[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 7, No. 3 (1997)

열중량 분석에 의한 DGEBA/MDA/PGE-AcAm/CTBN계의 열적 안정성 평가

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Estimation of Thermal Stability for DGEBA/MDA/PGE-AcAm/CTBN System by TG Analysis

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(1996년 12월 30일 받음, 1997년 2월 1일 최종수정본 받음)

초 록 Diglycidyl ether of bisphenol A(DGEBA)/4,4′-methylene dianiline(MDA)/phenyl glycidyl ether(PGE)-acetamide(AcAm)/carboxyl-terminated acrylonitrile butadiene copolymer(CTBN) 계의 열적 안정성을 평가하기 위해 열중량 분석법(TG)을 사용하였다. 활성화 에너지를 구하기 위해 Freeman & Carroll, Kissinger, Flynn & Wall 식을 사용하였다. Freeman & Wall 식을 이용하여 구한 활성화 에너지는 112.9 kJ/mol, Kissinger 식에 의한 값은 151.5 kJ/mol 이었으며, Flynn & Wall 식에 의해 구한 값은 168.3 kJ/mol이었다.

Abstract Estimation of thermal stability for diglycidyl ether of bisphenol A(DGEBA)/4,4′-methylene dianiline (MDA)/phenyl glycidyl ether(PGE)-acetamide(AcAm)/carboxyl-terminated acrylonitrile butadiene copolymer (CTBN) system was studied by thermogravimetry(TG) analysis. To get activation energy for thermal degradation, Freeman & Carroll, Kissinger, and Flynn & Wall expressions were used. The activation energy of Freeman & Wall expression was 112.9 kJ/mol, that of Kissinger expression was 151.5 kJ/mol and that of Flynn & Wall was 168.3 kJ/mol.

1. Introduction

With the increasing demands for polymer materials in power plant, electrical insulation, high temperature applications, etc., many researchers have studied the techniques and expressions to estimate the thermal stability of polymer components[1~8]. Many thermoanalytical methods such as thermogravimetry(TG), differential scanning calorimetry(DSC) and differential thermal analyzer(DTA) were employed and many expressions proposed by Freeman & Carroll[2,5,7], Kissinger[1,7], Flynn & Wall[1,3,5], Ozawa[4,5], Toop[6], Friedman[8], etc. were used. From these expressions and techniques, high quality kinetic data and lifetime were obtained.

In this study, the thermal stability of the epoxy system modified with carboxyl-terminated acrylonitrile butadiene copolymer(CTBN) was studied by Freeman & Carroll equation, Kissinger equation and Flynn & Wall equation, and the thermal degradation kinetics was compared. Freeman & Carroll equation[2,5,7] is

$$-\frac{\Delta \ln(dw/dt)}{\Delta \ln W_r} = \frac{Ea}{R}\frac{\Delta T^{-1}}{\Delta \ln W_r} - n \qquad (1)$$

where, dw/dt : rate of weight loss, W_r : weight of residue, Ea : thermal degradation activation energy, R : gas constant, T^{-1} : inversion of absolute temperature and n : reaction order. Activation energy of thermal degradation can be calculated from the slope of $-\frac{\Delta \ln(dw/dt)}{\Delta \ln W_r}$ vs. $\frac{\Delta T^{-1}}{\Delta \ln W_r}$.

Kissinger equation[1,7] is

$$Ea = -R\frac{d(\ln \beta/T_m^2)}{d(T_m^{-1})} \qquad (2)$$

where, T_m is the temperature at the maximum reaction rate.

