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Vitrification effect on the curing reaction of epoxy resin

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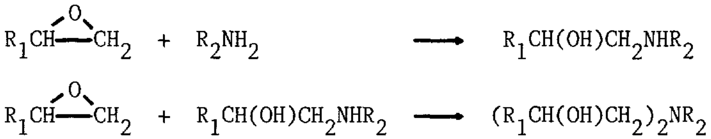
SUMMARY

The curing reaction of diglycidyl ether of Bisphenol A(DGEBA) with triethylene tetramine(TETA) was studied by the differential scanning calorimetry(DSC). The reaction was affected as the vitrification occurred when the glass transition temperature(T_g) of the reaction mixture exceeded the curing temperature. In order to describe the curing reaction in the rubbery state as well as in the glassy state, the reaction kinetic equation containing the generalized WLF equation term was proposed and the parameters were determined from the DSC data.

INTRODUCTION

The curing reaction of epoxy resin usually involves the reaction of oxirane group of the epoxy resin and the amine group of the polyamine. The major reaction mechanism with the polyamine has been proposed as follows(1,2);



$$R_1CH\overset{O}{\frown}CH_2 + R_2NH_2 \longrightarrow R_1CH(OH)CH_2NHR_2$$

$$R_1CH\overset{O}{\frown}CH_2 + R_1CH(OH)CH_2NHR_2 \longrightarrow (R_1CH(OH)CH_2)_2NR_2$$

Both gelation and vitrification occur during the curing reaction(3,4), the gelation occurring when the reaction product forms a three dimensional network, and the vitrification occurring when the liquid or rubbery reacting mixture is transformed into the glassy state as the molecular weight increases. Near the vitrification point, T_g of the partially cured reaction mixture reaches the curing temperature and the reaction is retarded due to the immobilization of the network segments. Gillham et al. have introduced the time-temperature-transformation(TTT) cure diagram(5-7) which is a plot of the time required to reach gelation and vitrification during the isothermal cure. In order to describe the relation between the reaction rate and the change of the physical state, they derived the reaction kinetic equation containing viscosity term.

In this study, a reaction kinetic equation is derived which can describe the change of the reaction rate at both glassy and rubbery state during the curing process of epoxy resin.

THEORY

In order to examine the change of the reaction rate during the vitrification process, the relationship between the glass transition temperature(T_g) and the conversion(X) of the partially cured reacting

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mixture must be derived. There have been some published results(8-11) about the relationship and Adabbo et al.(11) proposed the following Di Benedetto's equation(12);

$$\frac{T_g - T_{go}}{T_{go}} = \frac{(E_x/E_m - F_x/F_m)X}{1 - (1 - F_x/F_m)X} \qquad (1)$$

where T_{go} is T_g of the unreacted material, E_x/E_m is the ratio of the lattice energies for crosslinked and uncrosslinked polymer, and F_x/F_m is the corresponding ratio of segmental mobilities and is a function of the distance between the crosslink points. Several experimental T_g vs. X relationships have been reported with values of F_x/F_m between 0. to 1.0(5,11).

For the curing reaction of thermosetting polymers having high T_g, the reaction rate is dependent on the difference between the T_g of the reaction mixture and the curing temperature, $T-T_g$. When T_g exceeds the curing temperature during the reaction so that $T-T_g$ becomes less than zero, the reactants are converted into the glassy solid and the reaction is retarded because of the low diffusional mobility(13).

The curing reaction of the epoxy resin is exothermic and is assumed to be a simple n-th order reaction with Arrhenius temperature dependence(14,15). The kinetic equation can be written as follows;

$$\frac{dX}{dt} = A_T \exp(-E/RT)\,(1-X)^n \qquad (2)$$

where A_T is a temperature dependent frequency factor, and X is the conversion. For the reaction kinetics controlled by the intermolecular segment motion, a proper relation for A_T can be expressed as follows using the generalized WLF form(16,17);

$$\ln A_T = \ln A_{Tg} + \frac{A\,(T - T_g)}{B + |T - T_g|} \qquad (3\text{-}A)$$

where A_{Tg} is the temperature dependent frequency factor at T_g and A and B are the empirical constants.

The WLF equation describes the molecular mobility of amorphous polymer in the temperature range above T_g. In order to describe polymer relaxation responses, in temperatures above and below T_g by a single equation, a modified form of the WLF equation was introduced as follows(16);

$$\log a_T = \log \frac{t(T)}{t(T_o)} = - \frac{C_1\,(T-T_o)}{C_2 + |T-T_o|} \qquad (3\text{-}B)$$

where t(T) and $t(T_o)$ are the polymer relaxation times at temperature T and reference temperature T_o, C_1 and C_2 are empirical constants, and a_T is the time-temperature shift factor. The generalized WLF equation(3-B) is based on the extension of the free volume concept to the temperature below T_g. The available free volume is assumed to control the molecular mobility both in the liquid region above T_g and also in the glassy state well below T_g. Rusch analyzed the published experimental time-temperature shift factors, a_T from various sources and reported that the plot of $\log(1/a_T)$ for PMMA and polystyrene in both temperature ranges(16,18) show sigmoidal forms. The Eq.(3-B) agrees well with the experimental $\log(1/a_T)$ data in both temperature ranges while the classical WLF equation can be applied only in temperature range above T_g. So the generalized WLF form can be related as the frequency factor to the kinetic equation in order to represent the change of the intermolecular segment motion near the vitrification point during the curing reaction.

