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Kinetic Studies on the Curing Reactions of Fluoroepoxy Oligomer and Cycloaliphatic Amine

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Abstract. The curing kinetic analysis is an important technique for the characterization of the curing behavior of reactive polymeric systems. In this study, fluoroepoxy oligomer was synthesized from trifluoromethyl aniline and epichlorohydrin. The epoxide equivalent weight (EEW) and the number average molecular weight (M_n) of the systhesized fluroepoxy oligomer determined from acid titration and gel permeation chromatography were found to be 312.16 g/eq and 534 g/mol, respectively. The mixtures of the fluoroepoxy oligomer were mixed with the cycloaliphatic amine in various stiochiometric ratios (1:1, 1: 1.5 and 1:2). The effects of the stiochiometric ratio on the curing behaviors were studied using both isothermal and non-isothermal DSC methods. Ozawa's, Kissinger's and Friedman's methods were employed to investigate the kinetic parameters. The results showed that the peak temperature (T_p) increased with the increasing heating rate. The activation energy (E_a) calculated from Ozawa's and Kissinger's methods were much larger than that from Friedman's method.

Introduction

Fluoropolymers are widely used in many applications that extend from common household appliances to the high performance materials in aircrafts because of their unique non-adhesive and low friction properties as well as their superior heat, chemical and electrical properties to other polymers. These attractive properties stem from the high electron affinity, small atomic radius and low polarisability of fluorine [1]. Among the fluoropolymer, the fluorinated thermosetting polymer is interestingly developed due to its ease of processing. Like other thermosetting materials, the properties of fluorinated thermosetting polymer depend on processing parameters (time and temperature of cure) as well as the amount and type of hardeners. Almedia and Monteiro [2] reported that the compression behavior of the epoxy systems was controlled by the epoxy/hardener ratios. Evrikleai, et al. [3] studied the cure kinetics of epoxy-amine by FTIR technique. They found that curing rates and final conversions increased with increasing amounts of hardener. In this research, therefore, a fluorinated thermosetting resin, namely fluoroepoxy oligomer, was synthesized, and the effect of the amounts of hardener on the cure kinetics was studied using differential scanning calorimeter (DSC) in both non-isothermal and isothermal methods.

Experimental

Materials

Epichlorohydrin and m-trifluoromethyl aniline were supplied by Aldrich. Both chemicals were used as starting reagents for synthesizing fluoroepoxy oligomer. The handener used was a modified cycloaliphatic amine (EPIKURE™ Curing Agent 3380) from Momentive. The equivalent weight of hardener is 114 g eq^{-1}.

Synthesis and Characterization of DGTFA Epoxy Oligomer.

Fluoroepoxy oligomer was synthesized according to our previous study [4]. The epoxy equivalent weight (EEW) of the obtained product was determined by acid titration. The chemical structure was investigated using FTIR spectrophotometer. The average molecular weight was determined using gel permeation chromatography (GPC).

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DSC Measurements

All non-isothermal and isothermal cure kinetics were studied on differential scanning calorimeter (DSC). Fluoroepoxy and cycloaliphatic amine hardener were mixed in mole ratios of (fluoroepoxy to amine) 1:1, 1:1.5 and 1:2. For the non-isothermal measurements, the uncured resins (approx. 3-4 mg) were added to aluminum pans and analyzed dynamically with heating rate of 10 ℃ /min, 12 ℃/min, 15 ℃/min and 20 ℃/min in a nitrogen atmosphere. Measurements were carried out with an empty cell as reference from 10 ℃ up to 200 ℃. For the isothermal method, the measurements were carried out on uncured resins at 120, 125, 130, 135 ℃, respectively.

Results and Discussion

Synthesis and Characterization of DGTFA

The product so obtained was light yellow colored, viscous and water non-soluble liquid. Its density at 25 ℃ was 1.3803 g/cm^3. The epoxide equivalent weight (EEW) determined from acid titration was 312.16 g/eq. The number average molecular weight (M_n) was 534 g/mol. The evidence from the FTIR confirmed the successful synthesis of fluoroepoxy oligomer (Figure was not shown here). The absorption peak at 3381.60 cm^{-1} indicated the presence of –OH group. Bands at 2956.91 and 2912.84 cm^{-1} showed C-H stretching of CH_2 and CH, respectively. The overtone band in the region from 1700 to 2000 cm^{-1} was attributed to 1,3-substituted benzene. The peak at 1613.20, 1498.75 and 1165.96 cm^{-1} was attributed to the aromatic rings. The characteristic absorption band of CF_3 appeared at 1320.42 cm^{-1}. Absorption bands at 852.98 cm^{-1} showed the presence of epoxide group.