Flynn & Wall equation[1,3,5] is

$$Ea = \frac{-R}{0.457}\frac{d(\log \beta)}{d(T^{-1})} \qquad (3)$$

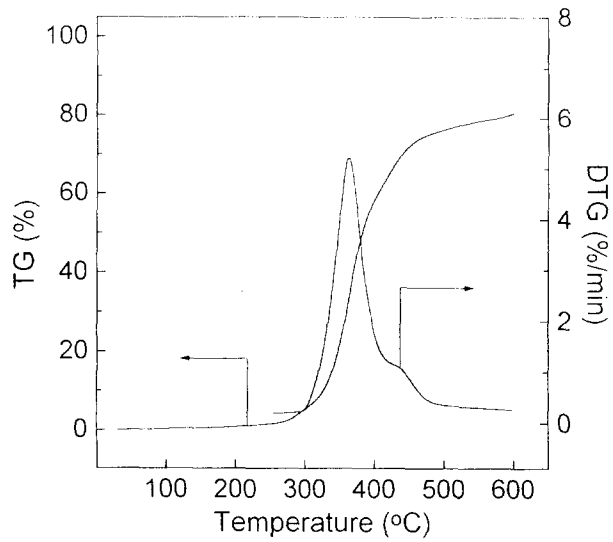

Fig. 1. TG and DTG curves for DGEBA/MDA(30 phr)/PGE-AcAm(10 phr)/CTBN(20 phr) system at the heating rate of 5℃/min.

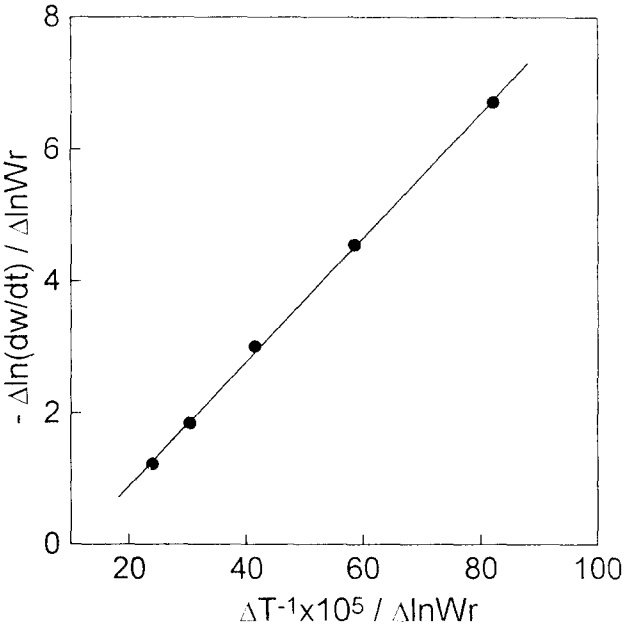

Fig. 2. Evaluation of activation energy through Freeman and Carroll equation for DGEBA/MDA(30 phr)/PGE-AcAm(10 phr)/CTBN(20 phr) system.

where, β is heating rate. From these three expressions, activation energies were obtained, respectively and the values were compared.

2. Experiment

Diglycidyl ether of bisphenol A(DGEBA) type epoxy resin supplied by Shell Co., a trade name of Epon 828 was used as a base resin and 4,4′-methylene dianiline (MDA) was as a amine curing agent. Synthesized phenyl glycidyl ether(PGE)-acetamide(AcAm) was introduced as a reactive additive and carboxyl-terminated acrylonitrile butadiene copolymer(CTBN) supplied by Goodrich as a trade name of Hycar 1300×8 was used as a toughner.

Table 1. Activation Energy for DGEBA/MDA/PGE-AcAm(10 phr)/CTBN(20 phr) at Different Heating Rates through Freeman & Carroll Equation.

Heating Rate (℃/min)	5	10	15	20
Activation Energy (kJ/mol)	96.7	112.2	129.7	113.1

DGEBA, PGE-AcAm(10 phr) and CTBN(20 phr) were well-mixed at 80℃ for 20 min and 30 phr of MDA was added, and this mixture was cured at 150℃ for 1hr after curing at 80℃ for 1.5hr[9~11]. To analyze the thermal degradation characteristics of the cured sample, TG analysis was carried out at the heating rate of 5, 10, 15 and 20 ℃/min. Nitrogen gas flowed at 80 ml/min to prevent the oxidation of the sample.

