[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 11, No. 9 (2001)

Azomethine 기를 가지는 신소재 액정 에폭시 (LCE)와 지방족 아민의 경화반응

김 상 욱†
서울시립대학교 화학공학과

Curing Reaction of Noble Liquid Crystalline Epoxy (LCE) with Azomethine/Aliphatic Amine

S.W. Kim †
Department of Chemical Engineering, The University of Seoul, Seoul 130-743

(2001년 7월 30일 받음, 2001년 8월 30일 최종수정본 받음)

Abstract α,ω-Bis(4-glycidyloxybenzylidene-4-aminophenyl)methane (BGBAM) was synthesized from the initial materials, 4-hydroxylbenzaldehyde (HBA), 4,4′-methylenedianiline (MDA) and epichlorohydrin. The DSC trace for BGBAM shows two endotherms associated with the liquid crystalline phase transition around 104.2℃ and the isotropic transition around 171.2℃, and it also has a broad exotherm in the range of 178~300℃ due to the anionic homopolymerization of BGBAM. DSC curve for the curing of BGBAM with hexamethylene diamine (HMD) shows an endothermic peak around 93℃ attributed to the melting of BGBAM. It also has three exothermic peaks around 128.4℃ and 180.2℃ associated with the epoxide-amine reaction and weak peak in the range of 200~263℃ related to the anionic homopolymerization between the unreacted epoxide groups. The activation energy values of cure reaction by Kissinger method are 66.5, 67.3 and 90.6 kJ/mol for T_{p1}, T_{p2} and T_{p3}, respectively. The kinetic parameters by isoconverional method are similar value to those from Kissinger method.

Key words : liquid crystalline epoxy, Kissinger method, isoconversional method, cure kinetics, azomethine

1. Introduction

High performance polymers have been developed recently, such as high modulus fibers and self-reinforced molded articles, as a direct result of increasing knowledge for structure-process-property relationships. Oriented materials have been produced as the result of two emerging technologies: the modification of conventional polymers and the design of rod-like liquid crystalline polymers (LCPs), both of which result in the extending application of LCPs.[1,2] Liquid crystalline polyphenyleneterephthalamide, commercialized by Du Pont under the trade name of Kevlar (ultra high modulus fiber) is the first example of the practical application of the LCPs. The liquid crystalline copolyesters Xydar produced by Dartco and Vectra by Celanese have very high tensile strength, stiffness and impact strength. The thermal expansion coefficient of these polymers is significantly lower than that of conventional polymers. Therefore the shrinkage of molded parts is negligible.[3,4]

Recently, ordered networks have become the subject of intensive research in the field of liquid crystal polymer materials.[5~8] This can partly be attributed to the fact that, although main-chain LCPs have excellent properties such as mechanical, thermal and optical properties, dimensional stability, etc., these properties in the transverse direction are rather poorer than those in the orientational direction. These problems can be overcome by the introduction of crosslinks between the main chains, which improves the dimensional stability of these ordered systems. Also, from the scientific point of view, ordered networks provide many new challenges, like the theoretical description of the mechanical deformation of such materials. Because of their high strength, dimensional stability and easy molding process, liquid crystalline thermosets (LCTs) will be used as replacements for complex shapes, metals and ceramic parts in the electronic, aerospace and other industrial applications. However, it is necessary to conduct the systematic studies to optimize the cure condition and to

† All correspondences should be addressed.

find out the relationship between structure and property for the final industry applications. So, many techniques and expressions have been proposed to investigate the cure kinetics, and differential scanning calorimetry (DSC) analysis is most important tool with the assumption that the exothermic heat of the cure reaction is proportional to the monomer conversion.[9~11]

All kinetic studies start with the rate equation, $\frac{d\alpha}{dt}$ which is written as the product of a composition-dependent term, $f_1(\alpha)$ and a temperature-dependent term, $f_2(T)$:

$$\frac{d\alpha}{dt}=f_1(\alpha)\cdot f_2(T) \quad (1)$$

The $f_1(\alpha)$ is expressed as

$$f_1(\alpha)=(1-\alpha)^n \quad (2)$$

where, n is reaction order. The $f_2(T)$ has been found in practical all cases to be well represented by Arrhenius' law :

$$f_2(T)=k=k_0 \exp\left(-\frac{Ea}{RT}\right) \quad (3)$$

where k is the Arrhenius rate constant, k_0 is pre-exponential factor, Ea is activation energy and R is the universal gas constant. For nonisothermal conditions, when the temperature varies with time with a constant heating rate, HR=dT/dt, Eq(1) is represented as follows :

$$\frac{d\alpha}{dT}=\frac{k_0}{HR}\exp\left(-\frac{Ea}{RT}\right)(1-\alpha)^n \quad (4)$$

