IR study of hydrogen bonding in novel liquid crystalline epoxy/DGEBA blends

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Summary
The hydrogen bonding of LCE/DGEBA blend was studied using FT-IR. IR spectra of hydroxyl region and carbonyl region were investigated according to the content of LCE. IR spectra of LCE/DGEBA blend before and after curing were compared. Most hydroxyl group in DGEBA rich blends formed intermolecular or intramolecular hydrogen bonding after curing, while free hydroxyl group was present in LCE rich blends. Intramolecular hydrogen bonding was popular in DGEBA rich blends due to the conformational reason. Most carbonyl group was hydrogen bonded with hydroxyl or amine group after curing and the fraction of hydrogen bonded carbonyl was high in DGEBA rich blends.

Introduction
Epoxy resins have been known as the thermoset with high mechanical and electrical properties. They have been used in the field of adhesive, protective coating and matrix for composite. In recent years, new epoxy resins with high heat resistance and dimensional stability were developed for the advanced industrial field. Tetrafunctional epoxy resin(1-4) and liquid crystalline epoxy(LCE) resin(5-20) have been studied in order to improve mechanical and thermal properties of common epoxy resin. In the previous paper we reported the synthesis and physical properties of novel LCE based on ester mesogenic unit(21). It showed excellent mechanical properties and glass transition temperature above 230 ℃. In addition, it was proved to be effective as a reinforcement in the blend with common epoxy resin since it had high aspect ratio. We also studied thermal properties of LCE/DGEBA blend and in that study the glass transition temperature of LCE/DGEBA blend was enhanced by about 40 ℃ by the addition of only 10 % of LCE(22). From thermal analysis, the curing rate of LCE was fast in LCE rich blends and the degree of cure was high in the DGEBA rich blends.
In this paper, we studied the hydrogen bonding of LCE/DGEBA blend using FT-IR. The hydrogen bonding of LCE/DDS blend in the hydroxyl region and carbonyl region was investigated before and after curing.
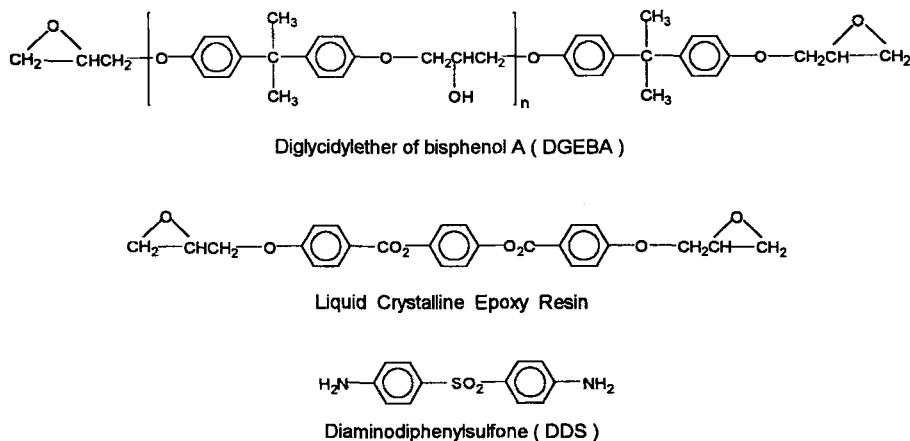
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Diglycidylether of bisphenol A (DGEBA)

Liquid Crystalline Epoxy Resin

Diaminodiphenylsulfone (DDS)

Figure 1. Chemical structures of epoxy resins and curing agent.

Experimental

Materials

The liquid crystalline epoxy(LCE) resin used in this experiment was synthesized in our laboratory. The synthetic method of LCE is described in previous paper(21). The nematic transition temperature of LCE was 181 ℃ and the isotropic transition temperature was 229 ℃. Diglycidylether of bisphenol A(DGEBA) was supplied by Kukdo Chem. Co. under the trade name of YD 128. Diaminodiphenylsulfone(DDS) was manufactured by Aldrich Chem. Co. and it was used without purification. Chemical structures of epoxy resins and curing agent are shown in Fig. 1.

