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Cure kinetics of high performance epoxy resin systems

Reaction with 4,4'-diamino diphenyl sulfone (DDS)

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SUMMARY

Isothermal cure kinetics of **EPON HPT** 1071/DDS system have been performed by means of differential scanning calorimetry. The maximum cure rate and the extent of conversion at various DDS concentrations were studied as a function of cure temperature. Maximum cure rate increases with increasing cure temperature and DDS concentration. At various DDS concentrations, the maximum cure rate occured between 19-22% conversion. In order to evaluate the kinetic parameters, numerical calculations by means of a Newton-Raphson technique and experimental results obtained from the peak of reaction rate curve were undertaken.

INTRODUCTION

In the aircraft/aerospace industries, tetraglycidylphenyl methylene dianiline (TGMDA)/diamino diphenyl sulfone (DDS) system has generally been used for the advanced composite applications(1-9). Various formulations of TGMDA/DDS system have retained good mechanical properties along with good processibility. However, this resin has been considered unacceptable for the hot/wet performance because of high moisture absorption(10-13).

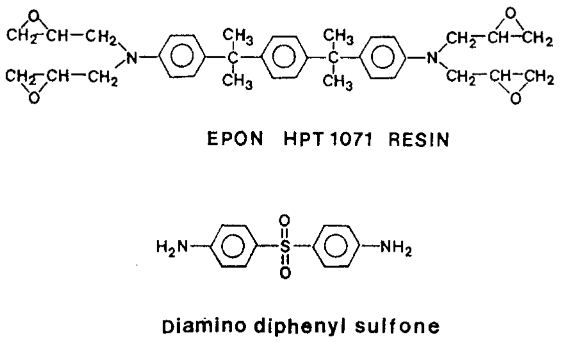
Recently, the **EPON HPT** resin, which can be suitable for the use under hot/wet conditions, has been introduced by Shell Chemical Company(14-17). The new resin is N,N,N',N'-tetraglycidyl-α, α'-bis (4-aminophenyl)-p-diisopropylbenzene (EPON HPT ™ Resin 1071).

A basic understanding of curing process in this resin system is essential for the resin handling, prepreg preparation, and the optimization of resin based composite processing. Differential scanning calorimetry(DSC) has been widely used for the study of epoxy cure kinetics. Several studies have been carried out to characterize the cure process of TGMDA/DDS system (4-9). However, there are very limited informations concerning the HPT1071/ DDS system. Especially, most of them are related to evaluate the mechanical properties of EPON HPT resins for composite(14-17).

It is the purpose of this study, therefore, to analyze the cure kinetics of various EPON HPT resin/DDS formulations by means of isothermal differential scanning calorimetry scans. In addition, temperature dependence of reaction rate and extent of cure were obtained and calculation methods for the kinetic parameter are discussed.

EXPERIMENTAL

The epoxy resin used in this study was EPON HPT 1071 supplied by Shell Chemical Company. This resin is N,N,N'N'-tetraglycidyl- α, α'-bis(4-aminophenyl)-p-diisopropylbenzene. The curing agent was 4,4'-diamino diphenyl sulfone (DDS), which was obtained from Ciba Geigy Ltd.. The structures of EPON HPT 1071 and DDS curing agent are given in Fig.1. These materials



EPON HPT1071 RESIN

Diamino diphenyl sulfone

Fig.1. Structure illustration of EPON HPT 1071 Resin and DDS Monomer.

were used as supplied without further purification.

Amine/epoxide molar ratio are 1.0 for HD1, 0.71 for HD2, and 0.54 for HD3. The curing agent and the epoxy resin were dissolved in acetone and the mixture was agitated completely with a mechanical stirrer, then evaporating acetone in vacuum oven at room temperature.

The thermal and kinetic data were obtained using a Perkin-Elmer 4 differential scanning calorimeter coupled to a microprocess controller. The instrument was calibrated for temperature and enthalpy with high purity indium. Samples of 5-15 mg in crimpped aluminium pans were cured in the DSC under isothermal condition using nitrogen atmosphere. An empty pan was used as the reference material. Complete heat of cure was obtained from 10 °C/min scan.

