073	2.299886	0	3.177781
150	3.026704	3.235167	2.219434	0	3.032004
160	3.061540	0	2.147405	0	2.646695
170	3.045388	0	2.163631	0	2.588444
180	3.025694	0	2.18936	0	2.634916
190	3.001278	0	2.23872	0	2.604632
200	0	0	0	2.914109	0
210	0	0	0	2.869834	0
220	0	0	0	2.841241	0
230	0	0	0	2.689422	0
240	0	0	0	2.567664	0
250	0	0	0	2.420649	0
260	0	0	0	2.170983	0
270	0	0	0	1.984024	0
280	0	0	0	1.892082	0

spectively, which explains the homopolymerization or trimerization of cyanate functional groups. Table I. quantifies the change of functional groups using the absorbance of the phenyl group at 1508 cm^{-1} as an internal standard. And main specific band attributions are summarized in Table II.

Figure 4 is the FTIR spectra of epoxy/cyanate after long-time heating treatment. Figure 4(a) was obtained after 90-s heating. Two adsorption peaks attributed to oxazolidinone appear at 1695 and 1750 cm^{-1} respectively, and the former is assigned to the vibration of C=N oxazolidinone and the latter is assigned to that of C=O in oxazolidinone. Moreover, as shown in Figure 5, with the increase of cure time, triazine and iminocarbonate decrease gradually. Simultaneously, the band of epoxide at 915 cm^{-1} also decreases, indicating that epoxide begins to react with other substances.

Dynamic FTIR

As can be seen from Table III and Figure 5, the epoxide at 915 cm^{-1} and iminocarbonate at 1666 cm^{-1} diminish gradually and disappear at last. Triazine appears at 130°C (corresponding to 6 min) and disappears at 180°C (12 min), illustrating that triazine is only an intermediate structure during curing of epoxy/cyanate. And a new adsorption peak emerges at 1695 cm^{-1} for the first time at 200°C , which is attributed to the vibration of C=N in oxazolidinone.

Combining DSC and FTIR analyses, it can be drawn that there are two steps of the reaction of cyanate and epoxy, namely, homopolymerization of cyanates at lower temperature (the first exotherm in DSC curves) and the copolymerization reactions at higher temperatures (the second exotherm in DSC curves).

Analysis of ^{13}C NMR

To more accurately investigate the intermediate structures during curing, ^{13}C NMR was adopted for further

TABLE IV
 ^{13}C NMR Chemical Shifts of Br-DGEBA and BADCy

Carbon	δ (ppm)
C1	109.003
C2	151.22
C3	114.929
C4	129.225
C5	149.236
C6	42.553
C7	34.688
C8	43.77
C9	49.985
C10	69.355
C11	151.178
C12	113.993
C13	127.734
C14	148.735
C15	69.700
C16	68.774