Curing of LCE/DGEBA blends

LCE/DGEBA blends were cured using DDS as the curing agent. DDS was used to produce high heat resistant material and to slow down the curing reaction of LCE/DGEBA blends. The amine curing agent was tetrafunctional and epoxy resin was difunctional. The mole ratio of DDS to epoxy resins was fixed with 0.45. LCE content to DGEBA was varied with 0, 10, 25, 50, 75, 90, 100 mol% and each blend will be named as LC 0, LC 10, LC 25, LC 50, LC 75, LC 90 and LC 100 according to the content of LCE. The curing mixture was prepared by dissolving LCE, DGEBA and DDS in chloroform/acetone mixed solvent and removing the solvent under reduced pressure at room temperature. Each blend was cured at 180 ℃ in convection oven for 60 min.

Spectroscopic measurements

All IR absorption spectra were recorded on MB 100 Fourier transformed infrared spectrophotometer(FT-IR Bomem Inc.). 16 scans were performed at a resolution of 4 cm^{-1}. Relative peak area of carbonyl region was calculated with deconvolution method by Lorenzian curve fitting.
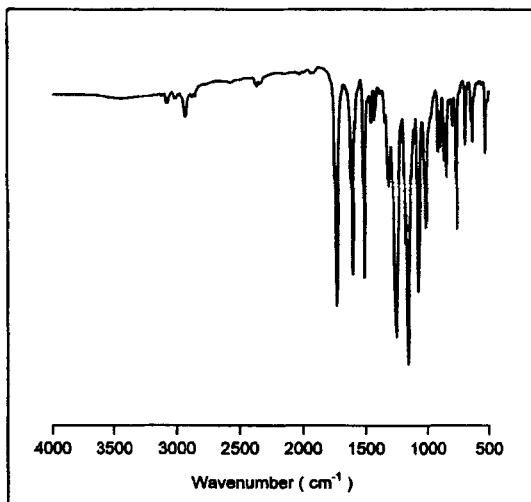
Figure 2. IR spectrum of LCE.

Results and discussion

Fig. 2 shows IR spectrum of LCE. The carbonyl stretching peak of LCE appears at 1732 cm^{-1} due to the aromatic ester mesogenic unit and epoxide ring deformation peak can be seen at 912 cm^{-1} and 896 cm^{-1}. The peak below 3000 cm^{-1} is assigned to the bending mode of aliphatic CH and the peak above 3000 cm^{-1} is attributed to the bending mode of aromatic CH. Peaks at 1510 cm^{-1} and 1594 cm^{-1} are caused by the stretching mode of aromatic C=C and the peak near 1250 cm^{-1} is due to the aromatic aryl ether unit. In the case of DGEBA, as it had no carbonyl functional unit, the peak at 1732 cm^{-1} was not observed. Instead of the carbonyl peak, DGEBA exhibited broad hydroxyl peak around 3500 cm^{-1}, which was not presented in this figure.. DGEBA also showed epoxide ring deformation peak at 912 cm^{-1} and 864 cm^{-1}. Other peaks of DGEBA were similiar with those of LCE.
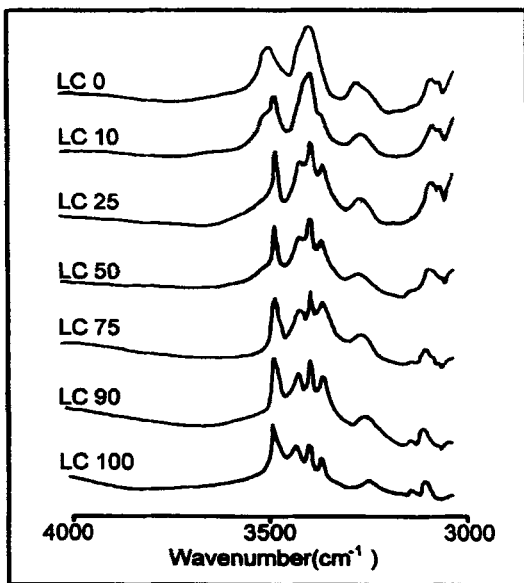

Figure 3. IR spectra of LCE/DGEBA blend in hydroxyl region before curing.

