

Cure Reaction of Epoxy Resin System with MN/HQ

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MN/HQ가 첨가된 에폭시 수지계의 경화반응 연구

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Abstract: We studied the cure kinetics of the DGEBA(Diglycidyl ether of bisphenol A)/MDA(4, 4'-methylene dianiline)/MN(Malononitrile)/HQ(Hydroquinone) system by Barrett method and Integral method with dynamic runs of differential scanning calorimetry(DSC). Kinetic parameters such as activation energy and pre-exponential factor were obtained and reaction order was estimated roughly supposing that present system was adjusted to n th order reaction. The MN(Malononitrile) was introduced as a chain extender and HQ(Hydroquinone) as a reactive accelerator or catalyst.

요 약: DGEBA(Diglycidyl ether of bisphenol A)/MDA(4, 4'-methylene dianiline)/MN(Malononitrile)/HQ(Hydroquinone)계의 경화 반응속도론을 differential scanning calorimetry(DSC)의 승온적 방법(dynamic runs)에 의해 Barrett method와 Integral method로 연구하였다. 활성화 에너지, pre-exponential factor와 같은 kinetic parameter들이 구하여 졌으며 반응 차수는 본계가 n 차 반응 속도식에 적용된다는 가정하에 추정되었다. MN(Malononitrile)은 본 반응의 사슬 연장제로, HQ(Hydroquinone)은 반응 가속제 또는 촉매로 도입되었다.

1. Introduction

We studied the reaction kinetics of epoxy cure by DSC(differential scanning calorimetry). The kinetic parameters have been determined from both isothermal and dynamic experimental data[1-3].

The epoxy cure reaction has sometimes been described by a simple n th order kinetics and autocatalytic expression.

2. Rate Expression

Various rate expressions have been proposed in the literature for the cure reaction of thermosets including epoxy.

n th order rate expression[4-5]

$$dx/dt = k(1-x)^n \quad (1)$$

where k is the rate constant, has been adopted to

describe cure kinetics.

For the reaction of epoxide and secondary amine hardeners a rate expression of Horie et al. is [6]

$$dx/dt = (k_1 + k_2x)(1-x)(B-x) \quad (2)$$

where k_1 and k_2 are rate constants and B is the initial ratio of epoxide to amine hydrogen equivalents.

To take into account the autocatalytic expression for many thermosetting systems, Kamal and Sourour suggested a generalized expression of [7]

$$dx/dt = (k_1 + k_2x^m)(1-x)^n \quad (3)$$

where m , n represent reaction orders.

Alternative expression is in the form of [8]

$$dx/dt = k(1+Cx^m)(B-x)^n \quad (4)$$

where C represents relative weighting for the autocatalytic part of the cure reaction which has also been proposed.

In general, the cure kinetics can be described by a rate law given by

$$dx/dt = kf(x) = Af(x)\exp(-E_a/RT) \quad (5)$$

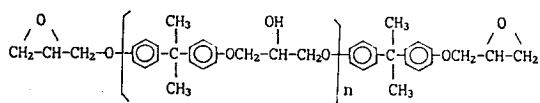
where $k (= A\exp(-E_a/RT))$ is the rate constant, A is the pre-exponential factor, E_a is the activation energy and $f(x)$ is an empirical function representing the conversion-dependent part of the rate expression.

With assumption that the rate equation of DGEBA/MDA/MN/HQ system was adjusted to n th order equation, cure kinetics of DGEBA/MDA/MN/HQ system was investigated by Barrett method and Integral method using DSC dynamic run.

3. Experiment

3.1. Materials

The Epoxy resin used was a commercial DGEBA (Diglycidyl ether of bisphenol A), EPON 828(Shell) with the following structure :



The Curing agent was MDA(4, 4'-methylene dianiline, m.p. 88~92°C). MN(malononitrile, m.p. 30~32°C) was used as a reactive additive and HQ (hydroquinone, m.p. 171~173°C) as a reactive accelerator or catalyst.

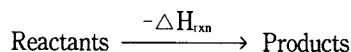
3.2. Method

DGEBA/MDA/MN/HQ system was prepared by mixing of DGEBA, MDA 30 phr and MN/HQ, where the ratio of MN: HQ was 4:1(5:1.25, 10: 2.5, 15: 3.75 and 20:5 phr).

