Effect of Cyanate Ester on the Cure Behavior and Thermal Stability of Epoxy Resin

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ABSTRACT: Epoxy resin (diglycidyl ether of bisphenol A, DGEBA)/cyanate ester mixtures were cured with a curing agent, 4,4'-diaminodiphenylsulfone, and the effect of cyanate ester resin on the cure behavior and thermal stability in the epoxy resin was investigated with a Fourier transform infrared spectrometer, a rheometer, a dynamic mechanical analyzer, and a thermogravimetric analyzer. Cure reactions in the epoxy/cyanate ester mixture were faster than that of the neat epoxy system. The cure reaction was accelerated by increasing the cyanate ester resin component. Glass transition temperature and thermal stability in the cured resins were increased with increasing cyanate ester resin component. This may be caused by the increase of crosslinking density due to the polycyclotrimerization of the cyanate ester monomer to form triazine rings and the reaction of cyanate ester resin with the epoxy network. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 85–90, 1997

Key words: epoxy; cyanate ester; cure; thermal stability

INTRODUCTION

Epoxy resin is one of the most important thermosetting resins. It has many desirable properties, such as high modulus, high strength, excellent chemical resistance, and good electrical resistance. Consequently, it is widely used for many important applications such as coating compounds, structural adhesives, insulating material for electric and electronic components, reinforced plastics, and matrix resins for advanced composite materials.[1,2] Unfortunately, epoxy resins have relatively high dielectric loss and poor water absorption properties and consequently have limited use in applications requiring high-speed signal propagation and transport for printed circuit board. Therefore, several researchers[3–6] have studied the modification of epoxy resin with bis-maleimide-triazine (BT resin), bismaleimide, and phenolic resin for printed circuit board applications. Here, the focus is on the modification of

epoxy resin with cyanate ester resin. Because cyanate ester resins have low dielectric loss properties, low water absorption, excellent heat resistance, and low volume shrinkage,[7–10] they are particularly useful in both the aerospace and the electronic industries. Aerospace applications include high-temperature adhesives and matrix resins for structural components. Electronic applications include printed-wiring circuit boards, thin cards, multichip module laminates, and chip encapsulants. Their transparency to microwave and radar energy makes them useful for the conical radome nose cones that house radar antennas of military and weather reconnaissance planes. Microcrack resistance is an important requirement for communications satellites, as is impact resistance for aircraft structures and engine pistons. Cyanate esters also find use in such friction materials as brake linings and grinding wheels and in high-performance adhesives and coatings.[11–14] In this article, I examine a diglycidyl ether of bisphenol A (DGEBA)/cyanate ester resin/amine curing agent mixture and investigate the effect of cya-

Table I Experimental Formulations

| Component	Epoxy Control	20 phr CE[a]	40 phr CE
DGEBA	75.4	75.4	75.4
AroCy L-10		20.0	40.0
DDS	24.6	24.6	24.6

[a] CE, cyanate ester.

nate ester resin content on the cure behavior and thermal stability of epoxy resin with a Fourier transform infrared (FTIR) spectrometer, a rheometer, a dynamic mechanical analyzer (DMA), and a thermogravimetric analyzer.
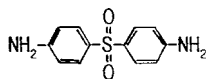
EXPERIMENTAL

An epoxy resin, DGEBA, was supplied by Kukdo Chemical Corp. (YD-127; EEW = 184 g/mol). The curing agent was diaminodiphenylsulfone (DDS). The bisphenol E–based cyanate ester resin, 4,4'-ethylidenediphenol (AroCy L-10) was supplied by Ciba-Geigy Corp. The structural formulae are shown as follows:
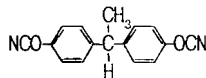
YD-127
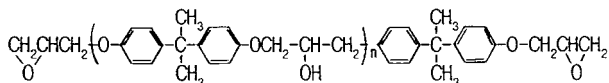
DDS

AroCy L-10

The DDS was dissolved in epoxy resin, and then cyanate ester resin was added to the epoxy/DDS mixture, ranging from 0 to 40 phr with respect to the epoxy resin used. The three formulations are shown in Table I. The mixture was mixed throughly at room temperature and degassed under a vacuum of 10^{-4} for 30 min to remove air and void. The bubble-free mixture was poured into a mold preheated to 145°C, inserted

in a convection oven, cured at 160°C for 3 h, and finally postcured at 200°C for 1 h. After curing, the sample was allowed to cool slowly to room temperature.

