行政院國家科學委員會補助專題研究計畫成果報告

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執行單位：國立高雄應用科技大學

中華民國九十一 年 十 月 三十 日
Cure Reaction of Dicyanate/Diepoxide/Diamine Hybrid System

Abstract
Cure reactions of a liquid aromatic dicyanate ester (1,1'-bis(4-cyanatophenyl)ethane, BEDCy) with a liquid bisphenol A epoxide (2,2-bis(4-glycidyloxyphenyl)propane, BADGE) and 4,4'-diaminodiphenyl sulfone (DDS) were studied through correlation of the in situ FTIR and DSC in dynamic scanning mode. Some reactions, such as polycyclotrimerization of dicyanate to form sym-triazine and formation of alkyl isocyanurate, were not observed in the combined curing system BEDCy/BADGE/DDS. Four principal reaction paths are proposed for this curing system (1) formation of oxazoline from the reaction between the epoxide and cyanate group, (2) reaction of oxazoline with primary amine to form a hydroxyl group, (3) reaction of oxazoline with the hydroxyl group to form an ether linkage, and (4) rearrangement of oxazoline to form oxazolidinone.

Key words: Diglycidyl ether of bisphenol A resin, Aromatic dicyanate ester, Diaminodiphenyl sulfone, Cure reaction

Introduction
In recent years some authors [1-4] have proposed a complex reaction mechanism for the polymerization of 2,2-bis(4-cyanatophenyl)propane and 2,2-bis(4-glycidyloxyphenyl)propane. This mechanism (herein referred to as Bauer pathway) was supported by model compound studies involving phenyl glycicyl ether, 4-chlorophenyl cyanate and its trimer. Shimp et al. [5] examined the Bauer pathway using phenyl glycicyl ether, p-cumylphenyl cyanate (a monofunctional analogue of bisphenol A cyanate) and its trimer by means of FTIR, GPC and LC analyses. The possible cross reactions between the cyanate and epoxy resin were also investigated via solid-state NMR by using monofunctional compounds.[6, 7] In previous studies[8] we have explored a possible reaction series in a real system of 1,1'-bis(4-cyanatophenyl)ethane (BEDCy) and 2,2-bis(4-glycidyloxyphenyl)propane (BADGE) through correlation of the in situ FTIR and DSC in dynamic scanning mode.

Kim [9] studied the effects of a cyanate ester on the cure behavior and thermal stability in the diglycidyl ether/dicyanate/diaminodiphenyl sulfone system, for which exact reaction pathways were not proposed.

The objectives of this work are to explore possible reaction series in a real BEDCy/BADGE/DDS system, rather than a system of model compounds, through correlation of the in situ FTIR and DSC dynamic scanning results. Before we attempted to examine this system, the precussory curing systems BADGE/DDS, BEDCy/DDS and BADGE/BEDCy were studied in advance by the same manner. Comparisons between these systems were also made in this work.

Experimental
1. Materials
2,2-bis(4-glycidyloxyphenyl)propane (BADGE), 1,1'-bis(4-cyanatophenyl)ethane (BEDCy), 4,4'-diaminodiphenyl sulfone (DDS) and n-nonlyphenol

Results and discussion
Before we attempted to analyze the cure reaction of BEDCy/BADGE/DDS system, cure reactions of BADGE/DDS with n-nonlyphenol, BEDCy/BADGE with p-nonlyphenol and BEDCy/DDS with n-nonlyphenol were first investigated separately.