Cure kinetics was estimated by dynamic runs carried out by DSC SEIKO I SSC-5000. Samples, contained in a closed pans, exactly 3mg in weight were scanned with different heating rates of 5, 10 and 20 °C/min in the range of 25 to 350 . The carrier gas was nitrogen at the flow rate of 50mL/min.

4. Results and Discussion

One of the common characteristics of thermosetting systems is the exothermic curing process.



Where ΔH_{rxn} is the heat of reaction.

The heat evolved during cure is proportional to the extent of reaction and the heat change in a reaction can be measured directly with DSC.

A typical differential enthalpic analysis curve given in Fig. 1 was obtained using the scanning calorimetry to evaluate the rate constants. The total area under the curve, A , corresponds to the total heat of reaction, ΔH_{rxn} , and the area, a , to the heat evolved up to certain temperature[9]. So that,

$$a/A = \Delta H / \Delta H_{rxn} = x \quad (6)$$

and

$$(dx/dt)_{DSC} = (dH/dt)_{DSC} / \Delta H_{rxn} \quad (7)$$

Where $(dx/dt)_{DSC}$ is the rate of heat generation, determined by DSC at any instant.

As mentioned above, the Barrett method and in-

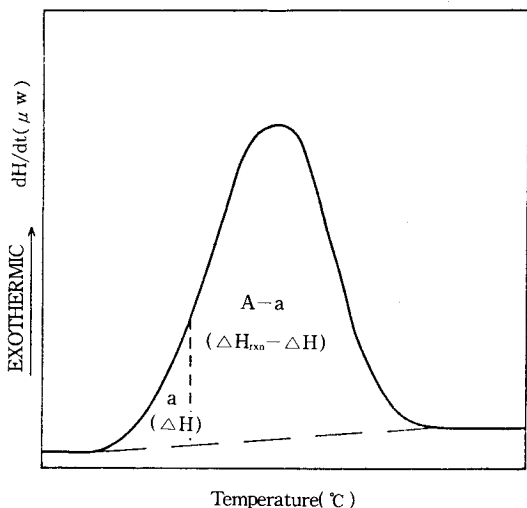


Fig. 1. Differential enthalpic analysis curve.

tegral method using the relationships of heat evolved and rate of heat generation with respect to a certain temperature are practical methods to obtain kinetic parameters.

4. 1. DSC Dynamic Run

The curing reactions of epoxy resins are highly exothermic. Fig. 2 is thermogram of DGEBA/MDA/MN/HQ system obtained at different heating rates using DSC dynamic run. The exothermic peak temperatures increased as heating rates increased with constant MN/HQ contents.

Fig. 3 shows exothermic peak temperatures decreasing with increasing MN/HQ contents at constant heating rates.

In case of the DGEBA/MDA/MN system without HQ, peak temperatures were constant regardless of MN contents. Therefore HQ should be served as a reactive accelerator or catalyst. In all cases, the hydroxyl groups generated during the reaction or provided by addition accelerated, the amine-glycidyl ether reaction remarkably[10].

4. 2. Barrett Method

The kinetics of the curing reaction was obtained from the DSC curve using the Barrett method. If the kinetic equation is written in terms of the con-

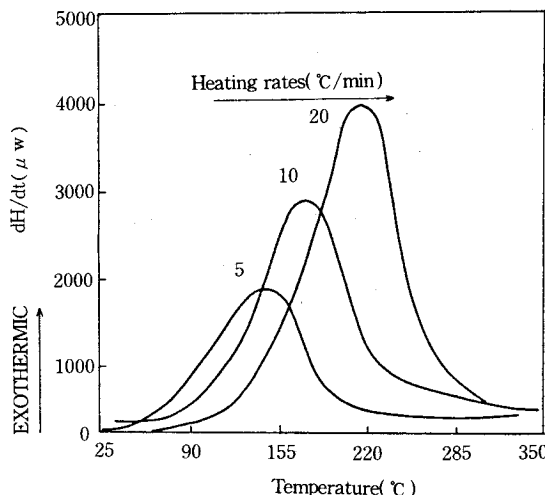


Fig. 2. Curing of the DGEBA/MDA/MN/HQ system using the dynamic run of the DSC at different heating rates(MN: HQ=10: 2.5 phr).