Isothermal experiments were run for HD1-3 at different temperatures. For epoxy curing, DSC was first equilibrated at the preset cure temperature and then the sample was introduced into the DSC cell. The thermal equilibrium of the sample and the reference holder was attained in less than 1

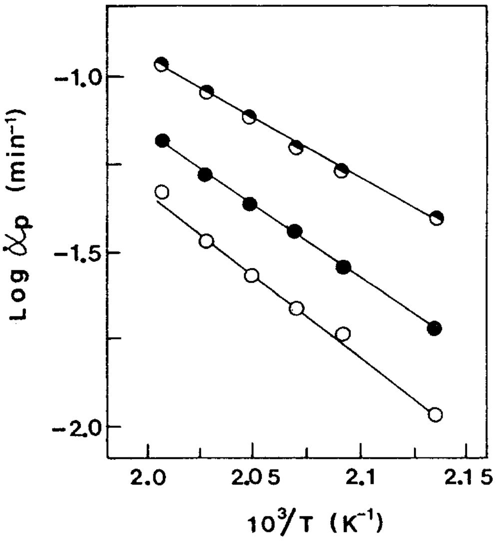


Fig.2. Cure rate at peak as a function of reciprocal cure temperature for HD1 (◐), HD2 (●), and HD3 (○).

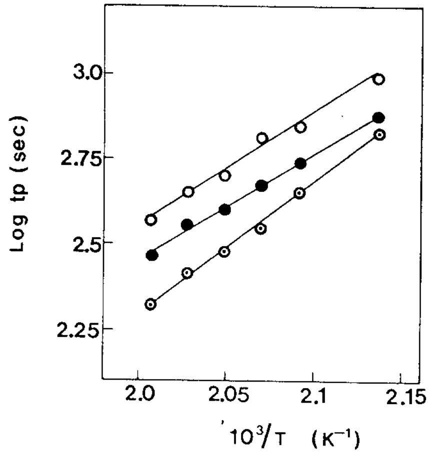


Fig.3. Cure time to peak as a function reciprocal cure temperature for HD1 (⊙), HD2 (●), and HD3 (○).

min after sample insertion.

RESULTS AND DISCUSSION

The cure rate equation used in this study was (18, 19)

$$\dot{\alpha} = d\alpha/dt = (k_1 + k_2\,\alpha^m)\,(1-\alpha)^n \qquad (1)$$

where α is the extent of cure, k_1 and k_2 are the kinetic rate constants, m and n are kinetic exponents. The reaction rate was determined directly from DSC thermograms

$$d\alpha/dt = (dH/dt)\ /\ H_{com}. \qquad (2)$$

where H_{com} is the complete heat of cure obtained from 10 °C/min scans. In order to get the extent of conversion, the DSC curves were integrated and the partial areas as a function of time were normalized with respect to H_{com} and sample weight.

Fig.2 represents the maximum isothermal cure rate as a function of reciprocal cure temperature. As can be seen in this figure, maximum cure rate increases with increasing cure temperature at a given epoxy formulation. Maximum cure rate also increases with an increase of DDS concentration.

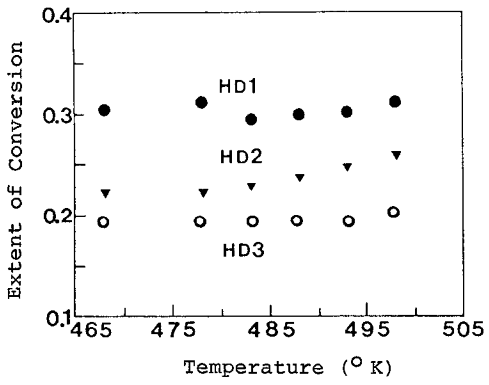


Fig.4. Extent of conversion at peak as a function of cure temperature for HD1-3.

The temperature dependence of the maximum cure rate can be described by an Arrhenius relationship. The temperature dependence of the cure time required to attain the maximum cure rate (t_p) is represented in Fig.3. The time required to reach the maximum peak decreases with increasing cure temperature. A linear relationship between cure time and temperature was observed at various epoxy formulations.