IR spectra of hydroxyl region of LCE/DGEBA blend mixed with DDS are presented in Fig. 3. Hydroxyl stretching peak and asymmetrical and symmetrical amine stretching peaks are shown in this region. DDS displays five characteristic peaks in this region. The peak at 3200 cm^{-1} arises from the overtone of NH$_2$ deformation and peaks between 3300 cm^{-1} and 3400 cm^{-1} are considered as free symmetrical NH$_2$ stretching and the peak at 3470 cm^{-1} is assigned to an asymmetrical amine stretching peak. These DDS peaks can be clearly seen in LC 100 because LCE does not show any peak in this region. However, as the content of DGEBA increases, peaks
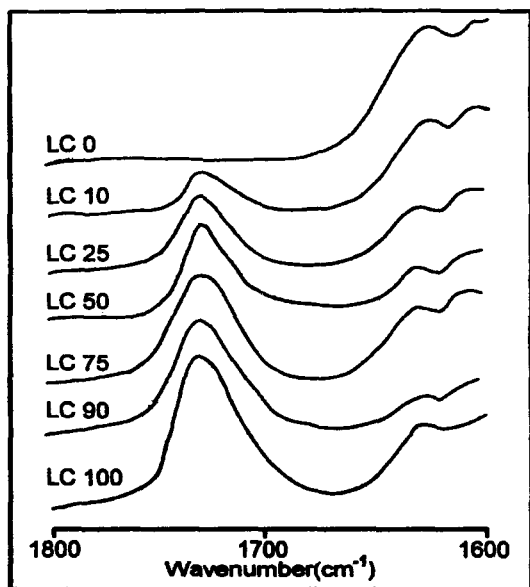
Figure 4. IR spectra of LCE/DGEBA blend in carbonyl region before curing.

between 3300 cm^{-1} and 3400 cm^{-1} are combined into one broad peak centered at 3350 cm^{-1} and the peak at 3470 cm^{-1} is merged to the peak at 3500 cm^{-1}, which is caused by the hydroxyl group of DGEBA. The free symmetrical NH$_2$ stretching peak appears as one peak due to the hydrogen bonding with the hydroxyl group of DGEBA in LC 0. The hydrogen bonding between hydroxyl group and amine is considerable in the case of DGEBA rich blends and the free hydroxyl peak is shown only in DGEBA rich blends. Fig. 4 demonstrates the carbonyl region of LCE/DGEBA mixed with DDS. The ester carbonyl peak was very sharp in LCE resin as there was no hydrogen bonded carbonyl group. However, carbonyl peak is broad in LCE/DGEBA blends due to the hydrogen bonding with the hydroxyl group of DGEBA and with the amine group of DDS. The carbonyl peak becomes broader as the content of DGEBA increases due to
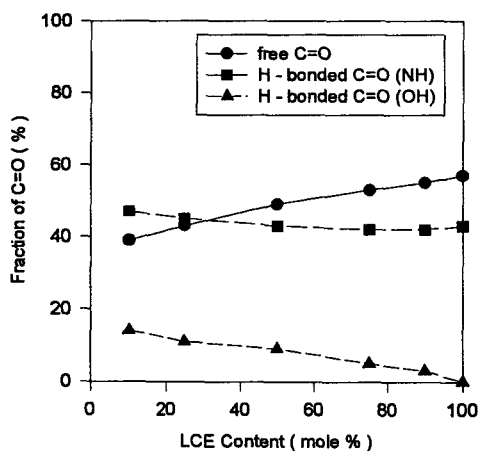