1. BADGE/DDS system
The curing system of BADGE/DDS with a weight ratio of 2:1 (mole ratio of 1:0.68) associated with 10 phr of n-nonlyphenol based on total resin was prepared to study the reaction mechanism via correlation of dynamic FTIR spectra and DSC thermograms. Figure 2a shows the DSC thermogram of this mixture system at a heating rate of 3 K/min. Only one broad exothermic peak can be observed (primarily in the range of 130-250 °C). This indicates that the cure reactions go on for a long time, but proceed in a consecutive way. In order to be able to compare the FTIR spectra and the DSC thermograms, we performed the infrared study for the dynamic cure of this
system at the same heating rate (5 K/min) from room temperature to 270 °C. Although there is a slight uncertainty as to the exact heating rate used for the FTIR work, the progressive temperature increase between the FTIR spectra and the corresponding DSC thermograms is comparable. The FTIR scans were performed at each 10 °C increment sequence of progressively ascending temperature during the heating.

Shown in Figure 3 are some pertinent FTIR representative spectra taken during the dynamic heating (in order to compare them with the DSC thermograms). We inspected each absorption peak which was changing its intensity (increasing or decreasing) compared with the internal standard absorption (−CH₃, 1510 cm⁻¹). Surprisingly, we found that intensities of characteristic DDS absorptions (544, 693, 719, 1105, 1144, 1278, 1595, and 3230-3460 cm⁻¹) increase as the heating temperature increases. This phenomenon is presumably due to the nature of DDS during the heating, which was demonstrated by dynamically heating neat DDS with an internal standard compound (2,2-diphenyl propane). Taking into account the temperature effect of DDS peaks, we observed that the absorption bands at 1105 cm⁻¹ (ether), 1145 cm⁻¹ (ether, secondary amine), 3410 cm⁻¹ (secondary amine) and 3500 cm⁻¹ (hydroxyl groups) simultaneously increase as the epoxide (912 cm⁻¹) and primary amine (1630 cm⁻¹) decrease during the dynamic curing. Epoxide groups and primary amines were almost completely consumed when the curing temperature approached 250 °C, which is compatible with the DSC observations. The main reactions in the BADGE/DDS system are proposed in Scheme I. The peak intensities of the hydroxyl groups (3500 cm⁻¹) and the secondary amines (3410 cm⁻¹) reach a plateau (in the vicinity of 230 °C) at the same time, indicating that the epoxide - secondary amine reaction (E-SA) does not play an important role beyond the temperature of 230 °C. This observation can only be rationalized by assuming that DDS acts as a bifunctional curing agent, i.e. the secondary amines formed from the curing of DDS does not react any further. This is presumably due to the fact that the reactivities of the primary amino hydrogens (k₁) in the aromatic amines are substantially greater than those of the secondary amino hydrogens (k₂), and hence the negative substitution effect occurs when the epoxide - primary amine reaction (E-PA) is completed [10]. Dusek[10] stated that although the data (k₂/k₁) presented may be somewhat controversial, analysis of data[11,12] shows that the ratio of the rate constants (k₂/k₁) per mole of amino group is 0.4-0.6 for aliphatic amines and 01-0.3 for aromatic amines. This indicates that it is negative substitution effect in aromatic amines. Although this negative substitution effect results in forming stable epoxy-amine adducts, the hydroxyl groups in these adducts can continuously react with epoxide groups to form ether linkages. Secondary amines undergo E-SA reaction only under the condition that there are no sufficient primary amines present in the curing system. With aromatic amines it is well established that the homopolymerization of the epoxide groups initiated by the hydroxyl group assumes a much greater significance in the curing process than in the case of aliphatic amines [13]. Therefore, it is reasonable to expect that reaction paths in Scheme I are generally available for a relatively low stoichiometric value of DDS. But, for a relatively high stoichiometric value of DDS (providing sufficient primary amines), only reactions 1 and 2 proceed.

II. BEDCy/BADGE system

The curing system of BEDCy/BADGE in a weight ratio of 1:1 associated with 10 phr of n-nonylphenol was prepared to study the reaction mechanism by the previous manner. Figure 2b shows the DSC thermogram of this mixture system at a heating rate of 5 K/min. Two distinct, but somewhat overlapping, exothermic peaks were observed. For comparison, shown in Figure 4 are some pertinent representative FTIR spectra during the dynamic heating (5 K/min). In previous studies [8] we have proposed reaction paths as illustrated in Scheme II. In the earlier stage, the former four reaction paths prevail. Reactions including the formation of triazine rings, isocyanurates, oxazine linkages and insertion of epoxide into cyannurate (i.e. traneseurification) were simultaneously observed.

