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Cure kinetics of high performance epoxy resin systems

Reaction with HPT curing agent from dynamic experiment

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SUMMARY

Cure kinetics of epoxy based on EPON HPT 1071 resin with EPON HPT 1062 curing agent were studied by dynamic differential scanning calorimetry experiment. Kinetic parameters were determined as functions of different epoxy formulations and heating rates. Total heat of cure was independent of heating rate, which was increased with decreasing the concentration of curing agent. The extent of cure at peak is nearly constant and independent of heating rate at a given curing agent concentration. Due to the diffusion controlled cure process, the activation energy of hydroxyl-epoxide reaction (peak 2) is higher than that of the primary amine-epoxide reaction (peak 1). The relationship between peak temperature and heating rate has been also undertaken in this study.

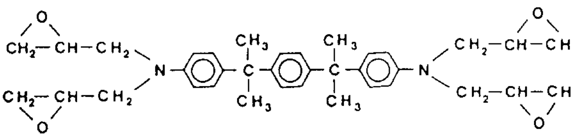
INTRODUCTION

Tetra functional epoxy resins have been applied for high performance composite matrix in aerospace/aircraft industries. In the past decade, TGDDM/DDS system, which has good mechanical properties and easy processability, has been used for the advanced composite (1-9). However, it has been reported that hot/wet performance of TGDDM/DDS system shows over six weight percents of moisture absorption (10). Especially, this poor hot/wet property affects not only the mechanical properties of epoxy resin but also a drastic drop in galss transition temperature and modulus (10-12). New epoxy resin systems, which have low moisture absorption and high glass transition temperature, have been developed (13-16). These resins are N, N, N', N'-tetraglycidyl- α, α'-bis(4-aminophenyl)-p-diisopropyl-benzene (EPON HPT ^{TM} resin 1071) and N, N, N', N'-tetra glycidyl-bis (3,5-dimethyl-4-aminophenyl)-p diisopropylbenzene (EPON HPT ^{TM} resin 1072).

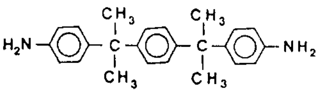
The low water absorption of EPON HPT system consequently provides good retention of hot/wet properties. In this paper, α , α'-bis (4-hydroxy-phenyl)-p-diisopropylbenzene (EPON HPT ^{TM} Curing-Agent 1062), which is a less polar amine than DDS, is used for the cure with EPON HPT resins.

The cure kinetics of high performance epoxy resins are essentially needed for the optimum use of matrix in the advanced composites. Several studies of cure kinetics have been carried out by means of dynamic DSC scans (17-21). The advantage of dynamic method is simple and valuable in itself, although the dynamic kinetic parameter is larger than that of the isothermal (19). It has been reported that this method was valid for the cure kinetics of epoxy-amine system (22).

The purpose of this study is to analyze the cure kinetics of various EPON HPT resin/EPON HPT curing agent formulations by differential scanning calorimetry (DSC). In addition, dynamic cure studies have been performed for the evaluation of cure kinetic parameters in EPON HPT epoxy resin/EPON



EPON HPT 1071 RESIN



EPON HPT 1062

Fig.1. The structures of EPON HPT 1071 Resin and EPON HPT 1062 Curing Agent.

HPT curing agent system.

EXPERIMENTAL

The epoxy resin used in this study was EPON HPT 1071 supplied by Shell Chemical Company. This resin was technical grade of N, N, N', N'-tetraglycidyl- α, α'-bis-(4-aminophenyl)-p-diisopropylbenzene. The epoxide equivalent weight of the resin was 166g/mol. The curing agent was α, α'-bis (4-hydroxyphenyl)-p-diisopropyl benzene, EPON HPT 1062 also supplied by Shell Chemical Company. These materials were used as supplied without further purification. The structures of the EPON HPT 1071 and EPON HPT 1062 monomers were illustrated in Fig.1. In addition, Table 1 and 2 represent the physical properties of these materials.

Amine/epoxide molar ratio are 1.0 for HH1, 0.71 for HH2, and 0.54 for HH3. The comonomer mixtures were prepared by dissolving the resin and the curing agent in methylene chloride, then evaporating the solvent in vaccum oven at room temperature.

Table 1. Physical Properties of EPON HPT 1071 Epoxy Resin.

Physical form	Dark colored solid
Epoxy equivalent weight	150 - 170
Melting point (ASTM D3461, Mettler, 1℃/min)	122 ℉
Melt viscosity at 230 ℉	18 - 22 poise (Brook field)
Tg	73 ℉ (DSC)

Table 2. Physical Properties of EPON HPT 1062 Curing Agent.

