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Modeling of Multi-Autocatalytic Cure Reactions of An Epoxy/Amine Terminated Polyetherimide/NMA System

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Summary

Amine terminated polyetherimide (ATPEI) as a modifier for epoxy resin was synthesized, then blended with a diglycidyl ether bisphenol A (DGEBA)/nadic methyl anhydride (NMA)/catalyst. A study on cure kinetics and morphology was conducted for a blend of a DGEBA/NMA/Catalyst/ATPEI (5phr) system. In the curing process, two major reactions were observed. Each reaction was identified, and a novel model equation for the cure kinetics is suggested.

Introduction

In recent years, in order to serve high-standard structural and mechanical applications, significant work on epoxy resin modifications work that introduced various thermoplastics, has been undertaken to improve the toughness of epoxy resin. For example, epoxy/polyetherimide (PEI: Ultem 1000) and epoxy/polyether sulfone (PES: Udel) blends have been used to investigate the mechanical properties – especially toughness - of modified epoxy resin while retaining a high glass transition temperature and high mechanical strength[1-4]. However, in the case of applications such as carbon fiber reinforcement composites (CFRC), the absence of reactive functional groups in thermoplastics has diminished the interfacial strength between the phases of thermoplastics and epoxy resin[5, 6].

For the purpose of solving this problem, amine terminated polyetherimide (ATPEI) as an end-group functionalized thermoplastics was introduced. In this study, the cure kinetics of an epoxy system containing the diglycidyl ether of bisphenol A (DGEBA) and nadic methyl anhydride (NMA) as a curing agent, as well as their blends with ATPEI at 5 phr (where phr represents the number of parts of ATPEI per hundred parts of DGEBA-based epoxy resin) were studied. Also, a novel model equation for the cure kinetics was introduced for this blend.

Experimental

Materials

The epoxy system was based on a commercial grade of DGEBA (Grade: YD-128, KUKDO Chemicals Co., Korea) with an average epoxy equivalent weight of 187.5 g/eq. The epoxy blends with ATPEI were cured with NMA as the curing agent and 2,4,6-tris (dimethylaminomethyl) phenol as the tertiary amine catalyst, both supplied by KUKDO Chemicals Co., Korea. 4,4'-(4,4'-isopropyliden diphenoxy) bisphthalic anhydride and m-phenylenediamine, both supplied by Aldrich Co., were used for the synthesis of ATPEI. The chemical structures of materials are shown in **Figure 1**.

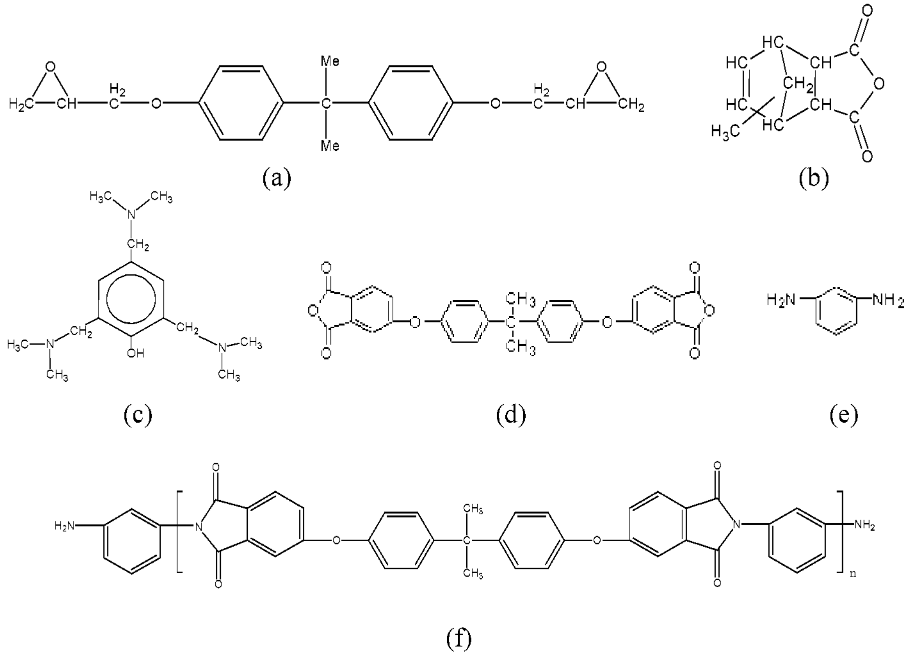


Figure 1. Chemical structures of materials : (a) diglycidyl ether of bisphenol A, (b) nadic methyl anhydride, (c) 2,4,6-tris(dimethylaminomethyl)phenol, (d) 4,4'-(4,4'-isopropyliden diphenoxy) bisphthalic anhydride, (e) m-phenylenediamine, (f) amine terminated polyetherimide (ATPEI)