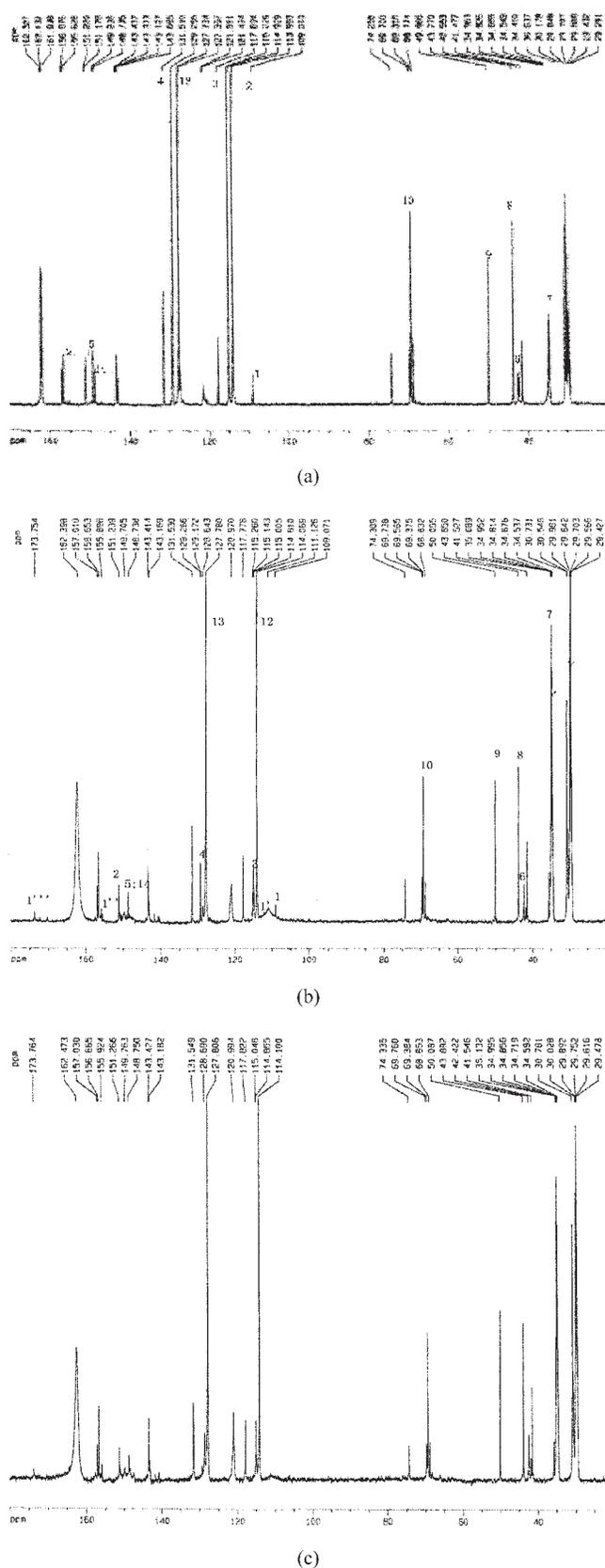


Figure 6 (a) ^{13}C NMR spectra of Br-DGEBA/BADCy system before heat treatment. (b) ^{13}C NMR spectra of manganese octoate-catalyzed Br-DGEBA/BADCy system heat treated for 1 min at 180°C . (c) ^{13}C NMR spectra of manganese octoate-catalyzed Br-DGEBA/BADCy system heat treated for 2 min at 180°C .

information on structure. On the basis of the results from manganese octoate-catalyzed Br-DGEBA/BADCy system, the attribution of ^{13}C NMR lines can be determined. Table IV and Figure 6(a) summarize the ^{13}C NMR chemical shifts obtained from the spectrum of the monomer and prepolymer before heat treatment.

Figure 6(b) is the NMR spectrum of Epoxy/Cyanate after 1-min reaction. In ^{13}C NMR, the characteristic line of the cyanate functional group is located at 109.003 ppm. During curing, most of the Br-DGEBA and BADCy lines diminished progressively. By comparison with the chemical shifts of initial sample, it is possible to detect one main intermediate and two other secondary products. It can be seen from Figure 6(b) that there are three new lines appearing at 173.754, 111.126, and 155.896 ppm. According to the chemical shifts, these three lines are assigned to triazine, iminocarbonate, and carbamate. During the evolution of the reaction medium, the resonance lines at 111.126 ppm (iminocarbonate) and 109.071 ppm (cyanate functional group) disappear, as shown in Figure 6(c) that provides the ^{13}C NMR spectrum of Epoxy/cyanate after 2 min of reaction. It should be pointed out that other metallic-catalyzed epoxy/cyanate systems were both investigated using NMR, but their spectra did not present pronounced difference in intermediate structures, compared with manganese octoate-catalyzed and noncatalyzed systems, suggesting that metallic catalysts do not change intermediate products or coreaction mechanisms.

