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IR study on the character of hydrogen bonding in novel liquid crystalline epoxy resin

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Summary

The hydrogen bonding of liquid crystalline epoxy resin with aromatic ester mesogenic group was investigated using FT-IR. The hydrogen bonding in the hydroxyl and carbonyl region was described. Free hydroxyl, intermolecular hydrogen bonding and intramolecular hydrogen bonding was observed in the cured LCE/DDS system. The amount of free hydroxyl was proportional to the content of curing agent and intramolecular hydrogen bonding showed adverse tendency with the content of curing agent. Carbonyl region was analyzed by curve fitting and the amount of hydrogen bonded carbonyl increased with the curing time and the content of curing agent.

Introduction

Epoxy resins have been widely used in the field of adhesive, matrix for advanced composite, protective coating material, electrical materials and so on. They have many advantages over common thermoset such as high mechanical properties, high electrical properties and good processibility. However, they are susceptible to thermal attack, so they cannot be used in the field which requires high thermal resistance. Therefore, many research groups have developed new high performance epoxy resin with high heat resistance(1-4).

Many studies about the characterization of the curing behavior of epoxy resin have been performed to analyze the curing mechanism of epoxy resin(5-12). Thermal analysis and spectroscopy were mainly used to characterize the curing mechanism of epoxy resin. Among these methods, FT-IR was very powerful to monitor the curing process by observing the change of functional group of epoxy. The degree of conversion was calculated by dividing the area of epoxy ring deformation peak with that of standard peak. However, few data were reported about the hydrogen bonding in epoxy resin in spite of the importance of the role of hydrogen bonding in determining the mechanical properties and curing behavior of epoxy resin. Bellenger et al.(5) and Harrod et al.(6)reported the hydrogen bonding of epoxy in the hydroxyl region. Some data were reported about the hydrogen bonding of epoxy when cured with anhydride curing agent. In recent years,

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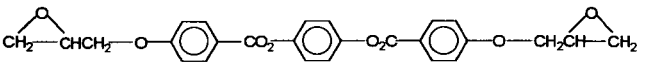
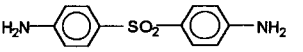


Liquid Crystalline Epoxy Resin



Diaminodiphenylsulfone (DDS)

Figure 1. Chemical structures of liquid crystalline epoxy resin and curing agent.

Carfagna et al.(7) observed the hydrogen bonding in liquid crystalline epoxy resin. In the previous paper(13), we reported the synthesis and physical properties of new liquid crystalline epoxy resin with high thermal stability to improve the heat resistance of the common epoxy resin. It showed glass transition temperature above 230 ℃ and its mechanical properties were excellent compared to the common epoxy resin. In this paper, we investigated the hydrogen bonding of liquid crystalline epoxy resin with aromatic mesogenic group as it plays a major role in determining the curing behavior of liquid crystalline epoxy resin. The peak change was monitored with the curing time and the content of curing agent. In addition the relationship between the amount of curing agent and the hydrogen bonding was examined.

Experimental

Synthesis of liquid crystalline epoxy resin

Synthesis of liquid crystalline epoxy resin was reported in the previous paper(13).

Curing of epoxy

Diaminodiphenylsulfone(DDS) was used as curing agent for the curing of epoxy resin. DDS was obtained by Aldrich Chemical Co. and it was used without purification. Liquid crystalline epoxy(LCE) resin was mixed with DDS in dichloromethane/acetone mixed solvent. After evaporation of the solvent at room temperature the mixture was dried perfectly in vacuum oven and stored at -10 ℃ to prevent the curing reaction of the mixture. Mole ratio of curing agent to LCE was varied with 0.25, 0.35 and 0.45. Each sample will be designated as EP5, EP7 and EP9 according to the content of curing agent. The mixture was cured at 180 ℃. Chemical structures of LCE and DDS are presented in Fig. 1.

Spectroscopic measurements

FT-IR(Bomem MB 100) was used to investigate the hydrogen bonding of LCE/DDS system. LCE/DDS samples were coated on the KBr pellet and they were analyzed after curing in the absorption mode. Resolution was 4 cm^{-1} and scanning number was 16.