Synthesis and characterization of ATPEI

Polyamic acid was obtained by the following procedure: m-phenylenediamine was dissolved with anhydrous NMP under a nitrogen atmosphere and reacted with 4,4'-(4,4'-isopropylidene diphenoxy) bisphthalic anhydride at room temperature for 24hr. Synthesized polyamic acid was imidized at 280℃ for 12 hr, resulting in the synthesis of ATPEI. The number average molecular weight was controlled by the Carother's relationship [7], as follows :

$$\overline{X_n} = \frac{1}{2}\frac{(1+r)}{(1-r)}, \qquad (1)$$

where $\overline{X_n}$ is the number average degree of polymerization and r is the stoichiometric imbalance between dianhydride and diamine. The target number for the repeating unit of ATPEI, the molecular weight of which is 592, was approximately 20, so the r value was fitted to 0.95.

Non-aqueous potentiometric titrations were used to determine the molecular weight of ATPEI. The end-point was detected as the maximum of the first derivative for the potential versus volume of titrant used. The end-point was then used to calculate the number of reactive groups in the synthesized ATPEI.

Preparation of blends

To make a 10 wt% solution of ATPEI, ATPEI was dissolved in methylene dichloride, then the solution was mixed with an epoxy prepolymer by using a high-speed stirrer for 2 hr. Next, the solvent was removed in a vacuum dry oven at 80℃ for 24 hr. Stoichiometrically balanced amounts of hardener and catalyst were added to the epoxy resin/ATPEI blend, then mixed by a mechanical stirrer at room temperature for 2 hr.

Differential scanning calorimetry

A differential scanning calorimeter analysis was conducted using Perkin-Elmer Pyris 1. For dynamic heating experiments, four different heating rates were selected: 2.5, 5.0, 7.5 and 10.0℃/min, from 50℃ to 350℃. To obtain the cure rate and the degree of conversion as a function of time, isothermal experiments were conducted at 120, 130, and 140℃. The degree of cure, α (i.e., cure conversion), was determined based on the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty}, \qquad (2)$$

where ΔH_t is the partial heat of reaction at time t, based on the results of the isothermal scan test, and ΔH_∞ is the average total heat of the reaction that was determined based on the results of the dynamic DSC scan. The cure reaction rates were obtained from the cure conversion data as a function of time by taking the derivative of α with respect to time.

Results and discussion

Characterization of synthesized ATPEI

The average number of molecular weight was 11,591 g/mol by the end-point analysis. It corresponded well to the results of the Carother's relationship as the calculated average number of molecular weight was 11,544 g/mol. From the FTIR analysis as shown in **Figure 2(a)**, the N-H absorption band appeared at 3500cm^{-1}, and the imide ring absorption band appeared at 1750cm^{-1} and 720cm^{-1}. The glass transition temperature of ATPEI was 180℃, as shown in **Figure 2(b)**. All of this data indicate

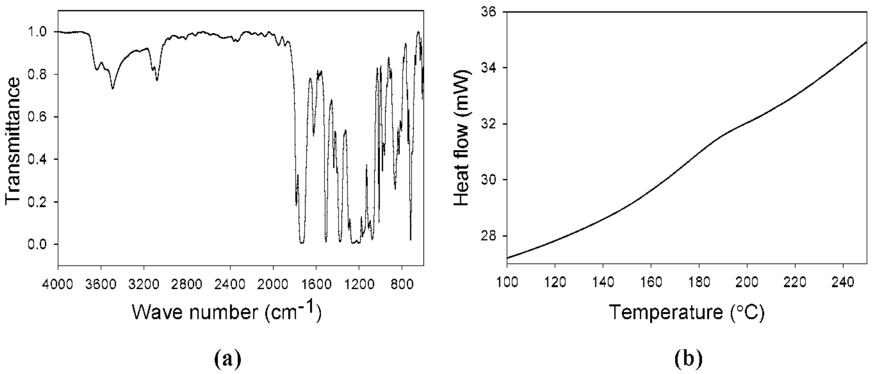


Figure 2. The characterization of amine terminated polyetherimide : (a) FTIR spectrum, (b) DSC thermogram

that ATPEI was polymerized successfully.