Figure 5. Calculated fraction of the carbonyl group before curing.

the higher probability of hydrogen bonding. The relative amount of hydroxyl group and amine group compared to carbonyl group increases with increasing DGEBA content and the amount of hydrogen bonded carbonyl group also increases. The carbonyl group is very polar and it can form a hydrogen bonding with hydroxyl and amine group easily. The hydrogen bonding between carbonyl group and hydroxyl group is stronger than that between carbonyl group and amine group since oxygen has higher electronegativity than nitrogen. Therefore, the former peak appears at lower
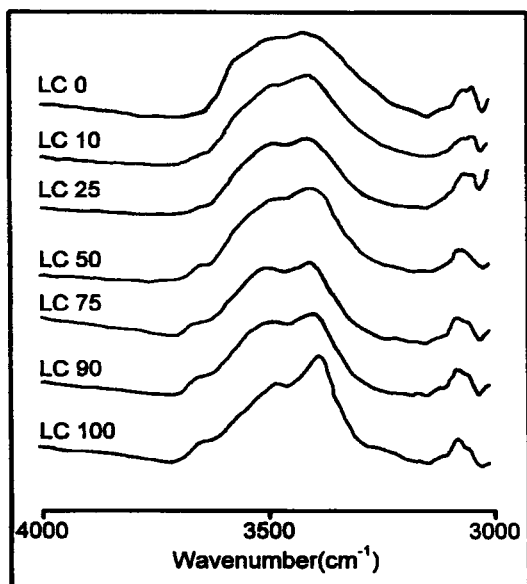
Figure 6. IR spectra of LCE/DGEBA blend in hydroxyl region after curing.

wavenumber than the latter peak. To calculate the relative peak area the carbonyl peak was separated into three peaks by Lorenzian curve fitting. One peak is free carbonyl peak centered at 1732 cm^{-1}, the other peak is carbonyl peak hydrogen bonded with amine at 1720 cm^{-1}, and the third peak is carbonyl peak hydrogen bonded with hydroxyl group at 1712 cm^{-1}. The relative peak area calculated from Lorenzian curve fitting is presented in Fig. 5. Relative fraction of carbonyl peak is displayed in this figure. In the case of LC 100, most carbonyl group remains as free carbonyl group and 35 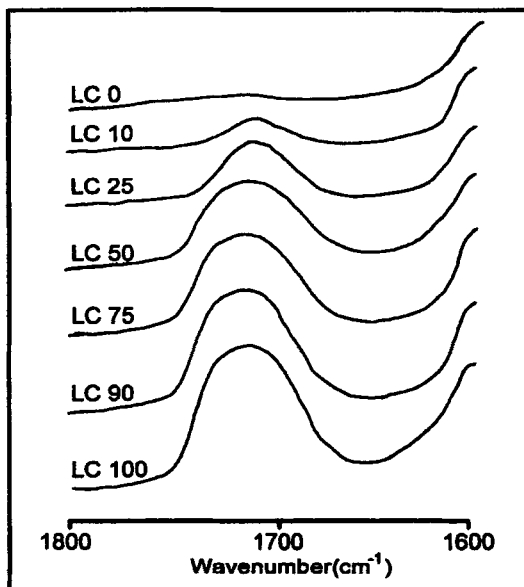% of carbonyl group is hydrogen bonded with amine. However, hydrogen bonded carbonyl group constitutes over 60 % of the carbonyl group in LC 0and this fraction increases as the content of LCE decreases. This tendency can be explained by considering that the decrease of LCE content leads to the decrease of the number of carbonyl group and causes the increase of hydroxyl group and relative amount of amine group based on carbonyl group.