In order to understand the chemorheological phenomena of the curing of thermosetting polymers like the epoxy resin, chemical reaction thresholds and rheological transition must be explained. The chemical reaction threshold may be related to $T-T_g$ (the vitrification point) and the rheological transition is related to T_g. The vitrification occurs when T_g of the reactant is equal to the curing temperature(3-7), but the reaction does not stop exactly at the vitrification point. Thus the chemical reaction threshold does not exactly coincide with the vitrification point. With decreasing the difference, $T-T_g$, the reaction rate decreases sigmoidally with abrupt decrease near T_g. So the temperature dependent frequency factor must include the generalized WLF equation in order to correlate the chemical reaction and vitrification point as follows;

$$\ln A_T = \ln A_{To} + \frac{A\,(T - T_g + D)}{B + |T - T_g + D|} \qquad (4)$$

where A_{To} is the temperature dependent frequency factor at $T_o (= T_g - D)$ and the correction parameter, D, is characteristic of the chemical system and can be varied with the chemorheological properties of the reaction system.

RESULTS AND DISCUSSION

The materials used in the experiment are shown in Table 1. The epoxy resin and the curing agent are diglycidyl ether of bisphenol A(DGEBA) and triethylene tetramine(TETA), same as the previous work(19). The conversion at time t was assumed as the ratio of the cumulative heat generated up to time t, H_t, to the heat of reaction at complete conversion, H_{RXN}, from the DSC thermogram.

$$X = H_t \,/\, H_{RXN} \qquad (5)$$

Table 1.
Materials

	Descriptions	Source
Epoxy resin	Diglycidyl ether of bisphenol A (YD -128) * epoxy equiv. 184 - 194 (g/eq.) * viscosity 11,000-14,000 (cps)	Kuk Do Chem.
TETA	Triethylene tetramine	Kuk Do Chem.

The T_g vs. X relationship was expressed using the Di Benedetto equation(9~12). Partially cured sample was obtained by rapid quenching of the DSC sample which was cured during the isothermal mode(10) and dynamic scanning mode. The T_g of the partially cured reacting mixture was

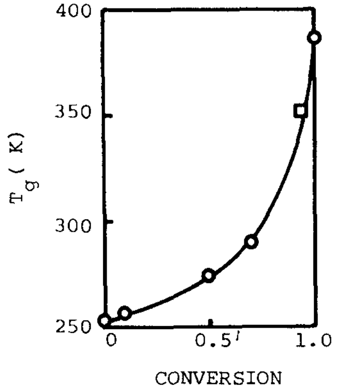

Figure 1. Glass transition temperature vs. conversion.
○ ; dynamic DSC result,
□ ; isothermal DSC result (60 °C, 9hr)
(solid line represents Di Benedetto's equation)

measured by DSC by heating under 10 °C/min. By measuring the residual heat of reaction in the quenched sample, the conversion attained during the partial curing could be calculated. Adabbo et al.(10) conducted the isothermal DSC experiment in the isothermal mode and reported that the measured T_g appeared at temperature 15 °C higher than the isothermal curing temperature. The T_g vs. X data were obtained from the DSC experiment and the best fitting parameters of Eq.1 were determined from the regression as follows,

$$\frac{T_g - T_{go}}{T_{go}} = \frac{(E_x/E_m - F_x/F_m)X}{1 - (1 - F_x/F_m)X} = \frac{(0.3 - 0.2)\ X}{1 - 0.8\ X}$$

The T_{go} obtained from the DSC data of the uncured reactant was 253 °C. Fig.1 shows the data points obtained from the experiment and the curve of the T_g vs. X calculated from the above equation, which shows a very good agreement.

The heat evolved during the curing reaction was measured with a du Pont 910 DSC and du Pont 990 Thermal Analyzer. The samples were heated under different scan rates to obtain the DSC thermograms of heat evolution vs. temperature as shown in Fig.2. The dual exothermic peak appeared at the scan rate lower than 1 °C/min was due to the vitrification. When the T_g of the partially cured mixture exceeded the cure temperature, the vitrification began to occur and the viscous liquid or elastic gel was transformed to the glassy solid. The curing reaction interrupted by the vitrification was resumed by subsequent heating of the reactant in the glassy state(19,20) above the T_g. Donnellan et al.(21) have reported the same dual peak during the DSC experiment for the resin system composed of DGEBA and 1,8 diamino-p-manthane.