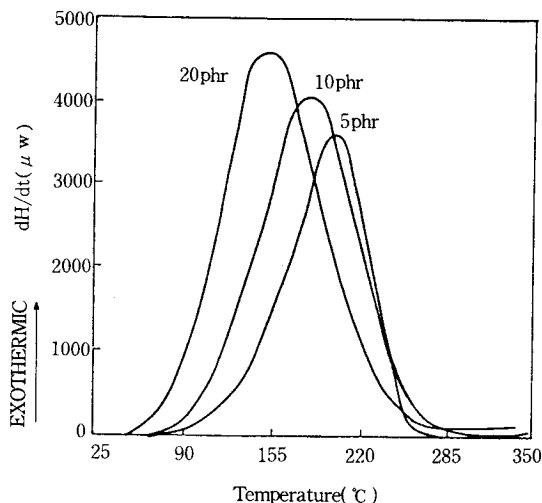


Fig. 3. Variation of peak temperature with different MN/HQ contents at constant heating rate 20 $^{\circ}C/min$.

version $x = \Delta H / \Delta H_{x_{no}}$, as

$$dx/dt = Af(x)\exp(-E_a/RT) \tag{8}$$

then

$$\ln[(dx/dt)f(x)] = \ln k = \ln A - E_a/RT \tag{9}$$

A plot of $\ln k$ vs. $1/T$ will be linear if $f(x)$ is se-

lected correctly. In that case, the activation energy could be calculated from the slope and pre-exponential factor, A, could be obtained from y-intersect.

$f(x)$ may be applied successfully with n th order kinetic expression. n , reaction order, have been determined by the experimental data using a linear least square fitting technique[11]. The overall reaction order(n) was too. The kinetics of epoxy-amine system have been found to be accurately decribed

by second order kinetic expression irrespective of temperature. At high catalyst concentrations, pseudo-second-order kinetics were observed[12, 13].

Fig. 4 shows plots of dynamic DSC run for $f(x) = (1-x)^2$ at three different heating rates. Increasing the heating rate leads to a lower pre-exponential factor, A, while the same activation energy with constant MN/HQ contents.

