A STUDY ON THE CURE KINETICS OF TETRA-FUNCTIONAL EPOXY RESIN/CARBOXYL FUNCTIONALIZED AMINE TERMINATED POLYETHERIMIDE BLEND

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Introduction

Recently, extensive studies on the modification of epoxy resin to improve toughness have been undertaken for high performance structural components. For example, epoxy / polyeherimide(PEI : Ultem 1000) and epoxy/polyether sulfone (PES:Udel) blends have been used to investigate the mechanical properties, while retaining a high glass transition temperature and a high mechanical strength[1-4]. Mechanical properties of the cured epoxy blends are controlled by the morphology which is affected by the compatibility of epoxy and PEI[6]. The introduced functional group of the latter, i.e. amine terminated PEI(ATPEI) influence significantly the morphology and interface of the cured epoxy blend[7]. To inverstigate the effect of functional group in the ATPEI, carboxyl functionalized amine terminated polyetherimide(COOH-ATPEI) as a functionalized thermoplastic was synthesized. In this study, the behavior of cure kinetics of an epoxy system containing the 4,4'-tetraglycidyl diaminodiphenyl methane (TGDDM) and diaminodipheyl sulfone (DDS) as a curing agent, and their blends with COOH-ATPEI at neat, 5, 10, and 15wt% were studied.

Materials and Method

The epoxy system was TGDDM(Grade : LER-430, viscousty : 14000cps, density : 1.17g/cm^3, supplied by LG chemical Co., Korea) with an average epoxy equivalent weight of 125g/eq. To make an epoxy resin / COOH-ATPEI blend, the latter was dissolved in methtylene chloride, and after that, the solution was mixed with the epoxy prepolymer by using a high-speed stirrer for 2hrs. Then, the solvent was removed in a vacuum drying oven at 100°C for 24hrs. 35 phr of DDS (=0.67 stoichiometric equivalent of epoxy) was slowly added, with continuous stirring, to the epoxy / COOH-ATPEI mixture in an oil bath at 180°C. A differential scanning calorimeter analysis was conducted using Mettler Toledo DSC 822e. To obtain the cure rate and the degree of conversion as a function of time, isothermal experiments were conducted at 160°C, 175°C, and 190°C.

Results and Discussion

Plot of the conversion versus time for 5wt% blend is shown in Figure 1. Figure2 is plot of the reaction rate versus time based on Figure 1. The reaction rate increased strongly to the peak value in the early stage of reaction and decreased smoothly in the late stage of reaction as time increased. This rate curves are typical shape of autocatalytic cure kinetics of epoxy/thermoplastics/amine hardener blend system. Table 1 shows that the final conversion was decreased by increasing the amount of COOH-ATPEI, and increased by increasing the

reaction temperature. The autocatalytic model which is shown in eq.(1) is a general equation based on a phenomenological approach and is used to analyze the cure kinetics of amine-cured epoxy systems[5-6]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n F(\alpha) \quad , \quad \text{where,.} \quad F(\alpha) = \frac{1}{1+\exp(C(\alpha-\alpha_c))} \quad (1)$$

where α is the conversion, k_1 and k_2 are the rate constants, m and n are the kinetic exponents of the reaction, m+n is the overall reaction order, f(α) is a diffusion control factor, C is a parameter of diffusion control, and α_c is the critical value of cure conversion. From eq.(1), using non-linear regression method , kinetics parameters and diffusion control factor were obtained, m   was about 1.0 or slightly larger than 1.0 and n was 2.5 ~ 3.1, increased by increasing amount of COOH-ATPEI, decreased by increasing curing temperature, the critical value of the cure conversion, α_c, was 0.6113 ~ 0.8249. As shown in Figure 3, a retardation of the conversion gradually occurred as the blends matrix became vitrified, so the cure reaction became rapidly diffusion controlled. The solid lines are calculated from eq.(1), the dotted line is without diffusion term, and symbol curves are the experimental data. The solid lines are well fitted with experimental data.

Conclusions
A study on cure kinetics was carried out for the blend of epoxy/DDS/COOH-ATPEI system. In the cure process, autocatalytic reaction was observed on whole of COOH-ATPEI blend system and identified by using a autocatalytic model equation for the cure kinetics. The reaction order, m, was about 1.0, and n was 2.5 ~ 3.1. The critical value of the cure conversion, α_c, was 0.6113 ~ 0.8249.
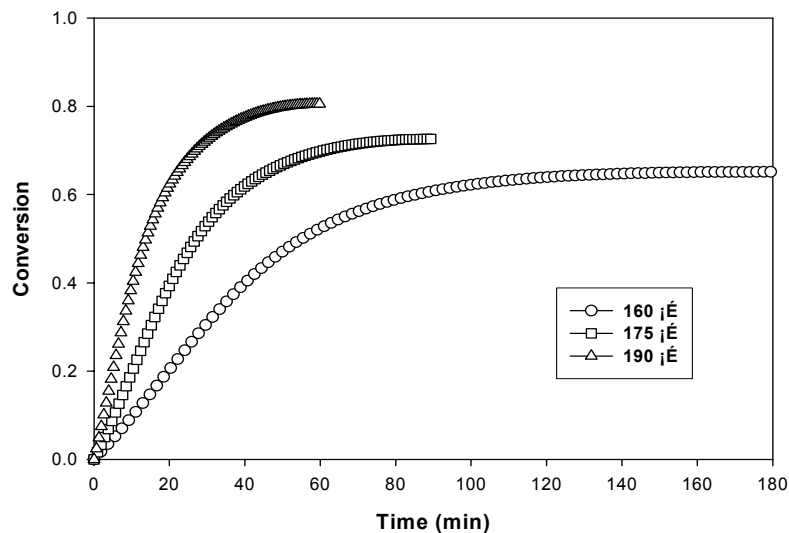