In order to calculate the kinetic parameters, many derivative modes by Kissinger, Ozawa, Flynn & Wall, etc. have been proposed, and here, Kissinger and Flynn & Wall modes are used.[12~15]

The Kissinger method is expressed as followings :

$$-\ln\frac{HR}{T_p^2}=\frac{Ea}{R}\cdot\frac{1}{T_p}-\ln\left[n(1-\alpha_p)^{n-1}\cdot\frac{k_0R}{Ea}\right] \quad (5)$$

where T_p and α_p are the temperature and conversion at the maximum conversion rate $\left(\frac{d\alpha}{dt}\right)_p$, respectively. The Ea value can be easily calculated from the slope of the straight line for $-\ln\frac{HR}{T_p^2}$ as a function of $\frac{1}{T_p}$. The y-intersection of the plot is

$$I=-\ln\left[n(1-\alpha_p)^{n-1}\cdot\frac{k_0R}{Ea}\right] \quad (6)$$

To obtain n value, k_0 of Eq.(6) is substituted to Eq.(4) and arranged for n as follows:

$$n=\frac{(1-\alpha_p)\cdot Ea\cdot[\exp(-I)]\cdot\exp(-Ea/RT_p)}{HR\cdot R\cdot(d\alpha_p/dT_p)} \quad (7)$$

Finally, the k_0 value can be calculated from Eq.(6) when the n value is known by Eq.(7).

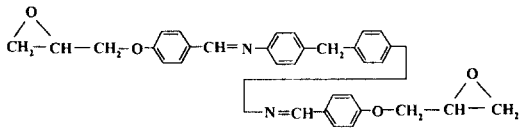
Flynn & Wall method is expressed as follows :

$$-\ln HR=\frac{Ea}{R}\cdot\frac{1}{T}-\ln\frac{k_0Ea}{R}+f_1(\alpha) \quad (8)$$

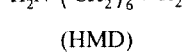
The Ea value can be calculated from the straight line of $-\ln HR$ against $\frac{1}{T}$ and k_0 from the y-intersection for a fixed conversion. There is no need to know the n value to calculate other kinetic parameters.

2. Experimental

A new liquid crystalline epoxy (LCE) with azomethine was α,ω-bis[4-glycidyloxy-benzylidene-4-aminophenyl]methane (BGBAM), which was synthesized as presented in the results and discussion section and an aliphatic curing agent was hexamethylenediamine (HMD, m.p=41℃) supplied by Junsei Chem. Co., Ltd. Their chemical structures are :



(BGBAM)



(HMD)

The mixture of BGBAM and HMD at the molar ratio of 1 to 1 was obtained by the following procedure: 1.5 g of BGBAM was put into about 10 ml of tetrahydrofuran and heated until a clear solution was obtained. The solution was cooled to 30℃, and a stoichiometric weight of HMD was added and stirred for about 5 min. Then the solvent was removed and dried in vacuum oven at room temperature for 48 h. The mixtures were stored at 13℃.

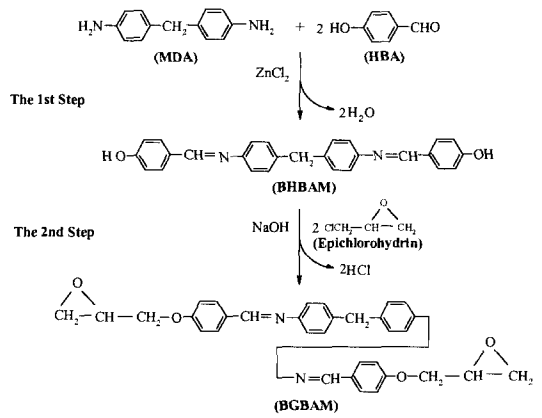
Dynamic DSC analysis was carried out in order to study cure kinetics by Kissinger and Flynn & Wall methods. The aluminum pan containing about 3 mg of the mixed sample was placed in DSC cell and it was heated at the constant heating rates from the room temperature to 300℃. The heating rates were 3, 5, 10 and 20℃/min under nitrogen purge gas flowing at 20 ml/min.