As DSC analysis shows, the coreaction of epoxy/cyanate presents two large exothermal peaks, suggesting that this reaction includes two successive steps during curing. And FTIR and ^{13}C NMR have demonstrated the existence of some intermediate products such as triazine, iminocarbonate, and carbamate. on the basis of these results, the following coreaction mechanisms, as shown in Figure 7, can be proposed.

1. In the first step, two intermediate products, $\text{R}'\text{-O}-\text{C}(\text{NH})=\text{O}-\text{R}'$ and $\text{R}'\text{-O}-\text{C}(=\text{O})\text{NH}_2$, can be determined, but the quantity of them is little because water and remaining phenol are very limited in epoxy/cyanate. Therefore, they are not main intermediate structures to take part in the later coreaction.

2. Cyclic dimer of cyanate ester, $\text{R}'\text{-O}-\text{C}_2\text{N}_2-\text{O}-\text{R}'$ is often produced before the formation of triazine.¹⁸ But in the present research, the characteristic adsorption peak and resonance peak of this dimer are not observed in FTIR and NMR.

3. Cyclic trimer of cyanate ester, $\text{R}'\text{-O}-\text{C}_3\text{N}_3-\text{O}-\text{R}'$ is often produced before the formation of triazine.¹⁸ But in the present research, the characteristic adsorption peak and resonance peak of this trimer are not observed in FTIR and NMR.

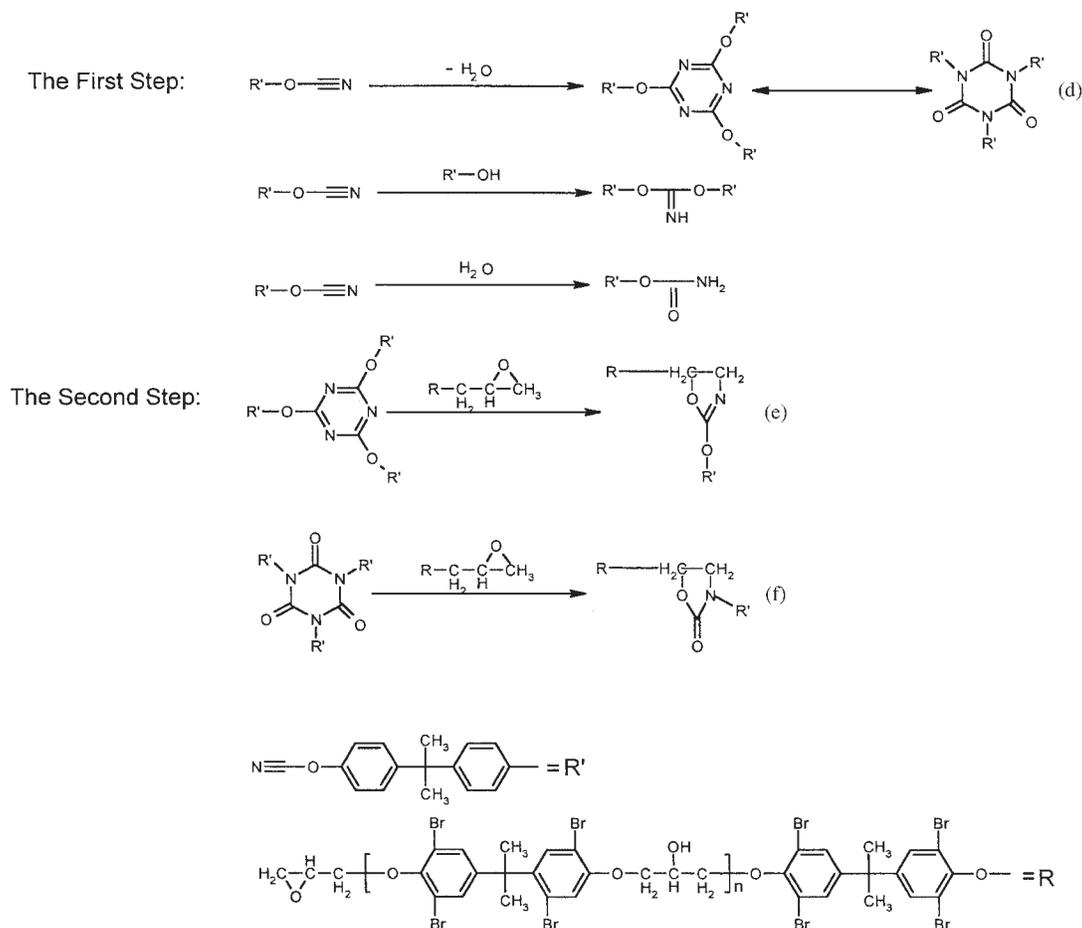
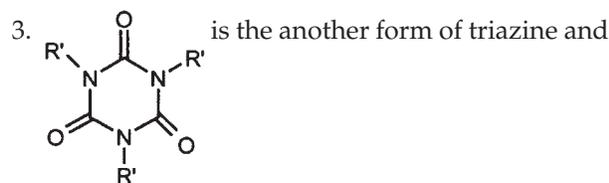