Cure Kinetics Analysis of Nonisothermal

The uncured mixtures of fluroepoxy and cycloaliphatic amine at the mole ratios of 1:1, 1:1.5 and 1:2 were tested at different DSC heating rates ranged from 10 to 20 ℃/min. A single exothermic peak was found for all of the studied systems. The total heat of reaction (ΔH) was varied between -58.5 and -63.5 kJ/g. The values of the exothermic peak maximum (T_p) at different epoxy systems are summarized in Table 1. At a particular mole ratio, T_p shifted to the higher temperature as the heating rate increased. Due to the shift of T_p in this manner, the apparent activation energy can be calculated by the Ozawa's and Kissinger's methods. For Kissinger's method, it assumes the maximum reaction rate occurs at the peak temperatures. The activation energy values (E) of curing can be determined from a plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$. Ozawa developed an alternative method to determine apparent E from T_p. This method is applied to thermal data using the following equation [5,6].

$$\ln\beta = \ln\left(\frac{A_\alpha E_\alpha}{R}\right) - \ln g(\alpha) - 5.3305 - 1.052\frac{E}{RT} \quad (1)$$

where g(α) is the integral conversion function, β is heating rate and R is ideal gas constant. The plot of lnβ versus $(1/T_p)$ obtained from DSC thermograms at different heating rates (β) should be a straight line where the slope allows the determination of the apparent E. The values of the apparent E determined from Kissinger and Ozawa's calculations are shown in Table 2.

Besides the Kissinger's and Ozawa's methods, Friedman's method was used to calculate the apparent E. Friedman's calculation is derived based on the Arrhenius rate law; the relation between curing rate (dα/dt) and temperature are shown in Eq. 2.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A - \left(\frac{E}{RT}\right) + \ln f(\alpha) \quad (2)$$

where α is the degree of conversion, A is the pre-exponential factor, and f(α) is the reaction model. The plot of ln(dα/dt) versus 1/T at constant α gives a straight line with slope $-E_a/R$ [6]. The results show again in Table 2.

It was found from Table 2 that the apparent E determined from Ozawa's and Kissinger's calculations decreased with increasing mole of the amine hardener in the epoxy system. Thus the excess mole of the modified cycloaliphatic amine (hardener) caused an accelerating effect on the

cure reactions. However, the phenomena were not found in Friedman's operation. This result may be attribution from the fact that Friedman's method exhibited high sensitivity of noise [6], as compared to those Kissinger's and Ozawa's operations. Moreover, the apparent E depends on the fraction of conversion (α). In this work, we performed the Friedman's calculations at the α of 0.5 which was far beyond the α at the peak maxima.

Table 1. Temperature at the maximum of the exothermic peak (T_p) at different heating rates.

Heating rate (°C/min)	T_p (°C)		
	Mole ratio of 1:1	Mole ratio of 1:1.5	Mole ratio of 1:2
10	143.2	144.5	142.7
12	147.3	147.0	147.8
15	149.8	150.9	151.3
20	154.6	155.5	155.6

Table 2. The apparent activation energies (E) of the fluoroepoxy and amine systems at various mole ratios (epoxy:amine).

Mole ratios	E (kJ/mol)		
	Ozawa's method	Kissinger's method	Friedman's method
1:1	104.1	102.5	55.8
1:1.5	88.3	85.8	72.4
1:2	74.3	73.0	70.4

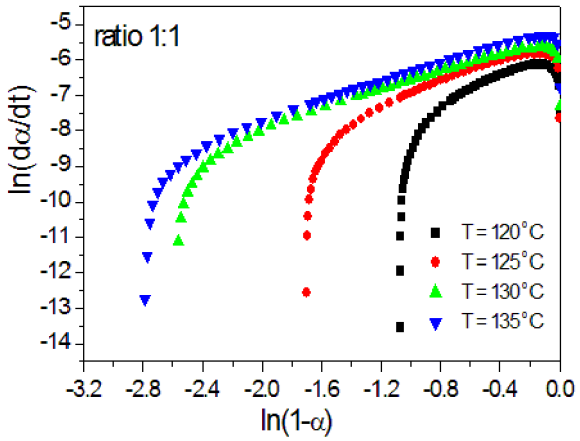

Fig. 1 The plot of ln(dα/dt) as a function of ln(1-α) using n-order equation at ratio 1:1.