The cure kinetics was measured with an FTIR spectrometer (Magna-IR, Nicolet Corp.). FTIR spectra were measured at appropriate interavals during isothermal curing.

The gel point was determined with a rheometer (PHYSICA RHEO-LAB MC20/UM) as a point of abrupt change in viscosity evolution. The parallel-plate rheometer was used to measure complex viscosity (poise) as a function of angular frequency (rad/sec) at 160°C in the oscillatory shear mode. The gap size was 1 mm, and the diameter of the plate was 50 mm. In order to avoid oxidative degradation, nitrogen was continuously purged during the measurements.

The glass transition temperature (T_g) was measured with a dynamic mechanical analyzer (DMA) (model 900, DuPont Corp.). The heating rate was 5°C/min, and the scanning range was from 25 to 300°C.

Thermogravimetric analysis (TGA) (model 951, DuPont Co.) was used to investigate the thermal stability of the cured resins. The scanning rate was 10°C/min in the presence of N_2.

RESULTS AND DISCUSSION

Figure 1 shows the change in FTIR spectra with curing at 160°C in the epoxy resin control formulation. As the cure reaction proceeds, an epoxide band at 908 cm^{-1} and an amine (NH bending) band at 1,620 cm^{-1} gradually decrease and then disappear.

Figure 2 shows the change in FTIR spectra with isothermal curing at 160°C in the mixture of epoxy and cyanate ester resins (40 phr). The epoxy and amine bands gradually decrease and eventually disappear in the same way as the epoxy resin. With curing, however, the cyanate band quickly decreases and finally disappears within 5 min. It may be due to the addition of aryl amine. The adducts either thermally degrade at 200°C to phenol and a cyanamide (detected at 2,210 cm^{-1}) (mono adduct) or undergo ring closure to 1,2,4-triazole (di adduct).[15] FTIR absorbance observed at 1,670 cm^{-1} in Figure 2 is likely the $\diagdown C = NH$ stretch of imidocarbonate or isourea. The cyanate —O— stretch at 1,365 cm^{-1} is observed at 0 cure
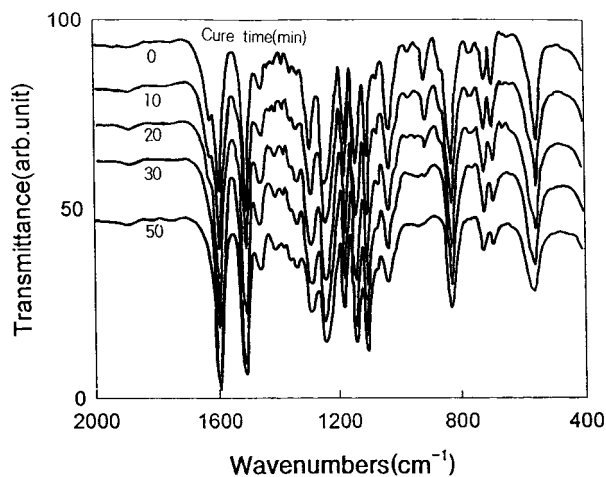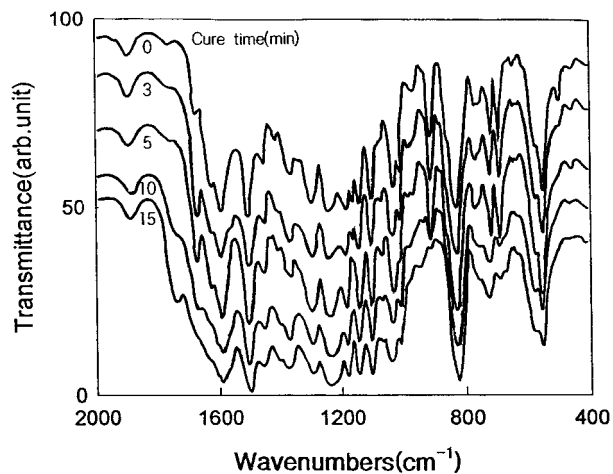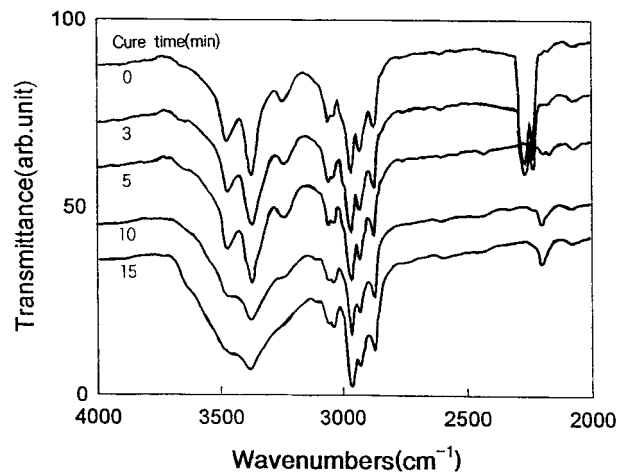
(a)
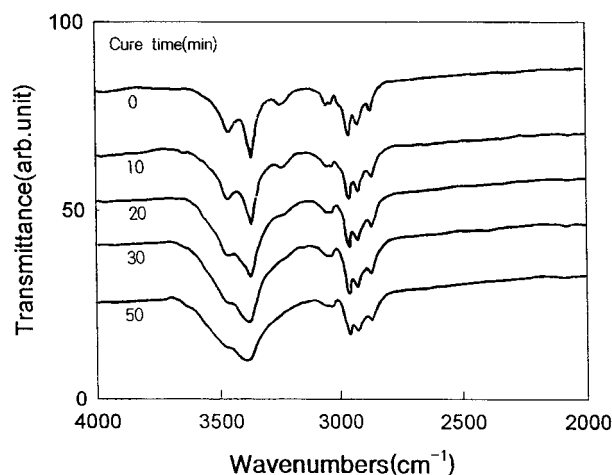
(b)