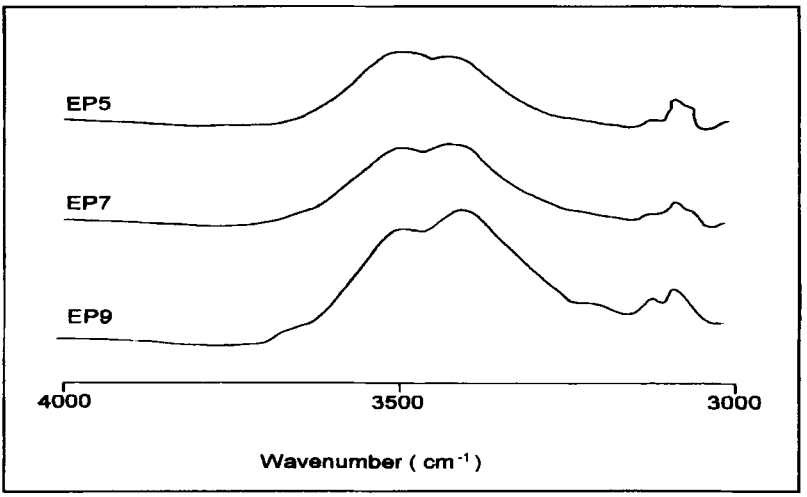


Figure 2. IR absorption spectra of hydroxyl region of cured LCE/DDS

Results and discussion

Fig. 2 shows IR spectra of LCE cured with DDS for 60 min at 180 ℃. This figure focuses on the hydroxyl region of the cured material. All samples exhibited intermolecular and intramolecular hydrogen bonding of the hydroxyl group in this region. The peak at 3400 cm^{-1} is related with the intermolecular hydrogen bonding of the hydroxyl group with amine and the peak at 3490 cm^{-1} is caused by the intermolecular hydrogen bonding between hydroxyl groups. The intensity of the peak at 3400 cm^{-1} tends to increase with increasing the amount of curing agent. This result can be expected as this peak is due to the hydrogen bonding between hydroxyl group in epoxy and amine group and between hydroxyl group and carbonyl group. 1° and 2° amine stretching peaks also appear in this region but these peaks cannot be investigated since they overlap with the hydrogen bonded hydroxyl peak. The peak at 3490 cm^{-1} is assigned to the hydrogen bonding between hydroxyl groups and is common in all samples and shows similiar shapes. Intermolecular hydrogen bonding between hydroxyl groups is attributed to the hydroxyl group produced by the curing reaction of epoxide ring with aromatic amine and the intensity of this peak increases as the curing reaction proceeds. Hydroxyl-hydroxyl hydrogen bonding peak appears at high wavenumber compared with hydroxyl-amine hydrogen bonding peak because the former is weaker than the latter. The bond dissociation energy of the former is known to be lower than the latter by about 2 kcal/mol(14). Intramolecular hydrogen bonding of the hydroxyl groups is displayed at 3550 cm^{-1} as a shoulder of the intermolecular hydrogen bonding peak in LCE/DDS. Intramolecular hydrogen bonding is clearly observed in EP 5 and its relative intensity decreases with increasing the content of curing agent. This behavior can be explained by considering the mechanism of intramolecular hydrogen bonding and degree of cure of the cured system. In