3. Results and Discussion

LCE monomer, BGBAM was synthesized by the following procedures as shown in Scheme I: 4-Hydroxylbenzaldehyde (HBA) 60 mmol and 4,4′-methylenedianiline (MDA) 30 mmol were reacted in ethyl alcohol 50 ml with $ZnCl_2$ catalyst at reflux temperature for 3 h. The aldehyde of HBA reacts readily with the arylamine of MDA giving an intermediate known as imine or Schiff base[16] with a water molecule as shown in the 1st step. This reaction is reversible, that is, the imine converts back to the aldehyde and amine. So, the water molecule should be distilled off from the reactants.

The intermediate α,ω-bis[4-hydroxybenzylidene-4-aminophenyl]methane (BHBAM) was recrystallized in 95% ethanol and it was converted into the BGBAM by the reaction with excess epichlorohydrin at base condition.

General DSC response for LCE monomer gives us a useful clue to characterize the phase transitions and Fig. 1 shows a dynamic DSC curve for the synthesized BGBAM at constant heating rate of 10℃/min. The DSC trace shows two endotherms and two exotherms. The endotherm around 104.2℃ is associated with liquid crystalline phase transition from solid crystal phase to smectic phase, which was confirmed by polarized optical microscope (POM) in a hot-stage as shown in Fig. 2. The other endotherm around 171.2℃ is for isotropic transition from smectic phase to isotropic liquid phase. And, the first exotherm is shown in the broad range of 178~300℃ whose maximum peak value is at 238.3℃, which is due to the homopolymerization of LCE monomer. And the second exotherm is sharp peak at 300~336℃, which is associated with the thermal decomposition of covalent bonding. The homopolymerization of



Scheme I. Synthesis of BGBAM and its structure.

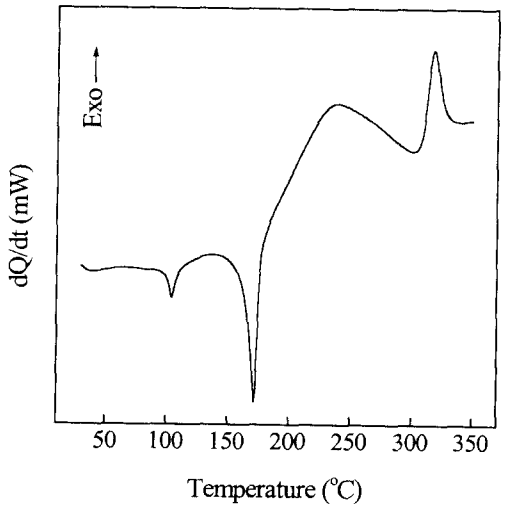


Fig. 1. Dynamic DSC curve for BGBAM at heating rate of 10℃/min.

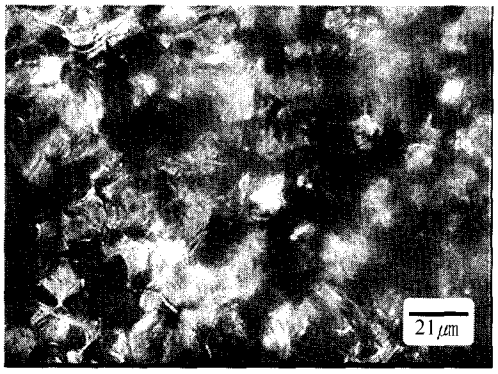


Fig. 2. Smectic birefringent pattern for BGBAM at 125℃.