Physical form	Crystalline solid
Color	Tan to cream
Melting point	151 - 154 ℃
Approximately equivalent weight / active hydrogen	100

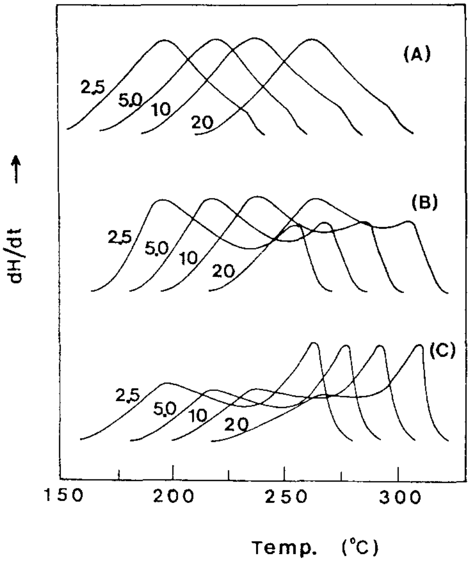


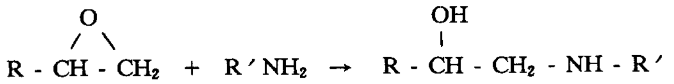
Fig.2. DSC dynamic thermogram of HPT 1071/HPT 1062 system. A) HH1 B) HH2 C) HH3

Thermal analysis was conducted by Perkin-Elmer4 differential scanning calorimeter (DSC) coupled with a microprocess controller. The sample size was 5-15 mg. An empty aluminum pan was used as the reference material and sample in crimmped pan was cured in the DSC under dynamic condition using purified nitrogen atmosphere. The dynamic experiments were performed with heating rate in the range of 2.5-20 K/min. The baseline was obtained from a second scan on the fully cured resin. The heat of reaction was determined from the area under the exothermic cure curve.

RESULTS AND DISCUSSION

Dynamic DSC scans were performed for HH1-3 at four different heating rates. These DSC thermograms are illustrated in Fig.2. At a constant concentration of curing agent, the initial curing temperature and the peak temperature increase with increasing the heating rate. As the concentration of curing agent decreases gradually, the first exotherm peak decreases and the second exotherm peak becomes prominently. In the case of HH3 (Fig.2 (c)), the second exotherm peaks are higher than the first exotherm peaks. Total heat of cure estimated from the area under the exotherm curve was independent of the heating rate. On the other hand, total heat of cure increases with decreasing the concentration of curing agent. In general, exotherm peak shifts to higher temperature with increasing the concentration of curing agent at constant heating rate (23). Due to the structural difference of the epoxy resin backbone, cure process of HPT 1071/HPT 1062 system is different from that of TGDDM/DDS system.

During epoxy curing, chemical reaction of epoxide-amine occurs as follows (24).



$$\mathrm{R-}\overset{\overset{\mathrm{O}}{/\ \backslash}}{\mathrm{CH-CH_2}} + \mathrm{R'NH_2} \rightarrow \mathrm{R-}\overset{\overset{\mathrm{OH}}{|}}{\mathrm{CH}}\mathrm{-CH_2-NH-R'} \qquad (1)$$

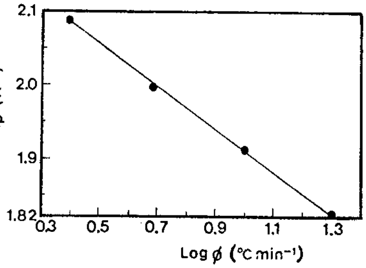
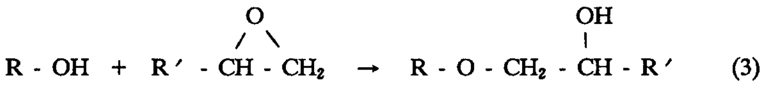


Fig.3. Reciprocal peak temperature as a function of logarithm heating rate for HH1.



$$R-OH + R'-\overset{O}{\overbrace{CH-CH_2}} \rightarrow R-O-CH_2-\overset{OH}{\overset{|}{CH}}-R' \qquad (3)$$

Based on the results that the second exotherm peak and total heat of cure increase with decreasing the concentration of curing agent, it can be concluded that the extent of epoxy groups consumed by other reactions rather than the primary amine-epoxide reaction is enhanced at low concentration of amine. In epoxy/amine system, the reactions of a series of hydroxyl groups with epoxide may be assumed as the other reactions.

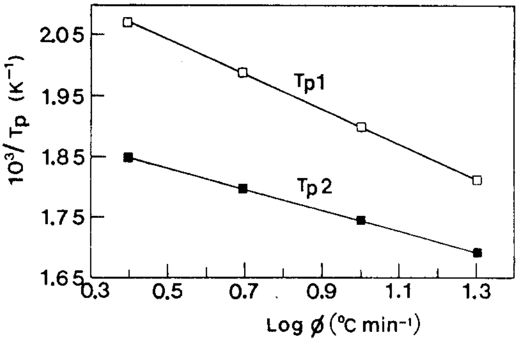


Fig.4. Reciprocal peak temperature as a function of logarithm heating rate for HH2.