Figure 7 Br-DGEBABADCy coreaction mechanism.



should be existing from the standpoint of theory.¹⁶ In this study, the characteristic adsorption peaks of (e) and (f) are detected at 1695 and 1750 cm^{-1} separately, which provide evidence to support the formation of (d) to some extent.

4. is the product of remaining phenol and cyanate groups, and FITR and NMR have demonstrated its existence during coreaction between epoxy and cyanate. But the specific details about its effect on the curing and how it reacts with other substances remain to be clarified.

Effect of catalyst on coreaction of cyanate/epoxy

Figure 8 and Table V give the effect of different metallic catalysts on the intensities of various main func-

tional groups. According to FTIR, it can be found that no new intermediate products or functional groups emerge after the use of catalysts when compared with noncatalyzed system, which effectively supports the fact that metallic catalysts do not change the coreaction mechanism and the intermediate structures. And, regardless of catalysts, the variation of triazine at 1367 cm^{-1} was little, which illustrates that the influence of catalysts on the formation of triazine can be neglected. But the absorption of iminocarbonate at 1666 cm^{-1} is the most pronounced in manganese octoate-catalyzed within the same time, followed by $\text{Cu}(\text{AcAc})_2$, copper octoate, and noncatalyzed.

Table VI shows the influence of different catalysts on the temperature of appearance and disappearance of characteristic adsorption peaks during dynamic heating. Compared to noncatalyzed system, characteristic adsorption band at 2270 cm^{-1} attributed to cyanate disappears at lower temperature. And the ones attributed to triazine (1565 cm^{-1}) and oxazolidinone (1695 cm^{-1}) appear at a much lower temperature in comparison with the noncatalyzed one. All these results indicate that the catalysts lower the reaction temperature and speed up the reaction.