IR spectra of LCE/DGEBA blend after 60 min curing are shown in Fig. 6. As the content of DGEBA increases, peaks around 3300 cm^{-1} become broader and are shifted to the high wavenumber by the intermolecular hydrogen bonding of the hydroxyl group. The peak at 3490 cm^{-1} is caused by the intermolecular hydrogen bonding between hydroxyl groups. As explained in the previous paper, intramolecular hydrogen bonding is found in the vicinity of 3° amine due to conformational restriction(23). In the case of LCE/DGEBA blends intramolecular hydrogen bonding is prominent in the DGEBA rich blends as there is much 3° amine, while the probability of intramolecular hydrogen bonding is very low in LCE rich blends, especially in LC 100 since less 3° amine exists in LCE rich blends compared with DGEBA rich blends. According to the result reported earlier, the degree of cure is proportional to the content of DGEBA(22). High degree of cure means that more 1° amine is converted into 3° amine, therefore intramolecular hydrogen bonding will mainly be found in DGEBA rich blends. In contrast to intramolecular hydrogen bonding, free hydroxyl group is clearly observed in LCE rich blends since rotational and translational motion of the growing chain is constrained by the interaction with the neighboring chain after

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Figure 7. IR spectra of LCE/DGEBA blend in carbonyl region after curing.

observed in the lower wavenumber in the case of content because there are many hydrogen bonding
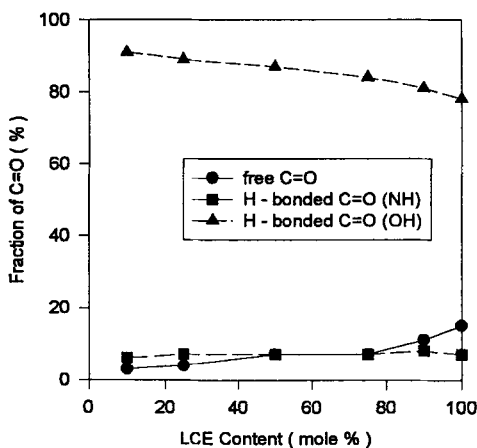

Figure 8. Calculated fraction of the carbonyl after curing.

gelation. Therefore, hydroxyl group can be hydrogen bonded with the neighboring chain. Judging from these results, we can conclude that most hydroxyl groups are hydrogen bonded in DGEBA rich blends, while free and hydrogen bonded hydroxyl groups appear in LCE rich blends due to the nature of the molecular structure.

IR spectra of carbonyl region after curing are shown in Fig. 7. The carbonyl peak was shifted to the lower wavenumber and broadened irrespective of the composition of the blend due to the hydrogen bonding of carbonyl group with hydroxyl group produced by the curing reaction. The carbonyl peak is the blend with high DGEBA content. As explained in Fig. 4, the carbonyl peak is made up of free carbonyl, carbonyl hydrogen bonded with amine and carbonyl hydrogen bonded with hydroxyl. To quantify each carbonyl peak, it was deconvoluted and its peak area was calculated by Lorenzian curve fitting.

Fig. 8 represents the fraction of carbonyl of LCE/DGEBA blend after 60 min curing at 180°C. As the content of LCE increases, the fraction of free carbonyl increases and that of hydrogen bonded carbonyl decreases. This can be explained by considering that the conversion of epoxide ring is low for the blend with high LCE content and more

hydroxyl group is present in the blend with high DGEBA content. It can be known from this result that the fraction of carbonyl hydrogen bonded with hydroxyl group considerably increased and that of free carbonyl decreased by the curing of LCE with aromatic amine.

Conclusion

The hydrogen bonding of LCE/DGEBA blend was investigated. Most hydroxyl group formed intermolecular or intramolecular hydrogen bonding irrespective of the composition of the blend. Intramolecular hydrogen bonding was popular in DGEBA rich blends and free hydroxyl group was observed in LCE rich blends. Free carbonyl, carbonyl hydrogen bonded with amine and carbonyl hydrogen bonded with hydroxyl were present in the carbonyl region and after curing most carbonyl group was hydrogen bonded with hydroxyl group produced by the curing reaction.

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