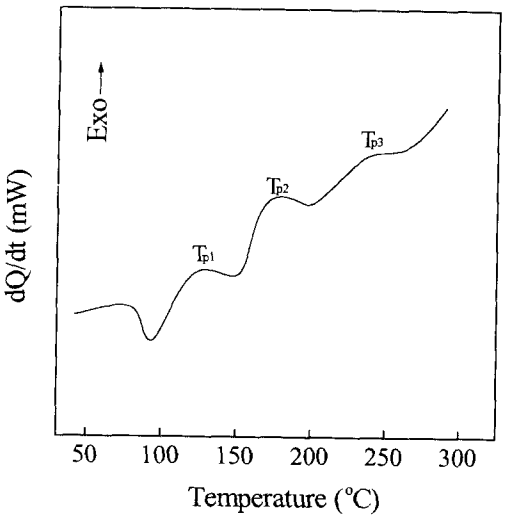


Fig. 3. Dynamic DSC curve for BGBAM/HMD system at 10 ℃/min.

the epoxide group with azomethine group is explained by the anionic polymerization.[17] The homopolymerization is initiated by the formation of a zwitterion with an azomethine cation and an alkoxy anion, and the anionic polymerization proceed until termination take

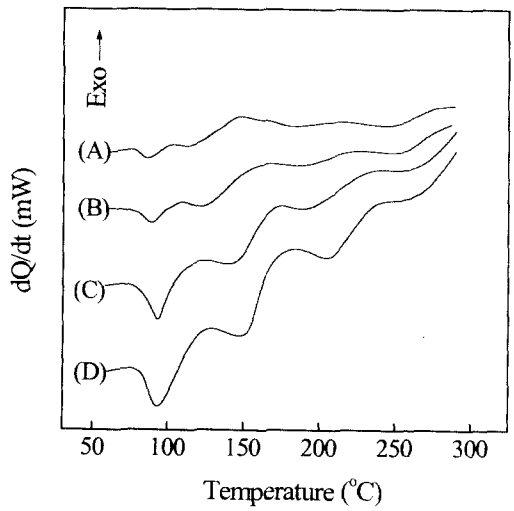


Fig. 4. Dynamic DSC curves for BGBAM/HMD system at various heating rates. Heating rate : (A) 3℃/min, (B) 5℃/min, (C) 10℃/min and (D) 20℃/min.

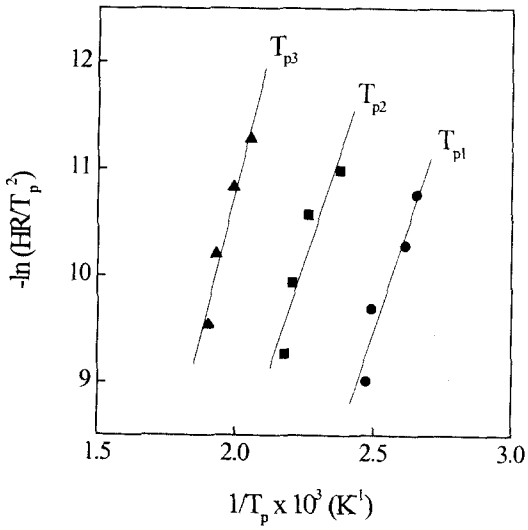


Fig. 5. Kissinger plots for three exothermic peaks.

place by the elimination of the azomethine from the end product, giving rise to a double bond and hydroxyl group.

Fig. 3 shows dynamic DSC curve for BGBAM cured with HMD at heating rate of 10℃/min. It contains an endothermic peak and three exothermic peaks followed by an exotherm overlapped with decomposition range over 263℃. The endothermic peak around 93℃ is attributed to the melting of BGBAM. The 1st exothermic peak around 93~150℃ centered at 128.4℃ and the 2nd around 150~200℃ centered at 180.2℃ are separated by the isotropic transition temperature as shown in Fig. 1. The two exothermic peaks are associated with the cure reaction of epoxide groups with primary or secondary amine groups. The 3rd weak exothermic peak in the range of 200~263℃ is related to the anionic homopolymerization between the unreacted epoxide

Table 1. Kissinger Relationship between Tp and HR for BGBAM/HMD System.

HR (℃/min)	T_{p1} (K)	T_{p2} (K)	T_{p3} (K)
3	376.6	421.0	486.9
5	382.6	441.7	501.9
10	401.5	453.3	518.1
20	404.6	458.7	525.6

Table 2. Kinetic Parameters for BGBAM/HMD System by Kissinger Method.