3. Results and Discussion

The typical TG and derivative thermogravimetry (DTG) curves for the epoxy system at a heating rate of 5 ℃/min were shown in Fig.1. On the TG curve, the sample was almost stable below 265℃ and the weight loss increased rapidly in the short temperature range of 265~483℃ due to the gasification of degraded low molecules. The total weight loss at 600℃ was 80.5%. On the DTG curve, the weight loss occurred at one stage and one shoulder appeared at some high temperature. T_m, the temperature at which maximum degradation rate appeared was 362.3℃. The TG and DTG data in Fig.1 were introduced into Freeman & Carroll expression(Eq.1) and the relationship between $-\Delta\ln(dw/dt)/\Delta\ln Wr$ and $\Delta T^{-1}\times 10^5/\Delta\ln Wr$ was plotted in Fig.2 with the assumption that the rate of degradation reaction was proportional to the rate of weight loss[1~5,12]. Activation energy was obtained from the slope of the straight line and the value was 0.144(Ea/R), so the activation energy of the epoxy system was 96.7 kJ/mol. By the same method, activation energies at different heating rates were calculated and the data were listed on Table 1. The average value was 112.9 kJ/mol and some difference was shown according to the heating rate. It may be because of the change of degradation mechanism due to the change of heat exposuring time on the sample.

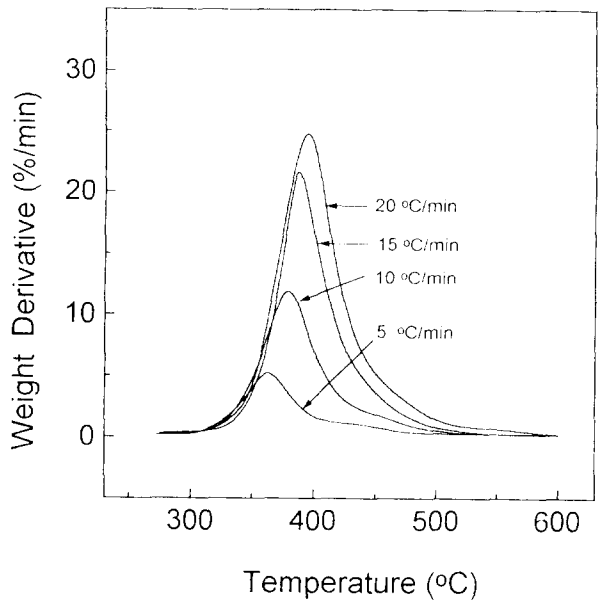

Fig. 3. DTG curves for DGEBA/MDA(30 phr)/PGE-AcAm(10 phr)/CTBN(20 phr) system at various heating rates.

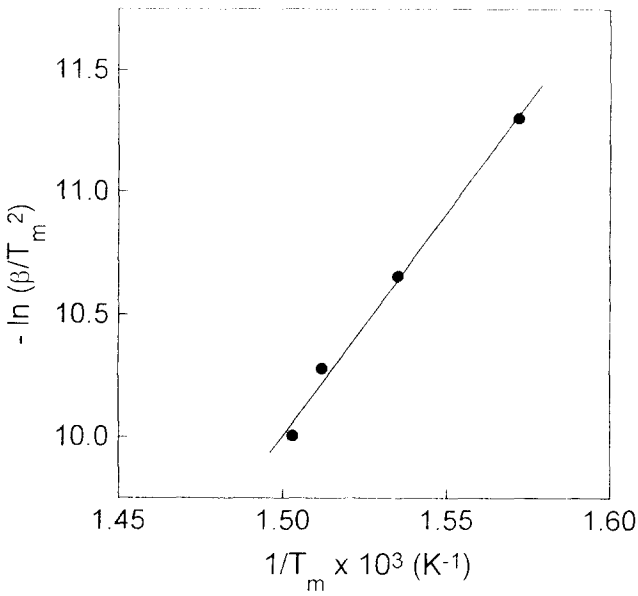

Fig. 4. Kissinger plots for DGEBA/MDA(30 phr)/PGE-AcAm (10 phr)/CTBN(20 phr) system.

To get activation energy by Kissinger expression(Eq. 2), DTG curves at four heating rates were displayed in Fig. 3. All curves showed that weight loss took place in one stage regardless of different heating rates, and the degradation rate rapidly increased in the initial stage until the maximum value, and after that point the degradation rate decreased. T_m values increased and DTG values at T_m increased with the increment of heating rate and and a shoulder at about 450℃ disappeared at 15 and 20 ℃/min. From the DTG curves, T_m at each heating rate β was obtained and the relationship between $-\ln\beta/T^2_m$ and $\frac{1}{T_m} \times 10^3$ was plotted in Fig.4. Activation energy was obtained from the slope of the straight line. The value was 18.16(Ea/R), so activation energy was 151.5 kJ/mol, which was some higher value about 40 kJ/mol than that of Freeman & Carroll expression. The difference of the activation energy between two methods was due to the different experimental procedure.