Figure 1 Change in FTIR spectra with curing at 160°C in the neat epoxy resin; (a) $400-2,000$ cm^{-1}, (b) $2,000-4,000$ cm^{-1}.

(a)

(b)

Figure 2 Change in FTIR spectra with curing at 160°C in the epoxy/cyanate ester mixture; (a) $400-2,000$ cm^{-1}, (b) $2,000-4,000$ cm^{-1}.

time, indicating that cyclotrimerization is beginning during mixing and degassing at 145°C. Other significant absorbances in Figure 2 are at 1,750 cm^{-1} (oxazolidinone from the reaction of epoxide with cyanate; see ref. 17) and 2,210 cm^{-1} ($-$C$\equiv$N of the cyanamide degradation product of the amine-cyanate isourea adduct; see ref. 17). Also, the addition of cyanate to hydroxyl is possible, particularly later in the reaction when hydroxyl is formed by the epoxide amine.[15]

Thus, one may associate an increase of T_g in the cured resins with an increase of crosslinking density by one or more of several reactions including cyanate with amine,[15] cyanate with hydroxyl,[15,16] cyanate cyclotrimerization, cyanate with epoxide,[17] and epoxide with cyanurate[17-19]
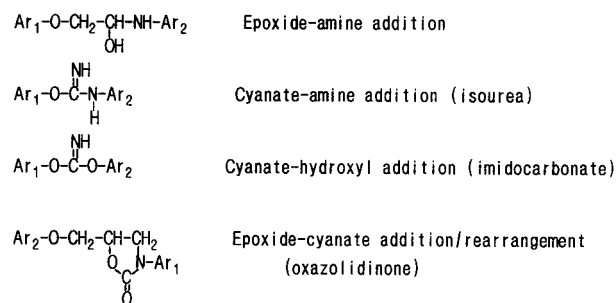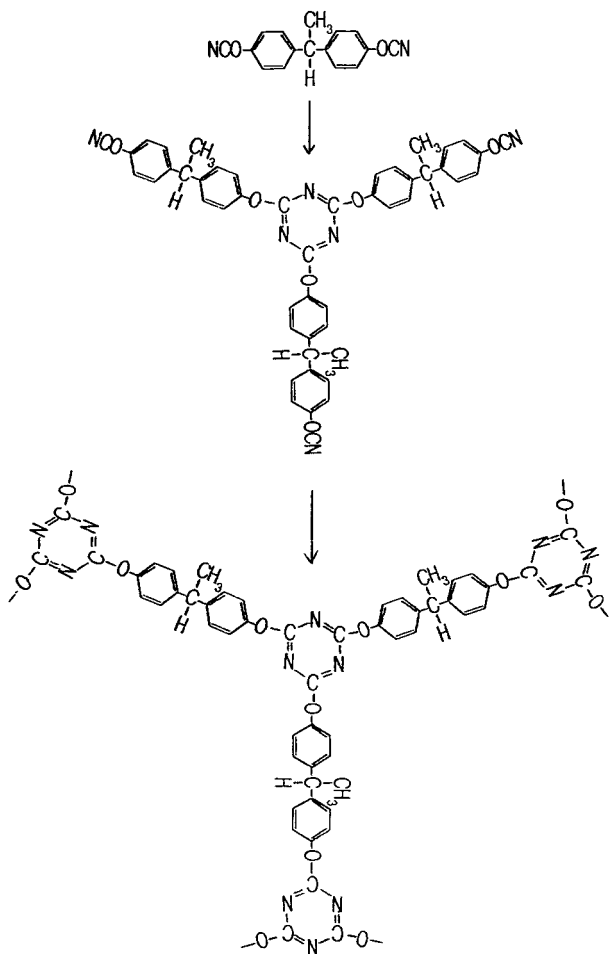
(Scheme 1) and/or the polycyclotrimerization reaction of cyanate ester monomer to form triazine rings (Scheme 2).

Scheme 1

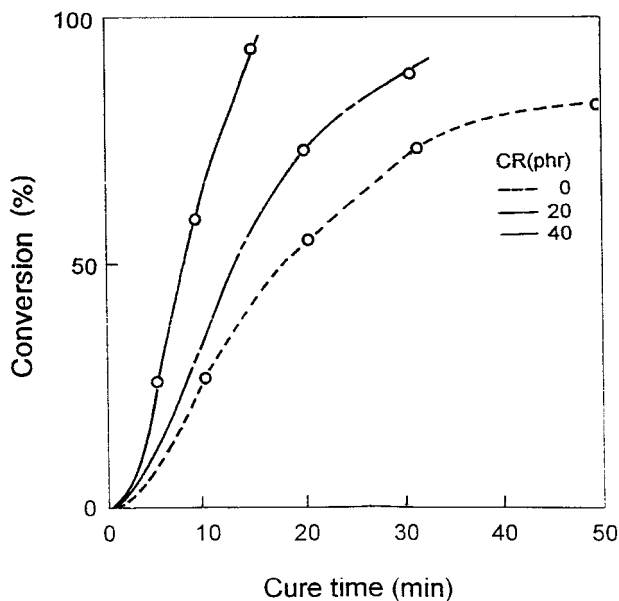**Scheme 2**   Dicyanate polycyclotrimerization

Figure 3   Epoxy conversion curves with curing at 160°C in the neat epoxy and epoxy/cyanate ester mixture.

that cyanate functionality is consumed faster than epoxide functionality (Fig. 4).