Parameter	Peak Temperature		
	T_{p1}	T_{p2}	T_{p3}
Ea (kJ/mol)	66.5	67.3	90.6
n	2.3	2.1	1.4
$k_0(10^8 min^{-1})$	1.6	6.1	15.9

groups with azomethine group.[17]

Fig. 4 shows dynamic DSC curves for BGBAM/HMD system at four different heating rates and all curves show the similar pattern to that of 10℃/min. To study the cure kinetics by Kissinger method, the temperature, T_p for each peak and heating rate, HR obtained from the curves of Fig. 4 are listed in Table 1. These data are introduced to the Kissinger equation (5) and the linear relationships are shown in Fig. 5. The linear equation for each peak is expressed as follows :

$$-\ln \frac{HR}{T_{p1}^2} = 8.0 \times \frac{1}{T_{p1}} - 10.5 \quad \text{(1st exothermic peak)}$$

$$-\ln \frac{HR}{T_{p2}^2} = 8.1 \times \frac{1}{T_{p2}} - 8.0 \quad \text{(2nd exothermic peak)}$$

$$-\ln \frac{HR}{T_{32}^2} = 10.9 \times \frac{1}{T_{p3}} - 11.1 \quad \text{(3rd exothermic peak)}$$

The activation energy values of cure reaction are calculated from the slopes, and those for T_{p1} and T_{p2} are 66.5 kJ/mol and 67.3 kJ/mol, respectively which means that the cure mechanism of the 1st and 2nd peaks are similar. In the initial stage of the 1st exotherm is mainly caused to the reaction between a primary amine and an epoxide ring with forming a hydroxyl group and as curing reaction proceeds, the hydroxyl group acts as a catalyst in other primary amine-epoxide reaction and secondary amine-epoxide reaction in the last state of the 1st exotherm and the whole of the 2nd exotherm. However, that for T_{p3} is 90.6 kJ/mol, which is rated to the anionic homopolymerization of the residual epoxide and this value is far higher than those of the T_{p1} and T_{p2}. The higher the activation energy is, the difficult cure reaction is.

Table 3. Kinetic Parameters for BGBAM/HMD System by Isoconversional Method.

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Ea(kJ/mol)	72.4	72.5	65.8	64.1	63.2	65.7	67.9	78.5	88.9	98.2
$k_0(10^8 min^{-1})$	1.4	1.8	4.2	6.6	5.0	5.9	7.2	10.8	11.9	15.1

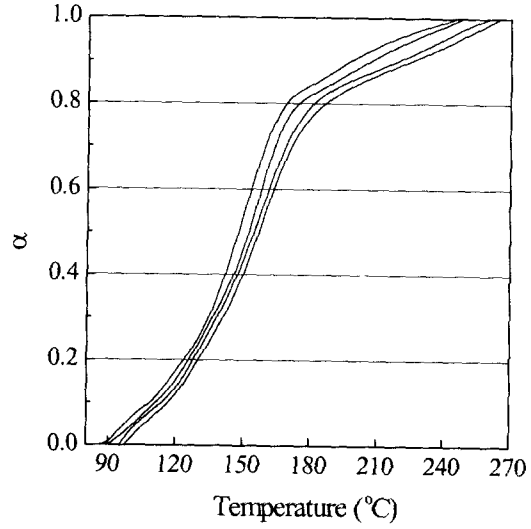


Fig. 6. Conversion and temperature curves for BGBAM/HMD system.

To calculate the reaction order, n for each peak, the y-intersection value is substituted to Eq.(7) and the calculated n value is introduced to Eq.(6) to get pre-exponential factor, k_0. These values are listed in Table 2 with the activation energy of cure reaction.

Fig. 6 shows the conversion curves at four heating rates for BGBAM/HMD system, which is obtained from integrating the DSC curves in Fig. 4 in order to investigate the cure kinetics by isoconversional method. The isoconversional temperatures are obtained from the four conversion curves at a selected conversion, and the relationship between $1/T \times 10^3$ and $-\ln(HR)$ is expressed as a straight line to estimate activation energy and pre-exponential factor for each selected conversion. Each slope is corresponding to Ea/R (Eq.8) and pre-exponential factor is calculated from the y-intersection. Table 3 shows the kinetic parameters by isoconversional method. As the conversion increases, activation energy increased, and the high activation energy means the difficult cure reaction. In the initial stage, noncatalytic cure reaction between epoxide group and primary amine group is the main reaction, which generates a hydroxyl group as an autocatalyst. As the cure reaction proceeds, the autocatalyst acts on the cure reaction between other epoxide and primary or secondary amine. Therefore, the activation energy decreases with increasing conversion until $\alpha=0.5$. But, it increases after that conversion due to the increasing diffusion restriction cause of the high viscosity and the formation of LC domains. The kinetic parameters by isoconversional method are similar value to those from Kissinger method.