III. BEDCy/BADGE/DDS system

A similar approach was used to investigate the curing of the BEDCy/BADGE/DDS system. This curing system in a weight ratio of 1:2:1 (BEDCy/BADGE/DDS) associated with 10 phr of n-nonylphenol was finally prepared to study the reaction mechanism of this hybrid system. Shown in Figure 2c is the DSC thermogram of this mixture system at a heating rate of 5 K/min. In the BADGE/BADGE system, two obvious exothermic peaks but shifted to a lower temperature range can be observed. What reactions correspond to each peak in Figure 2c? We doubt whether the reactions in this cure system result from all the combined reaction of the BEDCy/BADGE and BADGE/DDS systems. FTIR dynamic curing may provide us with more detailed information on the nature of the cure reactions.

III-a. Earlier stage of curing process

For comparison with the DSC thermogram, shown in Figure 5 are some pertinent FTIR representative spectra during the dynamic heating (5 K/min). These FTIR spectra show that dynamic heating from room temperature to 170 °C resulted in the consumption of most cyannurate groups. Surprisingly, we did not find the formation of the sym-triazine ring (1565 cm⁻¹) and the isocyanurate structure (1695 cm⁻¹) (via rearrangement from sym-triazine). The cyannurate groups are therefore consumed possibly by three different reactions. One of which is the reaction between BEDCy and BADGE, hereby forming an oxazine structure (−N−CH=−O−, 1678 cm⁻¹, ether 1365, 1295 cm⁻¹). Another one is the reaction between BEDCy and DDS to form an iso-urea structure (−C(=NH)=O−, 1678 cm⁻¹):  

\[
\begin{align*}
\text{BEDCy} + \text{DDS} & \rightarrow \text{Badger} + \text{Iso-Urea}
\end{align*}
\]

The third one is the reaction between BEDCy and a hydroxyl group to form an imidocarbonate structure (−O−C(=NH)−O−, 1678 cm⁻¹):  

\[
\begin{align*}
\text{BEDCy} + \text{OH}− & \rightarrow \text{Imidocarbonate}
\end{align*}
\]

The occurrence of the reactions in Equation 1 and 2 can be excluded from this system, because no absorption band for the iso-urea structure (1678 cm⁻¹) was observed for curing BEDCy/DDS system (not shown here for brevity), nor was an imidocarbonate structure (1678 cm⁻¹) detected for curing BEDCy with n-nonylphenol. Consequently, the reaction between BEDCy and BADGE to form the oxazine structure is the exclusive one which consumes all cyannurate groups in this stoichiometric formulation of BEDCy/BADGE/DDS system. The more significant evidence is that (a) the intensities of absorption bands 1678, 1365 and 1295 cm⁻¹ (characterizing the oxazine structure) reached the maximum value at the same time as the cyannurate groups (2268, 2237 cm⁻¹) were completely consumed when the heating temperature was up to 170 °C; and (b) the intensities of absorption bands 1678, 1365 and 1295 cm⁻¹ were simultaneously decreasing after passing 170 °C, and finally, completely vanished. This demonstrated that the peak at 1678 cm⁻¹ arose from the formation of the oxazine structure.

At this stage, the reactions (a) between the epoxide group
and primary amine to form a secondary amine and a hydroxyl group, and (b) between the epoxide group and hydroxyl group to form an ether linkage were not significantly detected, even if they did proceed. These inferences can be confirmed by the observations of (a) no obvious decrease in the intensities of the absorption bands of the primary amine (1630 cm\(^{-1}\)), and (b) no apparent increase in the intensities of absorption bands at 1105 cm\(^{-1}\) (ether), 1145 cm\(^{-1}\) (ether, secondary amine), 3410 cm\(^{-1}\) (secondary amine) and 3500 cm\(^{-1}\) (hydroxyl groups) when the temperature effect was taken into account as previously mentioned.