The autocatalytic model with a diffusion control factor

The autocatalytic model which is shown in **Eq.(3),** is a general equation based on a phenomenological approach and is used to analyze the cure kinetics of amine-cured epoxy systems and amine catalyzed anhydride-cured epoxy systems[8-14].

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n, \tag{3}$$

where α is the conversion, k_1 and k_2 are the rate constants, m and n are the kinetic exponents of the reactions, and $m+n$ is the overall reaction order.

A rate equation with a diffusion control factor, $f(\alpha)$, is a semi-empirical equation based on free-volume considerations, and the equation has been proposed to explain the retardation of cure reaction, due to the vitrification of epoxy resin, in the later stage of the reaction. The factor $f(\alpha)$ can be expressed as follows:

$$f(\alpha) = \frac{1}{1+\exp(C(\alpha - \alpha_c))}, \tag{4}$$

where C is a parameter of diffusion control and α_c is the critical value of cure conversion.

The final rate equation can be written as follows:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n f(\alpha) \tag{5}$$

The data for the reaction rate versus conversion at 120, 130, and 140℃ of the DGEBA/NMA/catalyst/ATPEI (5phr) blends, i.e., the DNCA system, is shown in **Figure 3**. The solid lines were calculated based on **eq.(5)** and the values for k_1, k_2, m, n, C and α_c are shown in **Table 1**. The calculations followed the Marquardt-Levenberg algorithm.

A modified autocatalytic model

Figure 3 shows that the calculated lines do not fit well with the experimental data, which shows two peaks at each reaction temperature. The two peaks indicate that two reactions were present. To verify the appearance of these two peaks, at 120℃, the DSC curing peaks of the DNCA system were compared with those of our previous study[12], that is, the DGEBA/NMA/Catalyst/PEI (DNCP) system. In the case of the DNCP system, the peak of the reaction rate appeared at approximately 20 min, but, in the case of the DNCA system, the first peak of the reaction rate appeared at about 7 min, and a moderate second peak of the reaction rate appeared at 20 min. Comparing the two peaks of the reaction rate for the DNCA system with those of the DNCP system, as shown in **Figure 4**, the first peak corresponds to the autocatalytic reaction of ATPEI with harder/DGEBA, and the second peak corresponds to the autocatalytic reaction of the catalyst with hardner/DGEBA. As a result, a new modified reaction rate can be expressed as follows:

$$-r = \frac{d\alpha}{dt} = \Sigma r_i = (-r_1) + (-r_2)\,, \qquad (6)$$

where $-r$ is the total reaction rate, and $-r_1$ and $-r_2$ are the partial reaction rates.
Each reaction model can be assumed to the autocatalytic mechanism, so $-r_1$ and $-r_2$ can be written as follows:

$$-r_1 = (k_{11} + k_{12}\alpha^{m_1})(1-\alpha)^n \qquad (7)$$

$$-r_2 = (k_{21} + k_{22}\alpha^{m_2})(1-\alpha)^n \qquad (8)$$

Thus, **eq.(6)** can be rewritten by combining the diffusion control factor, *f(α),* as follows :

$$-r = \frac{d\alpha}{dt} = (k_a + k_{12}\alpha^{m_1} + k_{22}\alpha^{m_2})(1-\alpha)^n f(\alpha)$$

$$= \frac{(k_a + k_{12}\alpha^{m_1} + k_{22}\alpha^{m_2})(1-\alpha)^n}{1+\exp(C(\alpha-\alpha_c))}\text{, where } k_a = k_{11} + k_{21} \qquad (9).$$

Figure 5 shows that the lines calculated by applying **eq.(9)** are fit well with the experimental data at each reaction temperature. The first peak solid line and the second peak (dotted line) were calculated based on **eqs.(7)** and **(8)**, respectively.