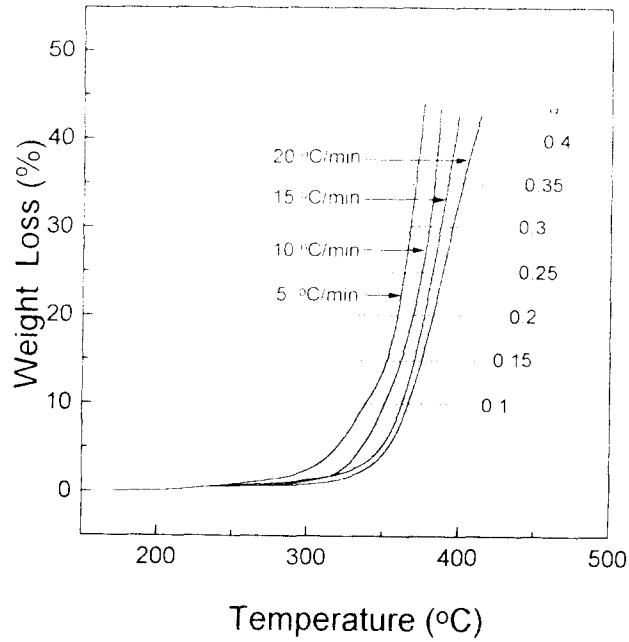

Fig. 5. TG curves for DGEBA/MDA(30 phr)/PGE-AcAm(10 phr)/CTBN(20 phr) system at various heating rates.

While Kissinger equation was very simple and easy method to get relatively exact activation energy, it did rely upon the peak temperatures to be known with a great deal of accuracy. However, it's very unfortunate that to get exact peak temperature was very difficult because the data usually had the least sensitivity due to the endotherms or exotherms associated with the weight loss process. So, the activation energy obtained from the other method should be compared with that obtained from Kissinger energy, and isoconversional method proposed by Flynn & Wall was used to compare. Flynn & Wall expression had the advantage that activation energy could be obtained at each degradation conversion.

Fig. 5 showed TG curves for DGEBA/MDA/PGE-AcAm(10 phr)/CTBN(20 phr) system at four different heating rates. With the increment of heating rate, the curve shifted to high temperature as shown in the DTG curves and decomposition temperatures, Td were 338.0 ℃, 356.5 ℃, 366.4 ℃, and 367.8 ℃ at 5, 10,

Table 2. $\log\beta$ and $\frac{1}{T}\times10^3$ of DGEBA/MDA/PGE-AcAm(10 phr)/CTBN(20 phr) for Flynn & Wall Expression.

$\log\beta$	$1/T\times10^3(K^{-1})$						
	α=0.1	0.15	0.2	0.25	0.3	0.35	0.4
0.699	1.659	1.624	1.606	1.591	1.580	1.567	1.557
1.000	1.611	1.587	1.570	1.555	1.544	1.533	1.523
1.176	1.584	1.566	1.554	1.541	1.530	1.521	1.510
1.301	1.575	1.555	1.539	1.526	1.514	1.503	1.495