In summary, the reaction path 1 in Scheme III is dominant and almost the exclusive one in the earlier stage.

### III-b Latter stage of curing process

FTIR spectra taken during the dynamic heating from 170 to 240 °C show the formation of an oxazolidinone structure (1753 cm\(^{-1}\)), a secondary amine (3410 cm\(^{-1}\)), a hydroxyl group (3500 cm\(^{-1}\)) and an ether linkage (1105, 1146 cm\(^{-1}\)), which eventually reach a saturation value at the end of the cure reaction (240 °C). The continuous disappearances of absorption bands of oxazoline (1678, 1365 and 1295 cm\(^{-1}\)), epoxide group (912 cm\(^{-1}\)), and primary amine (1630 cm\(^{-1}\)) were also simultaneously observed. Finally, absorption bands of the oxazoline structure, the epoxide and the primary amine completely vanished. It should be mentioned that the disappearing of the absorption peak at 1753 cm\(^{-1}\) in the earlier stage is the nature of the cure reaction of aromatic dicyanate (27). However, the marked increase in the absorption peak at 1753 cm\(^{-1}\) in the latter stage results from the formation of an oxazoline. From these observations, we infer that there should be three reactions in the latter regime (also for the low exothermic peak of DSC thermogram). These three reactions are proposed as paths 2, 3 and 4 in Scheme III. The reaction path 1 in the earlier stage and the reaction paths 2-4 in the latter stage were somewhat overlapping just as overlapping of the two exothermic peaks on the DSC trace occurred. Furthermore, the absorption intensity of the hydroxyl group (3500 cm\(^{-1}\)) does not decrease with the increase in that of the ether linkage. This indicates that the total formation rate of the hydroxyl group (path 3 and 4) is larger than its disappearing rate (path 4).

### Conclusion

There are 6 and 4 reaction paths for the precursory curing systems BEDCy/BADGE and BADGE/DDS, respectively. Nevertheless, the reaction mechanism for the combined curing system BEDCy/BADGE/DDS is not too complex. There are only 4 reaction paths (Scheme III) in this combined curing system, presumably due to the presence of DDS. Meanwhile, the reaction temperature has shifted about 30 °C lower. Some reactions in the BEDCy/BADGE system, such as polycyclotrimerization of dicyanate to form sym-triazine and hence the formation of alkyl isocyanurate via rearrangement from sym-triazine, were not observed in the BEDCy/BADGE/DDS curing system. The epoxide - secondary amine reaction to form tertiary amine is also unimportant in this curing system due to the negative substituent effect of the aromatic amine DDS.

### References

Figure 3. DSC thermograms of curing systems (a) BADGE/DDS in a weight ratio of 2:1, (b) BEDCy/BADGE in 1:1 and (c) BEDCy/BADGE/DDS in 1:2:1 at a heating rate of 5 °C min\(^{-1}\).

Fig. 3 Some pertinent FTIR representative spectra for BADGE/DDS (2:1) system during the dynamic heating from room temperature to 270 °C at a heating rate of 5 K/min.
Fig. 5  Some pertinent FTIR representative spectra for BEDCy/BADGE/DDS (1:2:1) system during the dynamic heating from room temperature to 240 °C at a heating rate of 5 K/min.

Scheme 2. Pathways proposed for the reaction of curing system BEDCy/BADGE.

(1) Epoxide + Dicyanate → Oxaizoline

(2) Epoxide + Primary amine → Hydroxyl group + Secondary amine

(3) Epoxide + Hydroxyl group → Hydroxyl group + Secondary amine + Ester

(4) Oxaizoline → Oxaizoline

Scheme 3. Pathways proposed for the reaction of curing system BEDCy/BADGE/DDS.