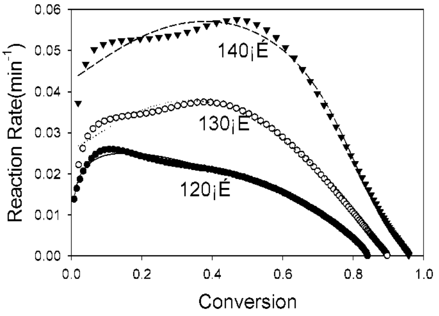


Figure 3. Reaction rate vs. conversion curves for the cure process of DNCA system

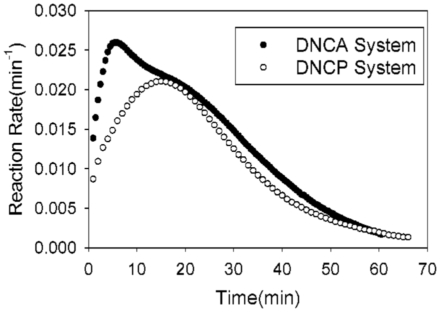


Figure 4. Reaction rate vs. time curves for the DNCP and DNCA systems at 120℃.

All parameters in **eq.(9)** could be obtained simultaneously by applying a nonlinear regression method and the calculated results are listed in **Table. 1.** It shows that the m_1, m_2 and n values for the modified autocatalytic model equation were in the range of 0.27~0.37, 3.09~3.78 and 2.19~2.97 in the DNCA system, respectively. The values of m and n for the general autocatalytic model (**eq.(5)**) were 0.83~0.92 and 1.63~1.83 in the DGEBA/NMA/Catalyst (DNC) system, and 0.86~1.07 and 2.21~2.39 in the DNCP system[12].

For the DNCP system and the DNCA system, the value of n increased compared to that of the DNC system, which may be due to the presence of PEI or ATPEI. For the DNC system and the DNCP system, the values of m were similar, i.e., approximately 1.0. However, for the DNCA system, the autocatalytic reaction by ATPEI was predominant in the early stage of the cure reaction, which is due to the relatively high activation energy of the anhydride curing system[15]. As a result, the values of m_1 were only in the range of 0.27~0.37. After that, the autocatalytic reaction by the catalyst affected the later stage of the cure reaction, so the values of m_2 were larger than those of m or m_1. Due to the presence of the amine functional group of ATPEI, the values of the critical conversion α_c were also larger than those of the DNC system or the DNCA system. This indicates that the values of m_1, m_2 and n were controlled by the reactions of ATPEI with hardner/epoxy, of the catalyst with hardner/epoxy, and of epoxy with hardner, respectively.

The values of m_1, m_2, and n depended strongly on the temperature, indicating that the reaction may be activated at higher temperature. The values of k_a, k_{12}, and k_{22} increased consistently according to temperature, following the Arrehnius relationship as shown in **eq.(10)** :

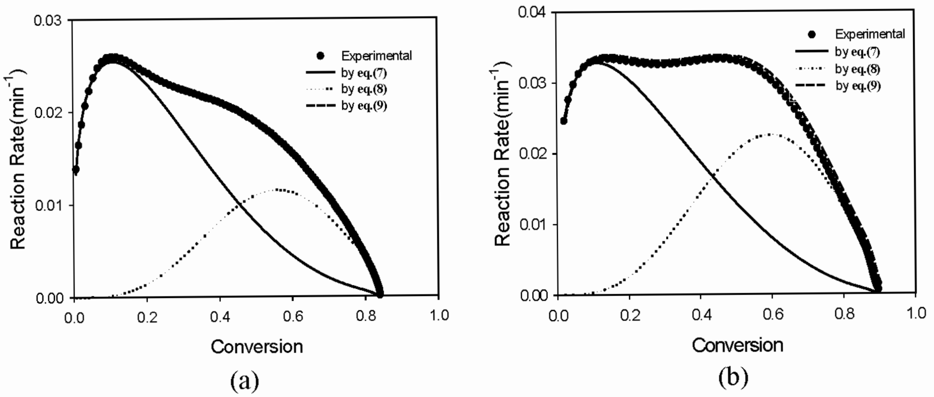
$$k_i = A_i \exp\left(\frac{-E_{a,i}}{RT}\right), \qquad (10)$$

where $i=a$, 11, and 21.