Figure 5 shows the variation of viscosity with cure time at 160°C in the neat epoxy and epoxy/ cyanate ester mixture. As the cure reaction pro-
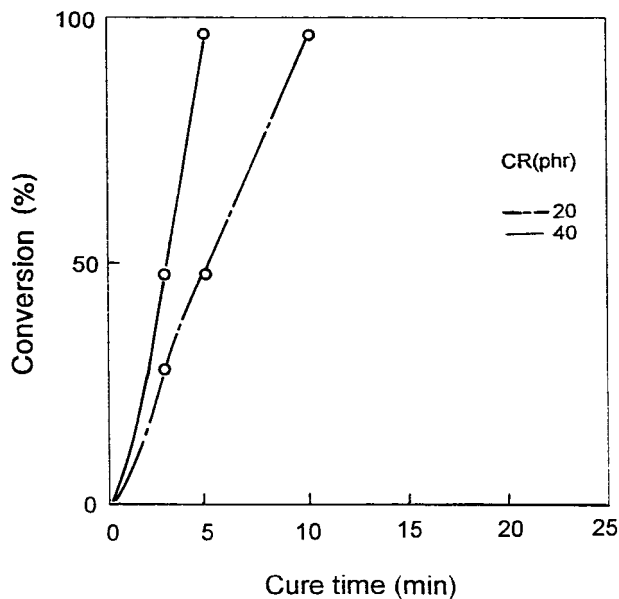
Figure 3 shows the time–conversion curves of the neat epoxy and the epoxy/cyanate ester resin mixture. The conversion was estimated by using the absorbance of the phenyl group at 1,602 cm^{-1} (as an internal standard) $A_{1,602}$:

Conversion (%) = 1

$$- [(A_{908}/A_{1,602})_t/(A_{908}/A_{1,602})_{t=0}] \times 100 \quad (1)$$

where $(A_{908})_t$ is the absorbance of the epoxy band at 908 cm^{-1} at reaction time t and $(A_{1,602})_{t=0}$ is the phenyl group at 1,602 cm^{-1} at reaction time $t = 0$. One sees that the degree of reaction in the mixture of the epoxy/cyanate ester resin is faster than that of the neat epoxy resin. The accerlation was increased with increasing a cyanate ester resin component. It seems that cyanate ester resin acts as a cocuring agent. By plotting cyanate conversion in a similar manner using the absorbance of the cyanate group of 2,270 cm^{-1}, one can see

Figure 4   Cyanate conversion curves of the epoxy/cyanate ester mixture. Using $A_{1,602}$ absorbance of the phenyl group at 1,602 cm^{-1} as an internal standard, the cyanate conversion was estimated by $1 - [(A_{2,270}/A_{1,602})_t/(A_{2,270}/A_{1,602})_{t=0}] \times 100$.
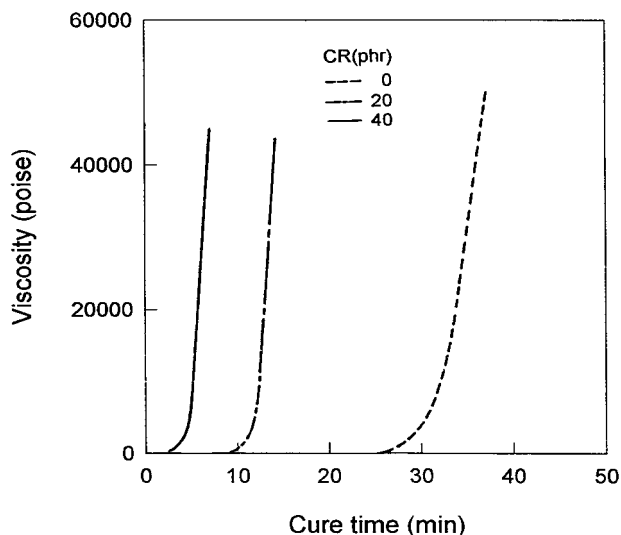
Figure 5 Time variations of viscosity during cure at 160°C in the neat epoxy and epoxy/cyanate ester mixture.

ceeds, viscosity gradually increases and then dramatically increases near the gel point. Here, the gelation time is obtained as a point of abrupt change in viscosity evolution. As was observed by FTIR analysis, the larger the content of cyanate ester resin, the faster is the reactivity.