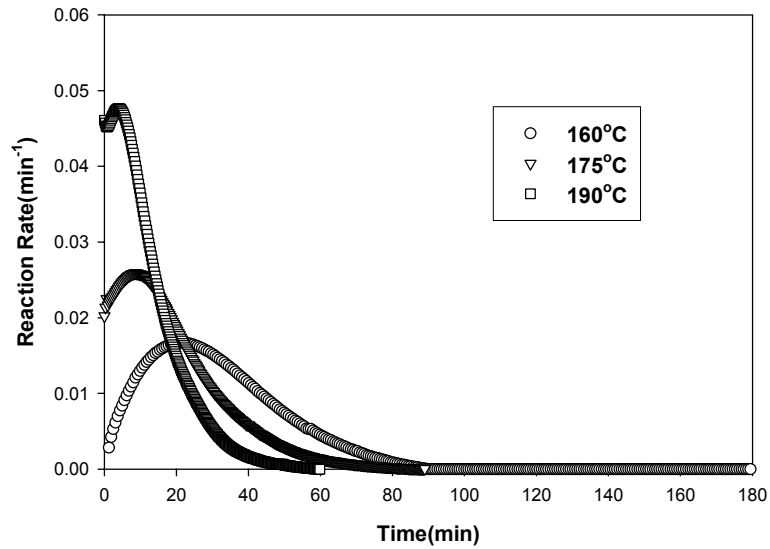Figure1. Conversion vs time of COOH-ATPEI 5wt% blend system

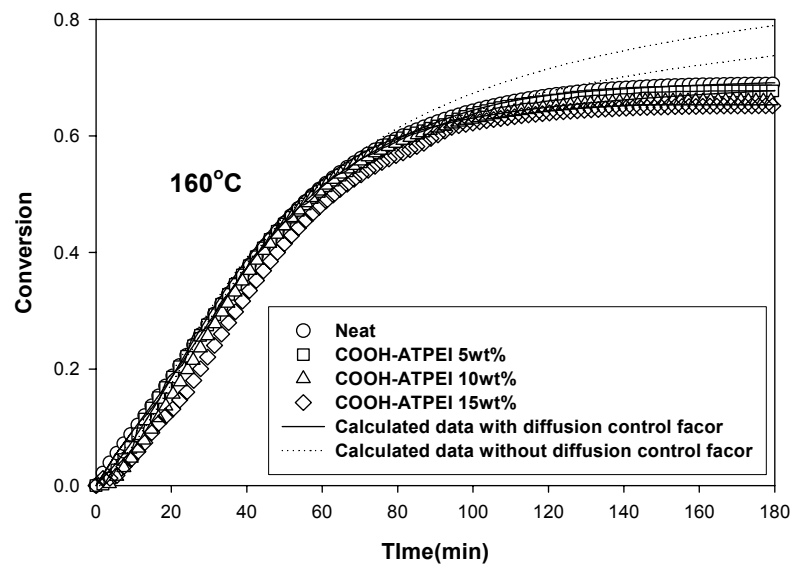Figure2. Reaction rate vs time of COOH-ATPEI 5wt% blend system

Figure3. Diffusion control of various COOH-ATPEI blend system on the conversion

Table1. Heats of reaction of neat epoxy and blends of exopy with various AB contents

	Temperature(oC)	ΔH_{iso}(kJ/mol K)	ΔH_R(kJ/mol K)	ΔH_T(kJ/mol K)	α_f
Neat	160	397.62	179.54	577.16	0.6889
	175	370.28	118.57	488.85	0.7574
	190	394.43	75.62	470.05	0.8391
COOH-ATPEI 5wt%	160	212.51	101.22	313.73	0.6773
	175	382.25	130.4	512.65	0.7456
	190	444.71	94.24	538.95	0.8251
COOH-ATPEI 10wt%	160	326.12	167.84	493.96	0.6602
	175	284.21	104.88	387.09	0.7342
	190	377.21	87.18	464.39	0.8122
COOH-ATPEI 15wt%	160	375.94	201.15	577.09	0.6514
	175	355.78	134.24	490.02	0.7260
	190	344.90	83.26	428.16	0.8055

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