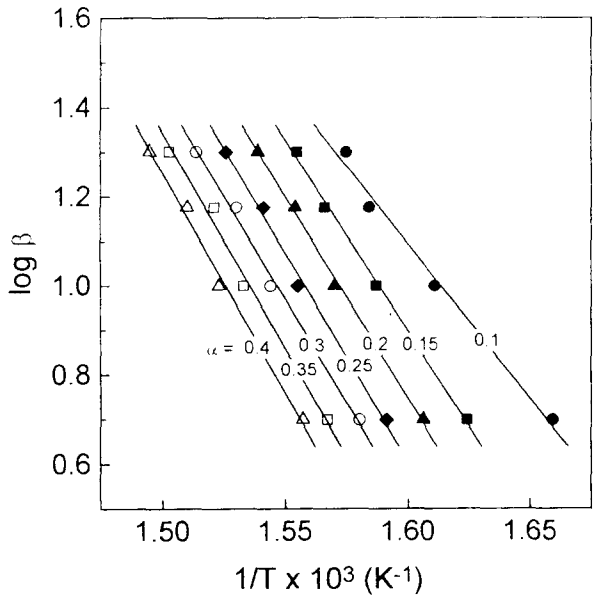

Fig. 6. Isoconversional plots for DGEBA/MDA(30 phr)/PGE-AcAm(10 phr)/CTBN(20 phr) system at various α.

15 and 20 ℃/min, respectively. The temperatures at a fixed conversion were measured at the cross points of dotted lines and the thermal curves of different heating rates, and the $\log\beta$ and $\frac{1}{T}\times10^3$ were listed on Table 2. Because taking the values too early on the curves was affected by volatilization of the some low molecules(e.g. moisture), so the fixed conversions were selected from 0.1 to 0.4 as shown in Fig. 5. A series of straight lines created from the relationship between $\log\beta$ and $\frac{1}{T}\times10^3$ on Table 2 was plotted in Fig.6 and the activation energies were calculated from the slopes(-0.457 Ea/R). If the sample degradation mechanism was the same at all conversion levels, all the slopes of the lines would be same. However, when the selected conversion was highered, the slope became steepered, so the activation energy was increased with the increment of degradation conversion as shown in Fig.7. The average activation energy for the conversion of 0.1~0.4was 168.3 kJ / mol. As thermal degradation was proceeding, the molecules which were easily broken from the network structure of the epoxy system were volatile at low temperature, however with the increment of degradation conversion, the molecules which was stable to some high temperature was residual. So, the activation energy would be increased with the increment of conversion.

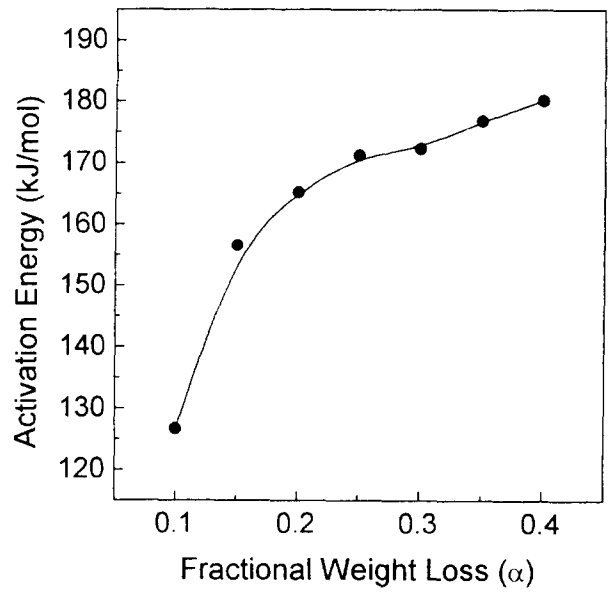

Fig. 7. Activation energy for DGEBA/MDA/PGE-AcAm(10 phr)/CTBN(20 phr) system through Flynn & Wall equation.

The order of activation energy obtained from three different expressions were Flynn & Wall(168.3 kJ/mol) > Kissinger(151.5 kJ/mol) > Freeman & Wall (112.9 kJ/mol). The values for Flynn & Wall equation and Kissinger equation had the same value, and Freeman & Carroll expression had a some low value.

4. Conclusions

From these results, the following conclusions were obtained.

1) At the heating rate 5 ℃/min, the epoxy system was almost stable below 265℃ and the weight loss increased rapidly in the short temperature range of 265~483℃.

2) In Freeman & Carroll equation, the value of activation energy was changed according to the heating rate and the average value was 112.9 kJ/mol.

3) In Kissinger equation, activation energy was 151.5 kJ/mol.

4) In Flynn & Wall equation, activation energy at different conversion was various and the average value was 168.3 kJ/mol.

Acknowledgement

This work was financially supported by Sun Kyong group.

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