4. Conclusions

α,ω-Bis(4-glycidyloxybenzylidene-4-aminophenyl) methane (BGBAM) was synthesized and DSC analysis was performed. The DSC trace for BGBAM shows two endotherms and one exotherm. The endotherm around 104.2℃ is associated with liquid crystalline phase transition from solid crystal phase to smectic phase and the other endotherm around 171.2℃ is for isotropic transition from smectic phase to isotropic liquid phase. And, the exotherm shown in 178~300℃ is due to the homopolymerization of BGBAM. The homopolymerization of the epoxide group with azomethine group is explained by the anionic polymerization. Dynamic DSC curve for BGBAM cured with hexamethylene diamine (HMD) contains an endothermic peak and three exothermic peaks followed by an exotherm overlapped with decomposition range over 263℃. The endothermic peak around 93℃ is attributed to the melting of BGBAM. The 1st exothermic peak centered at 128.4℃ and the 2nd centered at 180.2℃ are associated with the cure reaction of epoxide groups with primary or secondary amine groups. The 3rd weak exothermic peak in the range of 200~263℃ is related to the anionic homopolymerization between the unreacted epoxide groups. The activation energy values of cure reaction by Kissinger method are 66.5, 67.3 and 90.6 kJ/mol for T_{p1}, T_{p2} and T_{p3}, respectively. In isoconversional method, as the cure reaction proceeds, the activation energy decreases with increasing conversion until $\alpha=0.5$ due to the autocatalytic role of hydroxyl group acted on the cure reaction between epoxide and primary or secondary amine. But, it increases after that conversion due to the increasing diffusion restriction cause of the high viscosity and the formation of LC domains. The kinetic parameters by isoconverional method are similar value to those from Kissinger method.

Acknowledgement

This work was supported by The University of Seoul Research Fund (2000).

References

1. J.E. Mark, "Physical Properties of Polymers Handbook", AIP Press, New York, Ch.33 (1996).
2. J.Y. Lee, J. Jang, S.M. Hong, S.S. Hwang and K.U. Kim, Polymer, **40**, 3197 (1999).
3. US Pats., 3,869,429 and 3,869,430, H. Blades (E. I. Du Pont de Nemouers & Co., Inc.) (1975).
4. T.S. Chung, Polym. Eng. Sci., **26**, 901 (1986).
5. P.G. Higgs and R.C. Ball, Macromolecules, **22**, 2432 (1989).
6. S.M. Aharoni and S.F. Edwards, Macromolecules, **22**, 3361 (1989).
7. M. Warner and X.J. Wang, Macromolecules, **24**, 4932 (1991).
8. W. Mormann and C. Kuckerlz, Macromol. Chem. Phys., **199**, 845 (1998).
9. M.G. Lu, S.W. Kim and M.J. Shim, Korea Polym. J., **7**, 304 (1999).
10. J.Y. Lee, M.J. Shim and S.W. Kim, Thermochimica Acta, **371**, 45 (2001).
11. J.Y. Lee, M.J. Shim and S.W. Kim, J. Mater. Sci., **35**, 3529 (2000).
12. T. Ozawa, Bull. Chem. Soc. JPN, **38**, 1881 (1965).
13. J.H. Flynn, J. Therm. Anal. **27**, 95 (1983).
14. X.G. Li and M.R. Huang, Polymer Degradation and Stability, **64**, 81 (1999).
15. J.Y. Lee, M.J. Shim and S.W. Kim, Mater. Chem. Phys., **44**, 74 (1996).
16. S.N. Ege, "Organic Chemistry", D.C. Heath and Company, (1984) p385.
17. W. Mormann and M. Brocher, Macromol. Chem. Phys., **199**, 1935 (1998).