Fig.4. shows the extent of conversion at maximum cure rate as a function of cure temperature. Extent of conversion was independent of cure temperature. Meanwhile, the extent of conversion increases with increasing the curing agent concentration. It has also been observed that the maximum cure rate occurred between 19-32% at various DDS concentrations. It has been reported that autocatalytic reaction of epoxy has the maximum cure rate at 30-40% conversion (20). However, the extent of conversion at maximum cure rate was strongly dependent on the curing agent concentration. In the case of HD1, which has stoichiometric ratio of amine/epoxide, there is a good agreement with literature value (8). In isothermal cure study of TGMDA /DDS system, it has been reported that maximum cure rate occurred at 17-26 % conversion and maximum cure rate moved high conversion with an increase of DDS concentration (8).

The cure kinetics for the epoxy-amine system have been found to be accurately described by means of second order kinetic expression (10, 11, 13). Therefore, the overall reaction order for the epoxy-amine system was assumed to be second (m+n=2) in this study. In order to determine the kinetic parameter m, following equation was used.

$$m = \frac{\ln\left(\dfrac{(\dot{\alpha}_p/(1-\alpha_p)^n) - k_1}{(n\, k_1\, \alpha_p^{1-m}/(m-2\alpha_p))} \right)}{\ln \alpha_p} \qquad (3)$$

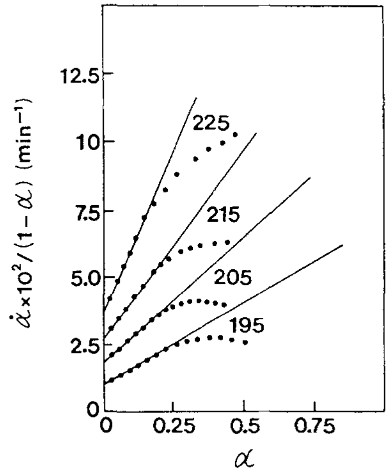


Fig.5. $\dot{\alpha}/(1-\alpha)^n$versus α^m for HD2 in the case of m=n=1.

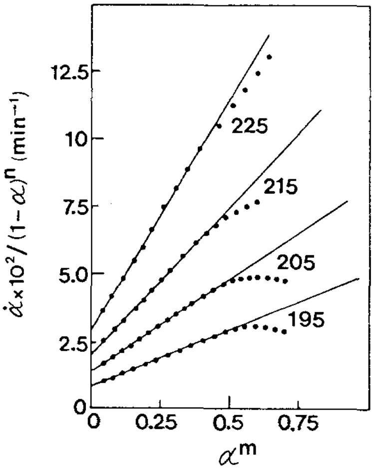


Fig.6. $\dot{\alpha}/(1-\alpha)^n$ versus α^m by using kinetic parameter in obtained from peak constant for HD2.

The quantities of initial reaction rate constant (k_1), extent of cure reaction (α_p) and cure rate ($\dot{\alpha}_p$) were readily determined at any given temperature using differential scanning calorimetry. These values may be then substituted in the above equation and the plot of $\dot{\alpha}/(1-\alpha)^n$ against α^m for HD2 is shown in Fig.5. Barton has reported that the cure reaction of TGMDA/DDS system provided linear plots up to approximately 20-30% conversion under the assumption of m=n=1(21). In the case of m=n=1, the early reaction of the HPT resin/DDS system up to approximately 25% conversion provides linear plots. As the cure temperature increases up to 225°C, cure rate is apparently slower than the theoretical prediction. Deviation of these plots would indicate a poor fit to above equation for m=n=1. There was a retardation in cure rate at higher conversion.

On the other hand, kinetic parameter m was calculated numerically by means of a Newton-Raphson technique (18). The data from this method are plotted in Fig.6. Compared to previous method, linearity of these plots shows a good fit to above equation for n=2-m. The data fit this model up to about 50% conversion and the deviation from theoretical value occurs at higher conversions.

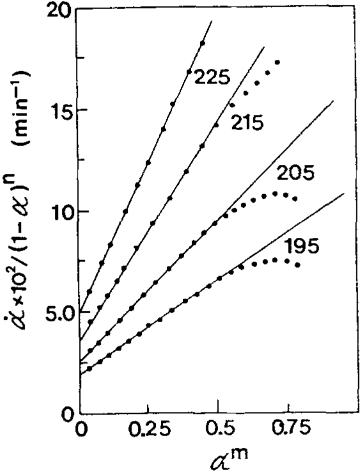


Fig.7. $\dot{\alpha}/(1-\alpha)^n$ versus α^m by using kinetic parameter in obtained from peak constant for HD1.