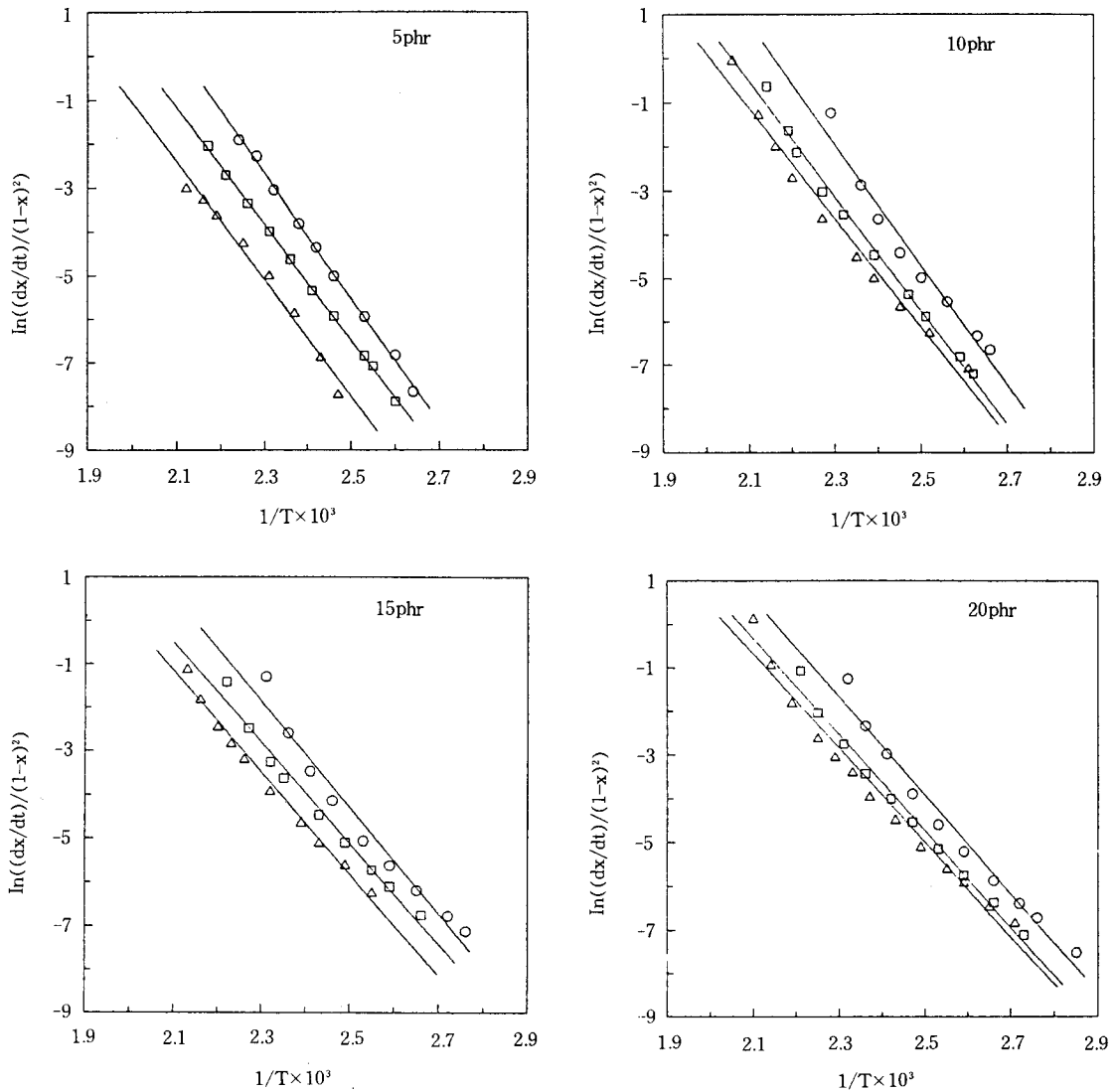


Fig. 4. Plots of dynamic DSC runs using Barrett method with different MN/HQ contents.

(○) 5°C/min, (△) 10°C/min, (◇) 20°C/min

4.3. Integral Method

Integral method[14] begins from following equation like Barrett method. As Barrett method uses both the rate dx/dt and the conversion x at every temperature, the integral method only needs the conversion.

$$dx/dt = Af(x)\exp(-E_a/RT) \quad (8)$$

defining $q = dT/dt$ as constant heating rate,

$$\int_x^0 dx/f(x) = A/q \int_{T_0}^T \exp(-E_a/RT) dT \quad (10)$$

Where $f(x)$ is $(1-x)^2$. By substituting $Z = E_a/RT$, $dZ = -Z^2 R/E_a dT$, equation (10) becomes

$$x/(1-x) = -AE_a/Rq (\text{°C/min}) \int_{Z_0}^Z [\exp(-Z)/Z^2] dZ \quad (11)$$

For $Z > 15$ which the actual curing range, integral

$$F(Z) = -\int_0^Z [\exp(-Z)/Z^2] dZ \quad (12)$$

may be approximate as[15]