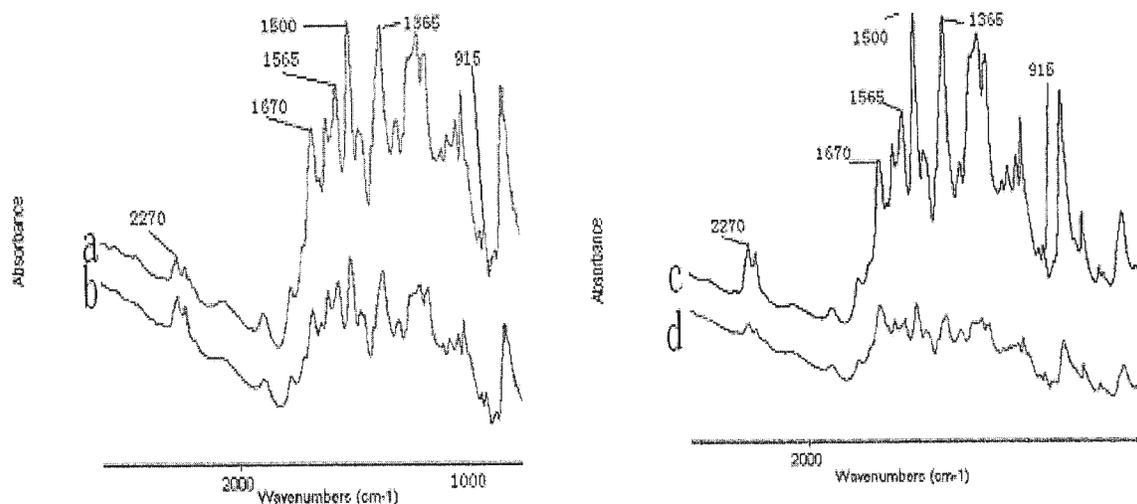


Figure 8 FTIR spectra of Br-DGEBA/BADCy systems heat treated under different catalysts: (a) $\text{Cu}(\text{AcAc})_2$ (135 s), (b) noncatalyzed (150 s), (c) $\text{Cu}(\text{AcAc})_2$ (90 s), and (d) manganese octoate (90 s).

Because the addition of catalyst can increase the reaction rate, there is a decrease in the gel time. Table VII lists the gel time of noncatalyzed and catalyzed systems. And it can be found that manganese octoate-catalyzed system possesses the smallest gel time.

CONCLUSIONS

The curing reaction between the diepoxy and dicyanate mixed resins in the presence of three different catalysts $\text{Cu}(\text{AcAc})_2$, manganese octoate, and copper octoate was investigated. Thus, the present study has enabled a representative path to be proposed for metallic catalyzed Br-DGEBA/BADCy system.

Compared to noncatalyzed epoxy/cyanate, the result shows that the overall reaction also occurs in two successive steps: first, cyclotrimerization of cyanate ester to produce triazine rings, coupled with the formation of some secondary intermediate products; and second, coreaction of epoxy and triazine rings to form oxazolidinone rings at high temperature.

In addition, the effect of metallic catalysts on the curing behavior was also investigated. The catalysts can accelerate the curing process, change the percentage of products, and decrease the curing temperature as well as gel time, which contribute to control the curing process. But, in fact, these metallic catalysts do not change the

TABLE V
The Influence of Catalysts on the Change of Characteristic Absorbance

Sample	Heating time (s)	A_{1367}/A_{1508}	A_{1565}/A_{1508}	A_{1667}/A_{1508}
Noncatalyzed	150	0.958771	0.83266	0.744543
$\text{Cu}(\text{AcAc})_2$	90	0.958011	0.767403	0.81547
$\text{Cu}(\text{AcAc})_2$	150	0.970464	0.85654	0.754219
Copper octoate	90	0.977053	0.766304	0.638285
Copper octoate	135	0.993208	0.886625	0.808255
Manganese octoate	90	0.942697	0.925843	0.989888

TABLE VI
The Temperatures ($^{\circ}\text{C}$) of Characteristic Change in the Presence of Different Catalysts

Change of adsorption peak	Noncatalyzed	Copper octoate	Manganese octoate	$\text{Cu}(\text{AcAc})_2$
Disappearance of 915 cm^{-1}	190	190	200	200
Disappearance of 2270 cm^{-1}	210	150	190	190
Appearance of 1565 cm^{-1}	200	130	170	130
Disappearance of 1565 cm^{-1}	220	180	230	160
Appearance of 1695 cm^{-1}	260	210	240	220

TABLE VII
Gel Time of Noncatalyzed and Metallic-Catalyzed Epoxy/Cyanate

	Gel time (s)
Noncatalyzed	165
Cu(AcAc) ₂	150
Copper octoate	105
Manganese octoate	75

two-step reaction mechanisms and the structures of intermediate products during curing.

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