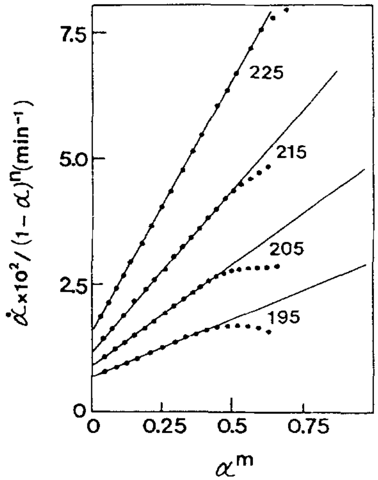


Fig.8. $\dot{\alpha}/(1-\alpha)^n$ versus α^m by using kinetic parameter in obtained from peak constant for HD3.

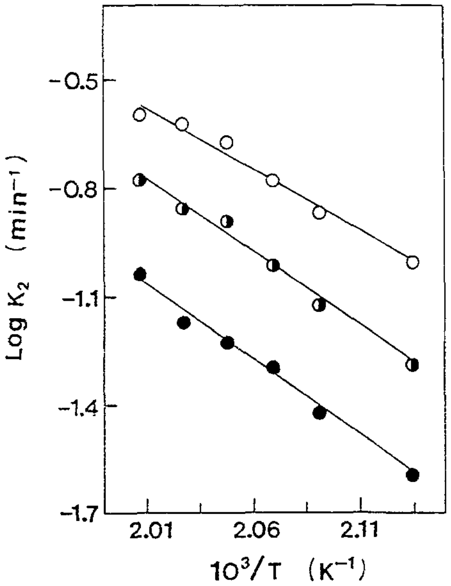


Fig.9. Cure rate constant (k_2) as a function of reciprocal cure temperature for HD1(○), HD2(◐), and HD3 (●).

The overall reaction order (m+n) was assumed to be 2 and the validity of above assumption was confirmed from this method. $\dot{\alpha}/(1-\alpha)^n$ against α^m for HD1 and 3 are also plotted in Fig.7 and 8, respectively. The calculated data from this model fit experimental data up to about 50% conversion. The intercepts and initial slopes of the plots were determined by linear extrapolation. The values of the reaction rate constant (k_2) are shown in Fig.9. In this figure, reaction rate constant should be an Arrhenius function of cure temperature. The plot between logarithm k_2 and reciprocal temperature would follow the linear relationship. From the Arrhenius plot, it is observed that the activation energy for the cure reaction of epoxy resin increases with decreasing the DDS concentration. A summary of the corresponding kinetic parameters for formulation HD1-3 is shown in Table I.

Table I. Summary of kinetic parameters for HD1-3.

	k_1	k_2	E_{a2} (kcal/g.mol)
HD1	$8.14 \times 10^7 \exp(-\frac{6.85 \times 10^4 \text{ J/g·mol}}{RT})$	$2.19 \times 10^6 \exp(-\frac{6.61 \times 10^4 \text{ J/g·mol}}{RT})$	15.741
HD2	$1.70 \times 10^6 \exp(-\frac{7.37 \times 10^4 \text{ J/g·mol}}{RT})$	$2.64 \times 10^7 \exp(-\frac{7.84 \times 10^4 \text{ J/g·mol}}{RT})$	18.656
HD3	$2.64 \times 10^7 \exp(-\frac{7.84 \times 10^4 \text{ J/g·mol}}{RT})$	$2.50 \times 10^7 \exp(-\frac{8.09 \times 10^4 \text{ J/g·mol}}{RT})$	19.270

CONCLUSIONS

Cure kinetics of EPON HPT 1071/DDS system have been studied using differential scanning calorimetry. Under the isothermal condition, maximum cure rate increases with increasing cure temperature and DDS concentration. Extent of conversion is independent of cure temperature.

Based on the assumption that the overall reaction for the epoxy-amine system is of the second order, the kinetic parameters are determined from the reaction rate and experimental data obtained from the peak of reaction rate curve. The data obtained from experimental results provide linear plot up to about 50% conversion, whereas the epoxy cure in the case of m=n=1 fits well up to approximately 25% conversion. Reaction rate constant (K_2) is dependent on the cure temperature.

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