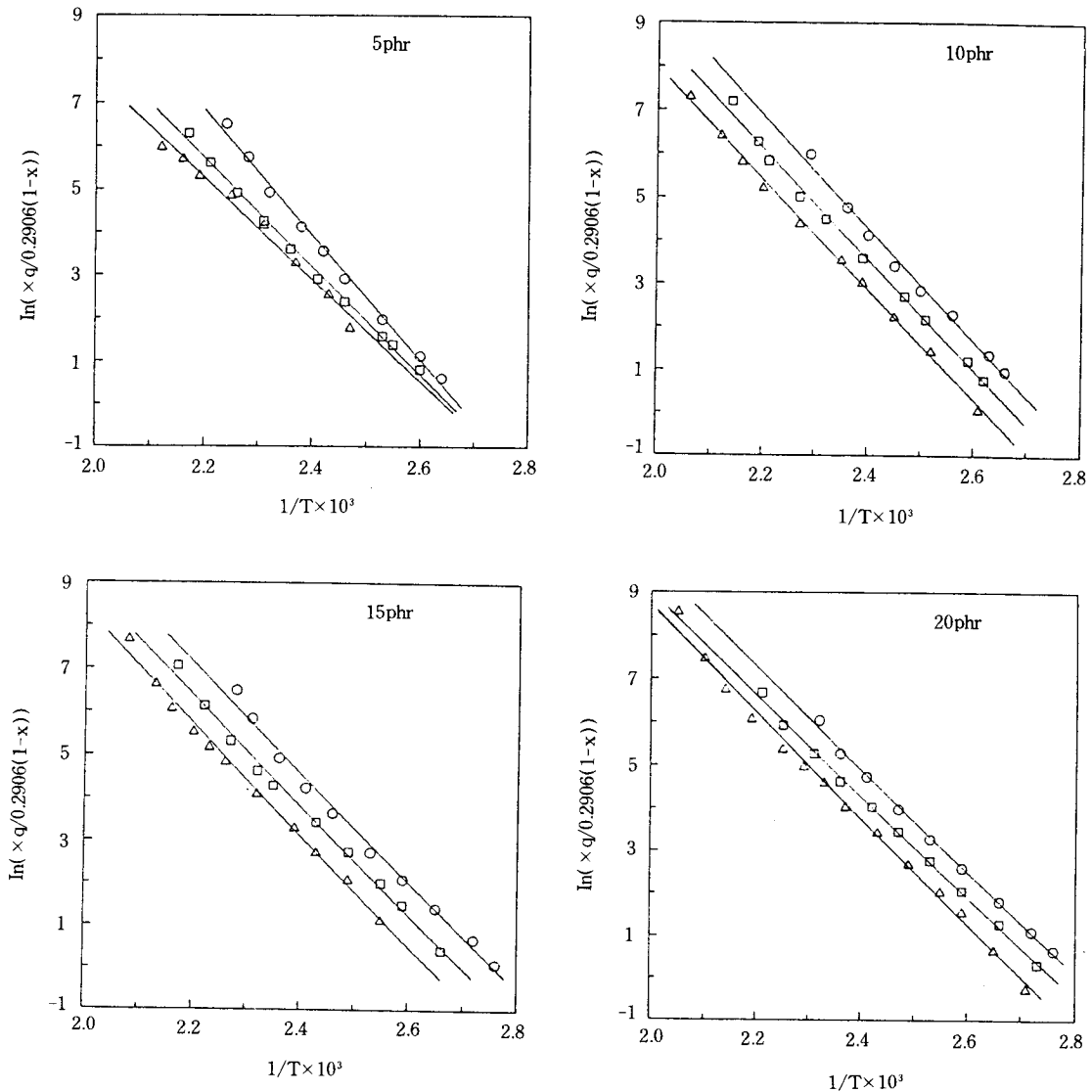


Fig. 5. Plots of dynamic DSC runs using Integral method with different MN/HQ contents.

(○) 5°C/min, (△) 10°C/min, (◇) 20°C/min

$$\ln F(Z) = -5.330 - 1.0516Z \quad (13)$$

then

$$\ln [xq/0.2906(1-x)] = -1.0516E_a/RT + \ln AE_a/R \quad (14)$$

Activation energy E_a and A was obtained by plotting equation (14). Fig. 5 shows plots of dynamic DSC runs by integral method with the experimental x vs. T results at different heating rates.

If equation (14) was transformed into $y=ax$,

equation (14) can be rearranged to the following form.

$$\ln [xq(\text{°C/min})/0.2906A(E_a/R)(1-x)] = -1.0516(E_a/R)/T \quad (15)$$

Fig. 6 shows plots of equation (15) at three different heating rates, conforming the reasonable accuracy of the proposed second order kinetic equation.