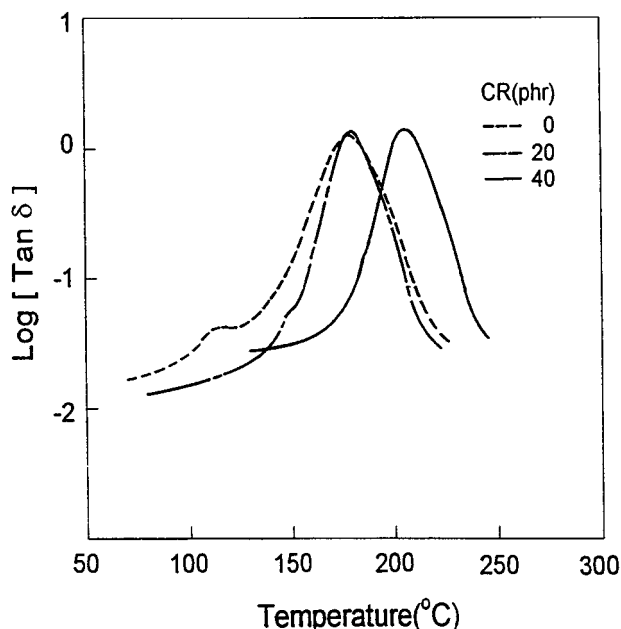Figure 6 shows the dynamic mechanical ther-

Figure 6 Dynamic mechanical thermograms of the neat epoxy and epoxy/cyanate ester mixture cured at 160°C for 3 h and postcured at 200°C for 1 h.
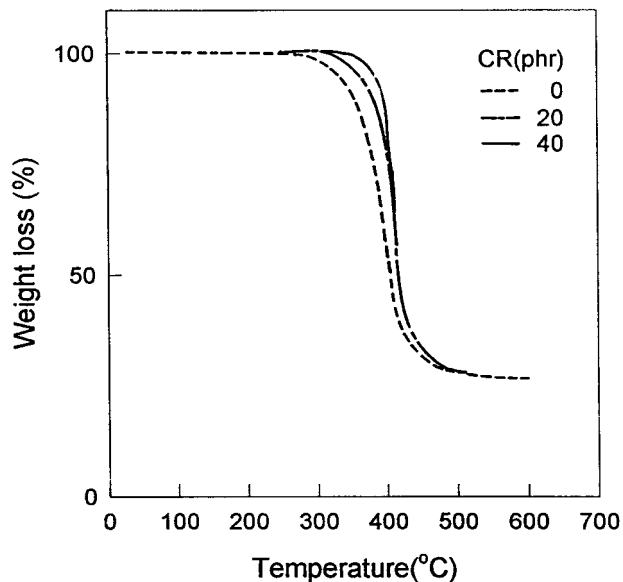

Figure 7 TGA thermograms of the neat epoxy and epoxy/cyanate ester mixture cured at 160°C for 3 h and postcured at 200°C for 1 h.

mograms of neat epoxy and epoxy/cyanate ester resin mixtures cured at 160°C for 3 h and postcured at 200°C for 1 h. As can be seen in Figure 6, the T_g of the cured castings was increased with increasing cyanate ester resin component. A high T_g may be the result of increasing crosslinking density due to the reaction of cyanate ester resin with the epoxy network.

Figure 7 compares the TGA thermograms of neat epoxy and epoxy/cyanate ester resin mixtures cured at 160°C for 3 h and 200°C for 1 h. The weight loss at 5% is shifted to higher temperatures with an increase of the cyanate ester resin component. That is, thermal stability is improved as much as 80°C by adding the cyanate ester resin.

CONCLUSIONS

The cure behavior, T_g, and thermal stability of epoxy/cyanate ester resin mixtures containing an aromatic diamine curing agent were investigated. FTIR analyses revealed that all functional group reactions are accelerated by adding a cyanate ester resin and indicate that one or more of several coreactions described in the literature (cyanate–amine, cyanate–hydroxyl, and/or epoxy–cyanate) are occurring. Cyanate ester resin acts as a cocuring agent in this system. The glass transition tem-

perature and thermal stability of the cured resins were increased substantially by increasing the cyanate ester resin component to 40 phr. Hybrid thermosetting resins formulated by the addition of aryl dicyanates to epoxy/aromatic amine systems offer faster processing, higher T_g, and improved thermal stability properties of interest to manufacturers of aerospace, electronics, composites, and adhesives.

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