In order to obtain the reaction kinetic parameters such as A_{To}, A, B, D, E, and n, the equation was converted to the following form using the scan rate, S_r.

$$\frac{dX}{dT} = \frac{A_T}{S_r} \exp\left(\frac{-E}{RT}\right)(1-X)^n \qquad (6)$$

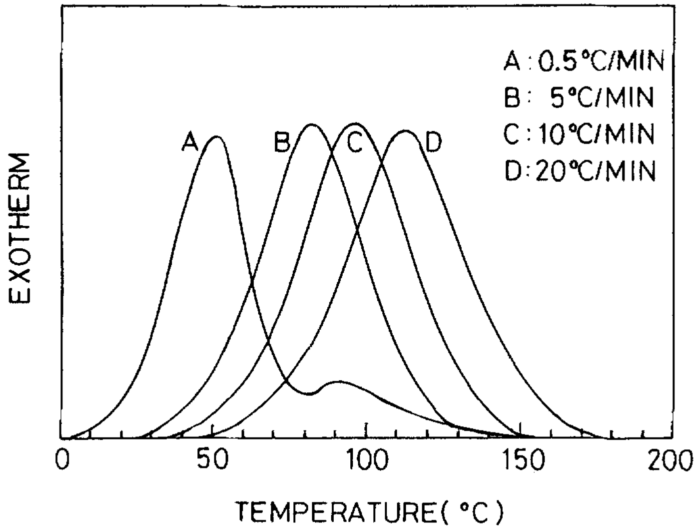

Fig.2. Thermograms obtained from the dynamic DSC method during the epoxy curing.

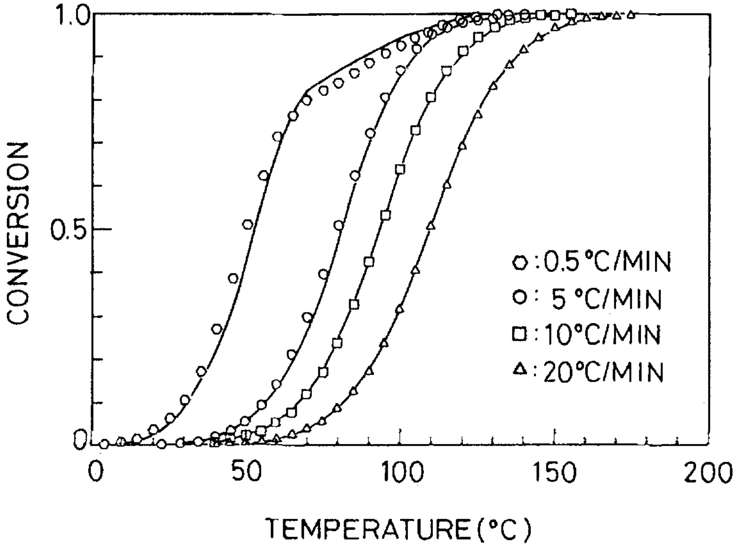

Fig.3. Experimental conversion data points and the conversion(lines) calculated from the kinetic equation.

$$A_T = A_{To} \exp\left(\frac{A\,(T - T_g + D)}{B + |T - T_g + D|}\right) \qquad (7)$$

$$S_r = dT/dt \qquad (8)$$

From the experimental data(T,X,dX/dT) and Eq.1(T_g vs. X), the parameters of equation(6) and (7) were determined through the Marquardt's multivariable nonlinear regression method(22) and Runge Kutta integration technique. The resultant parameters were

$A_{To} = 3.83 \times 10^8$ sec^{-1}
$A = 1$
$B = 2$ K
$D = -20$ K
$E = 18{,}600$ cal/mole
$n = 1.64$

Fig.3 shows that the conversion data obtained from the DSC exotherms agree fairly well with the conversion curves calculated from the above kinetic equation.

NOMENCLATURE

a_T	time temperature shift factor, dimensionless
A_T	temperature dependent frequency factor, /sec
A_{Tg}	temperature dependent frequency factor at T_g, /sec
A_{To}	temperature dependent frequency factor at T_o, /sec
A	empirical parameter in temperature dependent frequency factor, dimensionless
B	empirical parameter in temperature dependent frequency factor,K
C_1	empirical parameter in the generalized WLF equation, dimensionless
C_2	empirical parameter in the generalized WLF equation,K
D	correction parameter in temperature dependent frequency factor,K
E	activation energy, cal/mole
E_x/E_m	ratio of lattice energies for crosslinked and uncrosslinked polymer, dimensionless
F_x/F_m	ratio of segmental mobilities for crosslinked and uncrosslinked polymer, dimensionless
H_t	cumulative heat generated up to time t, cal/g
H_{RXN}	heat of reaction under complete conversion, cal/g
n	reaction order, dimensionless
S_r	scan rate of the DSC experiment, °C/sec
t	time, second
T	temperature, K
T_g	glass transition temperature of the partially cured reaction mixture, K
T_{go}	glass transition temperature of uncured reactant, 253 K
X	conversion, dimensionless

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