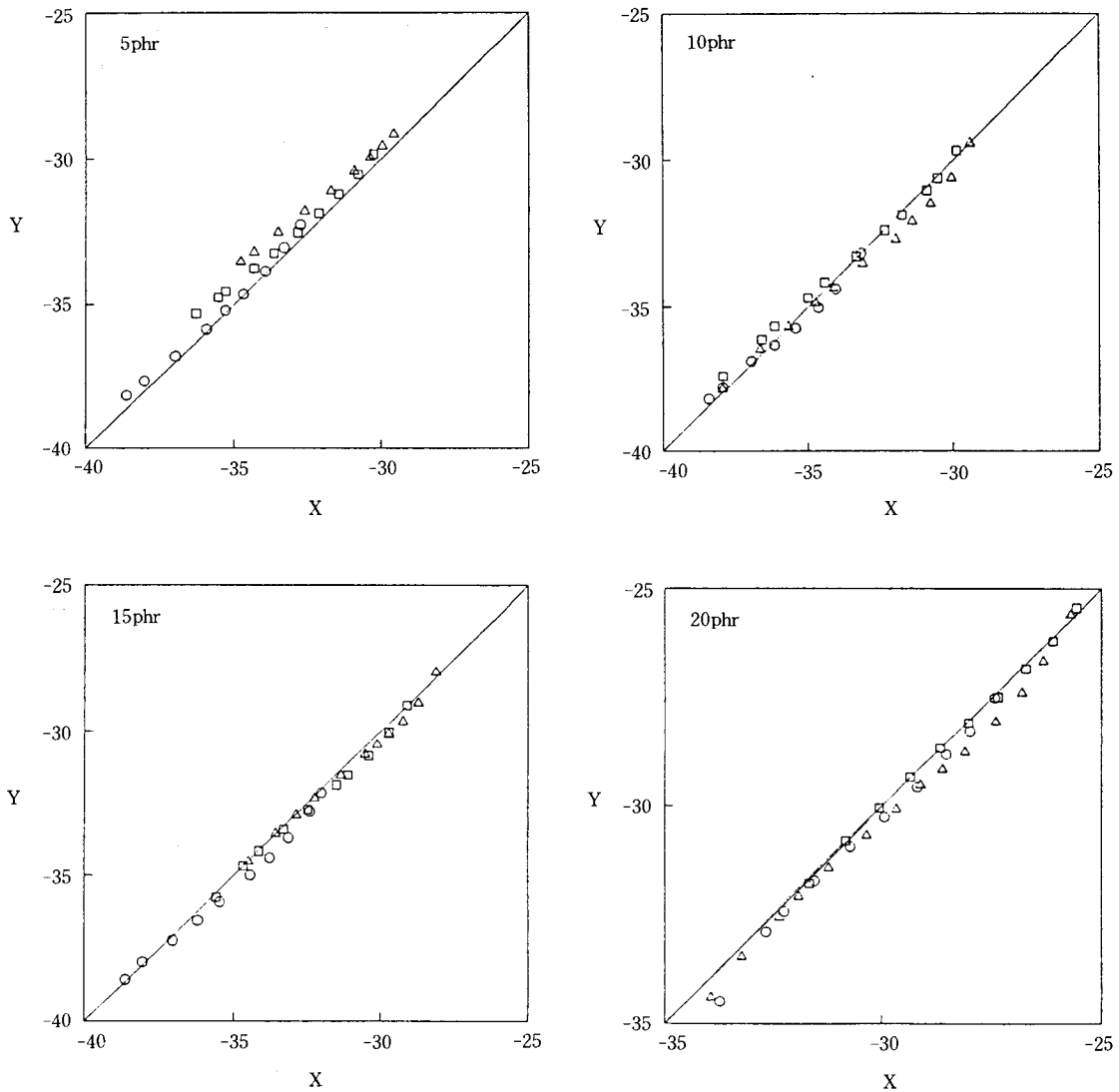


Fig. 6. Verification of the second order kinetic equation using Barrett method and Integral method with different MN/HQ contents: $Y = [xq(\text{°C/min})/0.2906A(E_a/R)(1-x)]$, $X = -1.0516(E_a/R)/T$.
 (○) 5°C/min, (△) 10°C/min, (◇) 20°C/min