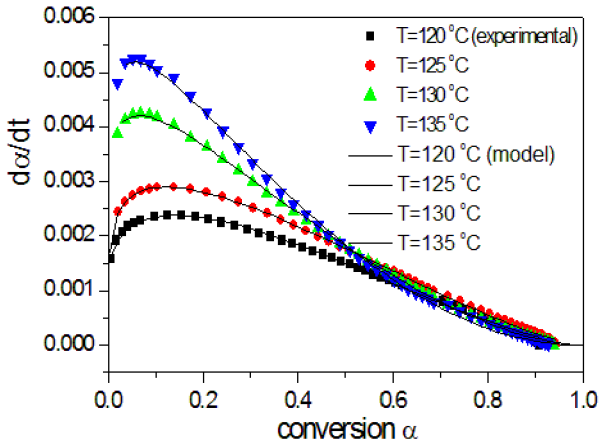

Fig. 2 Comparisons of experimental data with autocatalytic model in DGTFA/amine ratio1:1.

Cure Kinetics Analysis of the Isothermal

To explain the curing kinetics, the experimental isothermal data were fitted with two curing kinetic models, the n-order and autocatalytic models. The n-order model assumes that the reaction obeys the Eq.3:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (3)$$

where k is a rate constant and n is an order of reaction. By a linear plotting of Eq.3, it is possible to know the values of n and k. The plot of ln(dα/dt) as a function of ln(1-α) of the epoxy system with mole ratio of 1:1 are shown in Fig. 1. It was found that the reaction rate reached to the maxima at about 10% conversion. The experimental data were not fitted with the n-order model; nonlinear curves were found. Similar phenommena were also observed for other studied systems (Figs are not shown here).

For autocatalytic model expressed by Kamal, the isothermal curing behaviors are explained by Eq. 5.

$$\frac{da}{dt} = (k1 + k2a^m)(1-a)^n \quad (5)$$

where k_1 and k_2 are the externally catalyzed rate constant and the autocatalyzed rate constant, respectively. m and n are kinetic orders of the reactions. The Levenberg-Marquardt non-linear regression analysis was performed without any constraints to determine the kinetic parameters, k_1,

k_2, m and n. The plots of experimental data and the autocatalytic fitted values of curing rate as a function of conversion fraction only for the 1:1 epoxy system are shown in Fig. 2. The curve fitted from autocatalytic model coincided with the experimental data. Good fitting curves between the model and experimental data were observed. The cure kinetic parameters of all fluoroepoxy/amine systems along with χ^2 parameters are shown in Table 3.

In Table 3. the overall reaction order m+n were in range 4.6 of 1.55. The rate constants, especially the autocatalytic rate constant, k_2, increased with increasing amounts of amine hardener in the epoxy system. This acceleration effect became more significant at low cure temperature (120 ^oC), leading to that curing reaction of the systems with higher mole of hardener occurred more quickly.

Table 3. Cure kinetic parameters calculated from autocatalytic model.

ratio	Temperature (^oC)	k_1	k_2	n	m	χ^2
1:1	120	0.00124	0.00462	1.77	0.49	3.91E-09
	125	0.00161	0.00887	2.17	0.47	4.07E-09
	130	0.00054	0.00692	1.58	0.24	7.34E-09
	135	0.00034	0.00819	1.35	0.19	1.02E-08
1:1.5	120	0.01510	0.00570	3.03	0.74	6.14E-09
	125	0.00208	0.00694	3.76	0.85	2.40E-09
	130	0.00165	0.00908	2.06	0.45	1.25E-08
	135	0.00013	0.00856	1.47	0.18	1.06E-08
1:2	120	0.00088	0.01450	3.82	0.78	5.09E-09
	125	0.00163	0.00572	1.92	0.44	5.80E-09
	130	0.00263	0.00524	1.42	0.33	6.63E-09
	135	0.00301	0.00577	1.30	0.24	1.08E-08

Summary

The activation energies (E_a) from Ozawa's and Kissinger's methods were larger than that from Friedman's method. In the isothermal analysis, the total order of reactions m+n ranged from 4.6 to 1.55. The reaction of fluoroepoxy/amine systems preferred autocatalytic to the n-order reaction. The activation energy decreased with increasing amounts of the amine hardener; the amine hardener acted as an accelerator in this cure reactions.

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