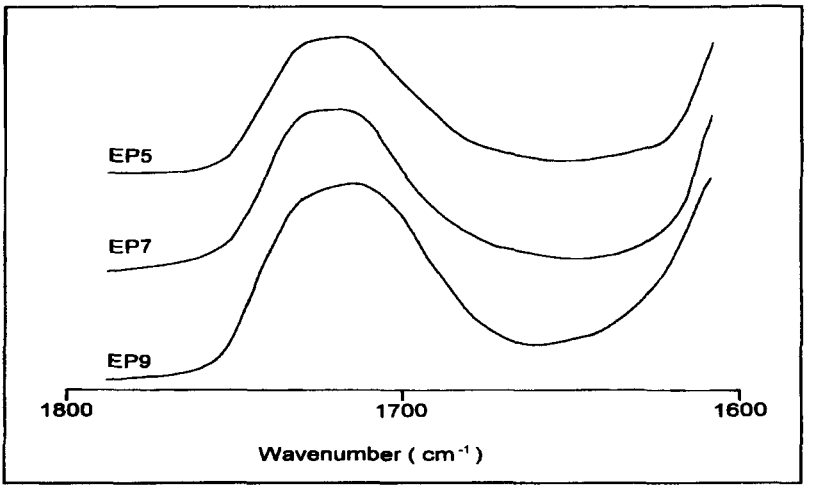


Figure 3. IR absorption spectra of carbonyl region of cured LCE/DDS

general, intramolecular hydrogen bonding can be observed in the neighborhood of the 3° amine because of the conformational restriction. Eight membered rings are mainly formed by the intramolecular hydrogen bonding though five membered rings are possible sometimes(5). Therefore, the probability of the intramolecular hydrogen bonding is directly proportional to the amount of 3° amine. In case of EP5 most amines exist as 3° amine, while considerable 2° amine coexists in EP 9. This leads to the relatively higher amount of intramolecular hydrogen bonding in EP 5 compared with in EP 9. In addtion, EP 9 has higher degree of cure than EP 5 and has more close packed strucure, which facilitates the intermolecular hydrogen bonding rather than intramolecular hydrogen bonding. Another peculiar peak is observed in this figure at 3650 cm^{-1}. This peak is assigned to the deformation of the free hydroxyl group which is not hydrogen bonded with other groups. It is attributed to the rigid rod character of the LCE molecule. Rigid mesogenic group mainly consists of ester unit and the rotational and translational motion of this unit is difficult by the conformational reason and interaction with the neighboring chain. Therefore, some hydroxyl groups remain as a free hydroxyl group and this phenomenon is prominent in EP 9 as chain motion is very restricted. From these results it can be concluded that in LCE/DDS system the amount of free hydroxyl group and hydrogen bonding with amine are proportional to the content of DDS and that of intramolecular hydrogen bonding is inversely proportional to the content of DDS.

Fig. 3 represents the carbonyl region of the IR spectrum for cured LCE/DDS system. The carbonyl peak is very broad since several peaks with different environment appear in this region. Free carbonyl, carbonyl hydrogen bonded with hydroxyl and carbonyl hydrogen bonded with amine coexist and all peaks are found in this region. Curve fitting result of carbonyl region is presented in Fig. 4. Free carbonyl peak is found at 1732 cm^{-1} and carbonyl peak hydrogen bonded

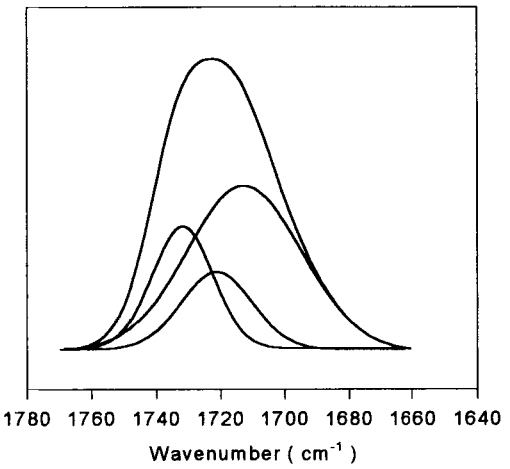


Figure 4. Curve fitting result of EP 7 in carbonyl region.

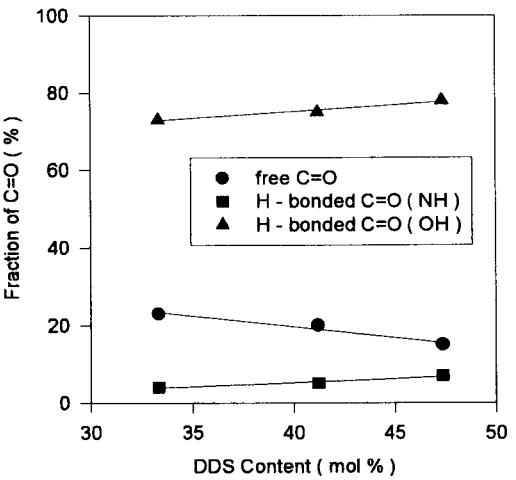


Figure 5. Calculated relative fraction of each carbonyl peak after curing according to the DDS content.