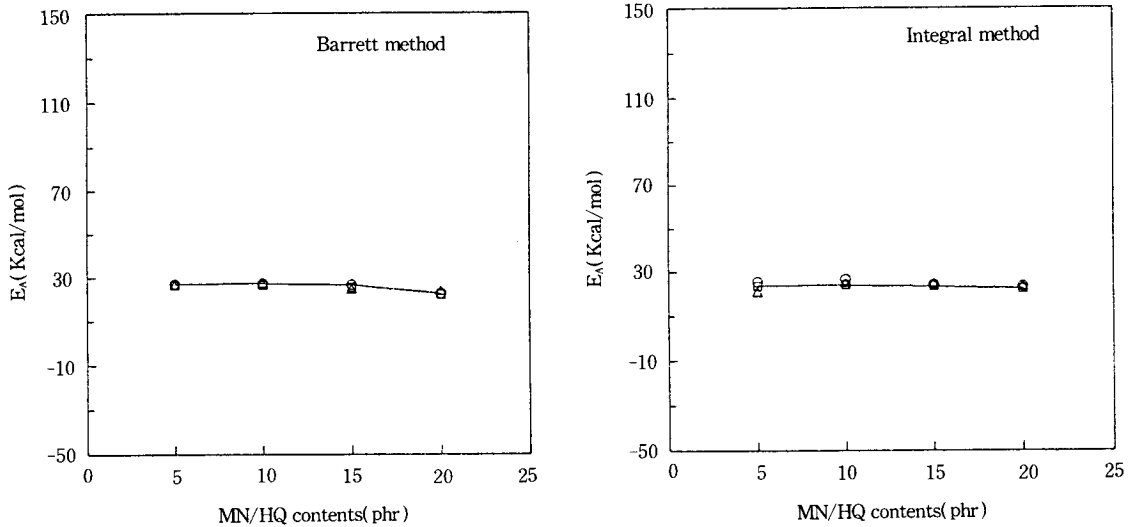


Fig. 7. Activation energy with different MN/HQ contents by Barrett method and Integral method. (○) 5°C/min, (△) 10°C/min, (◇) 20°C/min

Fig. 7 shows variation of activation energy values with different MN/HQ contents respectively. E_a values for the present system has been observed to increase then decrease with MN/HQ contents. In case of Barrett method, E_a values are in the range of 22 to 27Kcal/mol, Integral method are 21 to 26Kcal/mol. It is estimated that kinetic parameters obtained by the method presented here were larger when compared to values obtained from Kissinger equation[16] as followed equation (16).

The peak exothermal temperature varies with the heating rate(see Fig. 2). Kissinger equation is based on the relationship between heating rate and peak exothermal temperature.

Kissinger equation expressed for the pre-exponential factor for n th order reactions follows that

$$A = \frac{qE_a \exp[E_a/RT_p]}{RT_p^2 [n(1-x)^{n-1}]} \approx \frac{qE_a \exp[E_a/RT_p]}{RT_p^2} \quad (16)$$

It is considered that great difference of E_a and A between two method above mentioned was caused by that Kissinger equation was by definition for first-order reaction and that the method using present system consistently overestimated kinetic parameters[1]. Another shortcoming of Kissinger

equation is the requirement of an assumed reaction order[1].

The activation energy of the present system was lower than those of DGEBA/MDA/MN system without HQ(see Fig. 8).

Consequently, we could estimate that HQ served

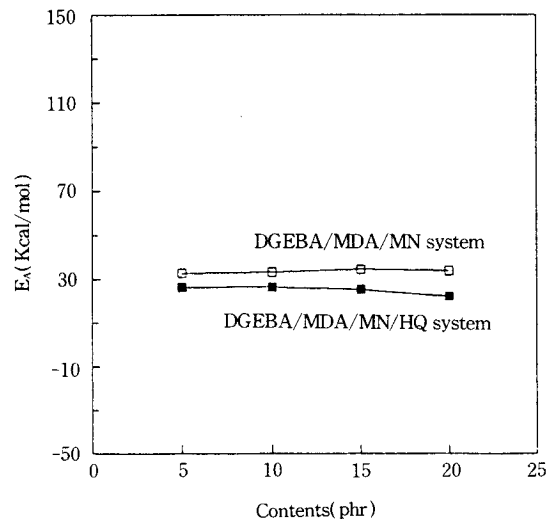


Fig. 8. Activation energy of DGEBA/MDA/MN/HQ system compared with DGEBA/MDA/MN system at heating rate 10°C/min.

as a reactive accelerator and lowered the activation energy in cure reaction.

5. Conclusion

The Barrett method and Integral method were appropriate to estimate the kinetic parameters, activation energy and pre-exponential factor of DGEBA/MDA/MN/HQ system.

Curing behavior was described with dynamic DSC curves and overall reaction order was too in the assumption that this present system was adjusted n th order reaction.

When HQ (hydroquinone) was added, both of the reaction starting temperature and the activation energy were lowered than DGEBA/MDA/MN system without HQ. For that reason, We convinced that HQ served as a reactive accelerator or catalyst.

Acknowledgement

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