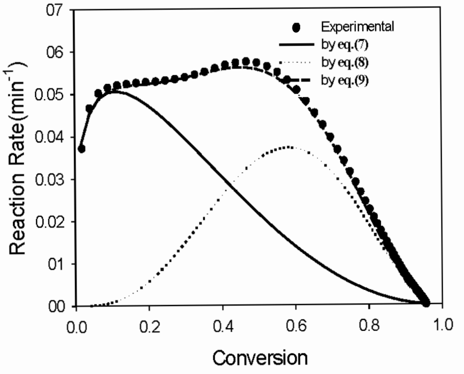
The relationship of ln k vs. (1/T) is shown in **Figure 6**. The levels of activation energy, $E_{a,12}$ and $E_{a,22}$, can be calculated based on the Arrehnius plot. The value of $E_{a,12}$ (53.75kJ/mol) for the epoxy/ATPEI reaction is similar to the values of $E_{a,22}$ (57.41 kJ/mol) for the epoxy/catalyst reaction, but lower than the value (i.e., 97kJ/mol) of the DNC system[12]. It indicates that the reaction of the DNCA system is easier than that of the DNC system.

Table 1. Kinetic constants of autocatalystic models on the DNCA system

T (℃)	m_1 or m	m_2	n	k_a (min^{-1})	k_{12} or k_1 (min^{-1})	k_{22} or k_2 (min^{-1})	α_c	C
General Model Equation(**eq.5**)								
120	0.4327		1.1641		0.0133	0.0384	0.8037	39.36
130	1.2419		1.0560		0.0263	0.1783	0.8573	33.40
140	1.1043		1.5832		0.0430	0.1336	0.8564	15.80
Activation Energy ($E_{a,i}$, kJ/mol· K)					85.13	79.26		
Modified Model Equation(**eq.9**)								
120	0.3707	3.7839	2.9677	0.0093	0.0524	0.8226	0.8270	99.41
130	0.3108	3.5216	2.4297	0.0125	0.0889	1.2367	0.8829	125.8
140	0.2735	3.0913	2.1893	0.0182	0.1160	1.9263	0.9526	230.58
Activation Energy ($E_{a,i}$, kJ/mol· K)				44.88	53.75	57.41		



(a) (b)



(c)

Figure 5. Reaction rate vs. degree of conversion plot for the cure process of DNCA system; experimental data(symbols) and calculated data(lines) at various isothermal conditions ; at 120℃(a), at 130℃(a), and at 140℃(a).

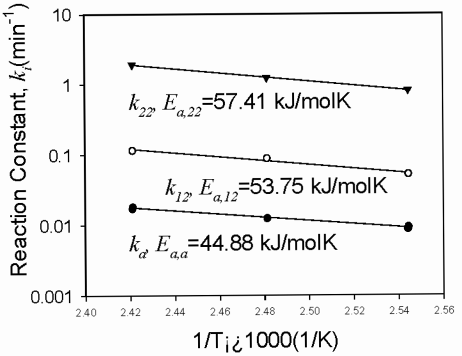
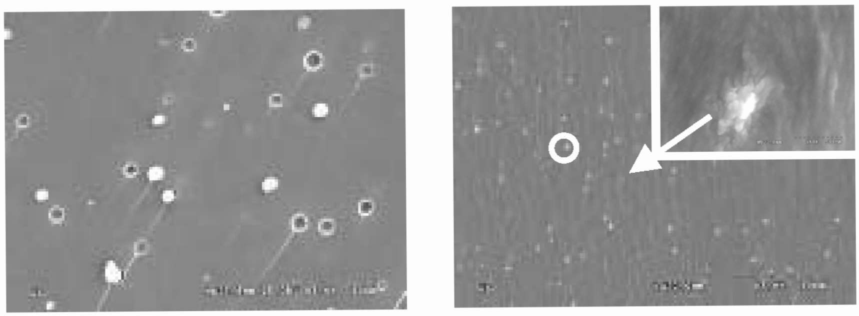


Figure 6. Arrhenius plot of the rate constant for isothermal runs.



(a) (b)

Figure 7. SEM photography of DNCP (PEI 5phr) (a) and DNCA(ATPEI 5phr) (b) systems.

Morphology

The SEM photographs of the fracture surface shown in **Figure 7** show that the morphology of phase separation is clearly distinctive between the DNCP system and the DNCA system. This result indicates that the reaction of the amine groups of ATPEI with epoxy resin caused the small, rough and vague particles in the DNCA system.

Conclusion

The blend of epoxy/NMA/Catalyst/ATPEI showed two peaks in the plot of reaction rate vs. conversion. Due to the presence of amine functional groups, another autocatalytic reaction appeared in the early stage of the cure reaction. By introducing one more autocatalytic term in the general autocatalytic model, the curing kinetics well be analyzed. SEM photographs showed that small, rough, and vague particles in the DNCA system are due to the presence of amine functional groups of ATPEI.

Acknowledgement

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