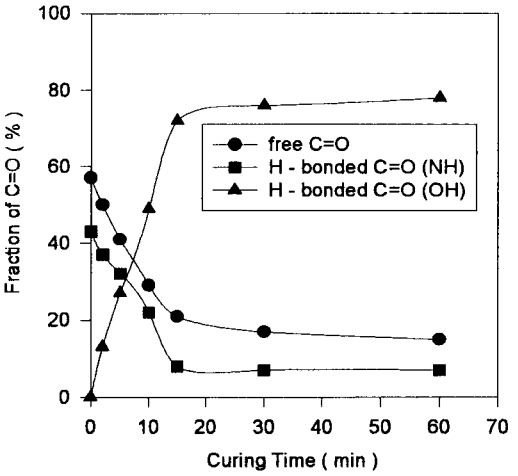


Figure 6. Calculated relative fraction of each carbonyl peak of EP 9 according to the curing time.

with amine is at 1720 cm^{-1} and carbonyl peak hydrogen bonded with hydroxyl is at 1712 cm^{-1}.

To measure the relative fraction of each peak, carbonyl region was deconvoluted and each peak area was calculated using curve fitting. Calculated data by this procedure are presented in Fig. 5. Most carbonyl group is hydrogen bonded with amine or hydroxyl group and only 20 % of the carbonyl goup is present as a free carbonyl group. The fraction of the hydrogen bonded carbonyl group is proportional to the content of curing agent and that of free carbonyl group is inversely proportional to the content of curing agent. This result is due to the fact that the more curing agent is present, the more hydroxyl group is produced and the more unreacted amine group is present. In other words, curing agent plays a role in providing hydrogen bonding site and increases the hydrogen bonding with the carbonyl group.

To investigate the change of the carbonyl peak, it was analyzed according to the curing time. Relative fraction of the carbonyl peak in EP 9 is represented in Fig. 6. The fraction of free carbonyl peak and carbonyl peak hydrogen bonded with amine tends to decrease with the curing time and that of the carbonyl peak hydrogen bonded with hydroxyl group increases with the curing time and relative fraction of each peak was kept almost constant after 30 min curing. The carbonyl hydrogen bonded with hydroxyl group is not found before curing as there is no hydroxyl group in LCE synthesized in this experiment. The fraction of the carbonyl peak hydrogen bonded with hydroxyl group increased with increasing the

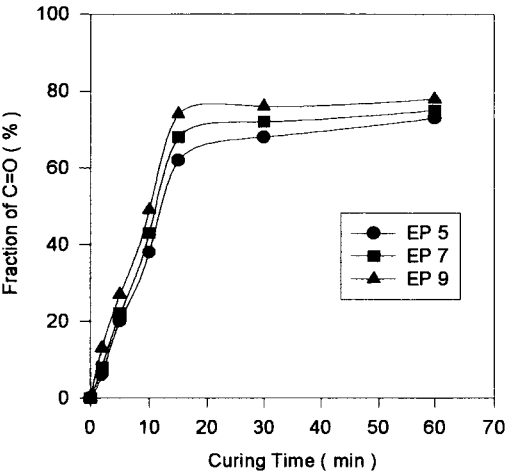


Figure 7. Calculated relative fraction of the carbonyl hydrogen bonded with hydroxyl group according to the curing time.

curing time because more hydroxyl group was produced by the curing reaction of epoxide ring with amine.

The relative fraction of the carbonyl hydrogen bonded with hydroxyl group is presented in Fig. 7 according to the curing time. EP 5 and EP 9 showed similiar tendency with the curing time, but the change was fast in the case of EP 9 compared with EP 5. This indicates that the curing reaction of EP 9 is faster than that of EP 5. This result is consistent with the fact that curing is fast in the system with high content of curing agent. The rather high faction of the carbonyl hydrogen bonded with hydroxyl group in EP 9 reveals that the degree of cure is proportional to the amount of curing agent.

Conclusion

The curing behavior of LCE/DDS system was investigated using FT-IR. As the content of DDS increased, free hydroxyl and hydroxyl hydrogen bonded with amine also increased, while intramolecular hydrogen bonding decreased. The fraction of free carbonyl and carbonyl hydrogen bonded with amine decreased considerably with the curing time due to the curing reaction of epoxide ring with amine. The curing reaction of EP9 was faster than that of EP5 and the fraction of hydrogen bonded carbonyl was proportional to the content of DDS. Most carbonyl groups were hydrogen bonded with hydroxyl group irrespective of the content of DDS and the fraction of free carbonyl was only 20 % after 60 min curing at 180 ℃.

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