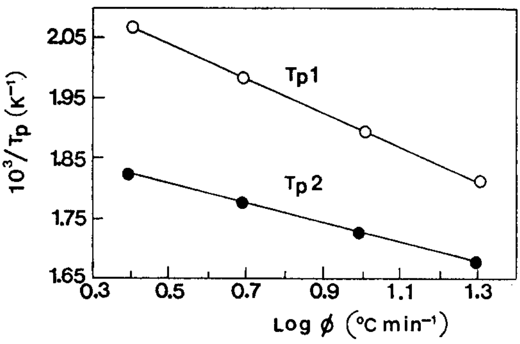
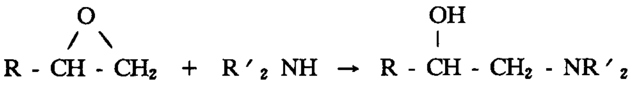


Fig.5. Reciprocal peak temperature as a function of logarithm heating rate for HH3.

Table 3. Peak exotherm temperature (T_p) for HH1-3.

Heating rate	HH1	HH2		HH3	
(°C/min)	T_p	T_{p1}	T_{p2}	T_{p1}	T_{p2}
2.5	206	210	268	210	275
5.0	229	230	283	232	290
10.0	250	253	300	255	307
20.0	275	279	319	280	324

T_{p1} : peak exotherm temperature at peak 1.
T_{p2} : peak exotherm temperature at peak 2.



$$R-\underset{}{CH}\overset{O}{\frown}CH_2 + R'_2NH \rightarrow R-\overset{OH}{\overset{|}{CH}}-CH_2-NR'_2 \qquad (2)$$

The hydroxyl groups formed by the amine-epoxide addition reaction are capable of reaction with epoxide group. When the amine is present in less than stoichiometric concentration, reaction of epoxide and hydroxyl may occur.

Table 4. The extent of cure (α_p) for HH1-3.

Heating rate	HH1	HH2		HH3	
(°C/min)	α_p	α_{p1}	α_{p2}	α_{p1}	α_{p2}
2.5	0.491	0.401	0.960	0.247	0.901
5.0	0.504	0.380	0.940	0.251	0.910
10.0	0.492	0.360	0.940	0.240	0.900
20.0	0.500	0.371	0.920	0.239	0.902

α_{p1} : The extent of cure at peak 1
α_{p2} : the extent of cure at peak 2

Table 5. Activation energy (Ea) for HH1-3.

HH1	HH2		HH3	
Ea	E_{a1}	E_{a2}	E_{a1}	E_{a2}
15.7	15.07	24.67	15.01	26.44

E_{a1} : activation energy at peak 1
E_{a2} : activation energy at peak 2

Peak exotherm temperatures (T_{p1} and T_{p2}) vary in a predictable manner with the heating rate as can be seen in Fig.2. The peak temperatures from dynamic scans are given in Table 3. In addition, the extents of cure at the peaks 1 and 2 for all formulations are summarized in Table 4. It is observed that the extents of cure at the peaks 1 and 2 are nearly constant and independent of the heating rate at a given curing agent concentration.

Reciprocal peak temperature as a function of logarithm heating rate for HH1-3 are plotted in Fig.3-5, respectively. A linear relationship between reciprocal peak temperature and heating rate has been observed for all formulations. Form these results, it is expected that the activation energy for the cure reaction of epoxy should be dependent only on the functional groups of the curing agents. The corresponding values of activation energy are also summarized in Table 5. At a given concentration of curing agent, the activation energy of peak 2 is higher than that of peak1. This phenomenon is due to the different cure reaction between peak 1 and peak 2. In HPT 1071/HPT 1062 system, reaction at peak 1 is mainly due to the primary amine-epoxide reaction. On the other hand, hydroxyl-epoxide reaction dominates at peak 2. Compared to the peak 1, the resin viscosity increases at peak 2 during the cure reaction and the diffusion controlled cure process dominates at high cure temperature. In addition, the activation energy of epoxy cure increases with decreasing the concentration of curing agent.

CONCLUSIONS

Cure kinetics of EPON HPT 1071 resin/EPON HPT 1062 curing agent system were investigated by dynamic differential scanning calorimetry experiment. The total heat of cure was independent of the heating rate. However, the total heat of cure increased with decreasing the concentration of curing agent. At a given curing agent concentration, the extent of cure at maximum cure rate was independent of cure temperature and heating rate.

A linear relationship between heating rate and reciprocal peak temperature was observed for all formulation. The activation energy for the cure reaction was dependent only on the fuctional groups of the curing agents. The activation energy of peak 2 was higher than that of peak 1 due to the diffusion controlled cure process.

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