

에폭시수지/CTBN-ATPEI-CTBN triblock 공중합체/NMA 시스템의 경화거동과 상분리 현상에 관한 연구

김민영*, 이정훈, 황승철, 김원호
부산대학교 화학공학과
(k3613@netian.com*)

A study on the cure kinetics and phase separation of the Epoxy/CTBN-ATPEI-CTBN triblock copolymer/NMA

Minyoung Kim*, Jung Hoon Lee, Seungchol Hwang, Wonho Kim
Department of Chemical Engineering, Pusan National University
(k3613@netian.com*)

Introduction

In recent years, to improve the toughness of epoxy resin in order to serve high-standard structural and mechanical component applications, significant work on epoxy resin modification introducing various thermoplastics has been undertaken. Representatively, epoxy/polyetherimide (PEI : Ultem 1000) and epoxy/polyether sulfone (PES:Udel) blends have been used to investigate the mechanical properties of modified epoxy resin, especially, toughness, while retaining a high glass transition temperature and a high mechanical strength.[1-4] But, by introducing thermoplastics modifier, improvement of fracture toughness are less than that of the case of introducing rubber (e.g. CTBN or ATBN) modifier within epoxy resin.

For the purpose of solving this problem, carboxyl terminated nitrile rubber (CTBN) - amine terminated polyetherimide (ATPEI) - CTBN triblock copolymer (ABA type) as a functionalized thermoplastic was introduced. In this study, the behavior of cure kinetics and phase separation of an epoxy system containing the diglycidyl ether of bisphenol A (DGEBA) and nadic methyl anhydride (NMA) as a curing agent, and their blends with ABA triblock copolymer up to 40wt% were studied. Also, a novel model equation for the cure kinetics was introduced for this blend as a multi-autocatalytic cure reaction system.

Experimental

To make an epoxy resin/ABA triblock copolymer blend, it was dissolved in methylene chloride, and after that, the solution was mixed with an epoxy prepolymer by using a high-speed stirrer for 2hr. Next, the solvent was removed in a vacuum drying oven at 80 °C for 24hrs. Stoichiometrically balanced amounts of hardener and catalyst were added to the epoxy resin/ABA triblock copolymer

blend, and then mixed by a mechanical stirrer at room temperature for 2hrs.

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, 10.0°C/min, from -50°C to 350°C. To obtain the cure rate and the degree of conversion as a function of time, isothermal experiments were conducted at 120°C, 140 and 160°C. Morphological investigation was undertaken on the fractured specimens by using SEM. Where etching was necessary, fractured sample was immersed in methylene chloride and sonicated in a water bath for 1hr, then dried completely before sputter coating.

Results and discussion

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 and amine catalyzed anhydride-cured epoxy systems[5-7].

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

where α is the conversion, k_1 and k_2 are the rate constants, m and n are the kinetic exponents of the reactions, $m+n$ is the overall reaction order, $f(\alpha)$ is a diffusion control factor, C is a parameter of diffusion control, and α_c is the critical value of cure conversion.

In the present study, the data for the reaction rate versus conversion at 120, 140, 160°C of the DGEBA/NMA/catalyst/ABA triblock copolymer (20wt%) blends, i.e., the DNCT system, are obtained and the data at 120°C are shown in Figure 1. The calculated solid line was obtained from eq.(1), i.e., with the diffusion control factor. However, Figure 1 shows that the calculated line does not fit well with the experimental data which show two peaks at 120°C. The two peaks mean that two reactions were present. For the sake of the verification of the appearance of these two peaks, at 120°C, the DSC curing peaks of the DNCT system were compared with those of our previous study[6], that is to say the DGEBA/NMA/Catalyst/PEI (20wt%) system, i.e., the DNCP system. For the case of the DNCP system, the peak of the reaction rate appeared at about 20 min, but for the case of the DNCT the peak were at 5 min and 18 min, the first peak system and the second peak for the case of the DNCT correspond to the autocatalytic reaction of triblock copolymer with (hardner/DGEBA) and the autocatalytic reaction of the catalyst with (hardner/DGEBA), respectively. As a result, a new modified reaction rate can be expressed as follows :

$$\begin{aligned} -r = \frac{d\alpha}{dt} &= (k_a + k_{12}\alpha^{m_1} + k_{22}\alpha^{m_2})(1-\alpha)^n f(\alpha) \\ &= \frac{(k_a + k_{12}\alpha^{m_1} + k_{22}\alpha^{m_2})(1-\alpha)^n}{1 + \exp(C(\alpha - \alpha_c))}, \text{ where } k_a = k_{11} + k_{21} \end{aligned} \quad (2).$$

Figure 2 shows that the calculated line by applying eq.(2) is well fitted to the experimental data at

120°C. All parameters in eq.(2) could be obtained simultaneously by applying a nonlinear regression method and it shows that the m_1 , m_2 and n values for the modified autocatalytic model equation were in the range of 0.5, 2.4~3.0, 3.3~3.5 in the DNCT 20wt% system, respectively. The values of m and n for the general autocatalytic model (eq(1)) were 0.8~0.9 and 1.6~1.8 in the DGEBA/NMA/Catalyst, i.e., the DNC system, and 0.6~1.0 and 1.5~2.6 in the DNCP 20wt% system[6]

The fractured surfaces of various epoxy resin/ABA triblock copolymer blend compositions were examined using SEM. To be obtained a better contrast, some of these surfaces were etched with methylene chloride to remove the ABA triblock copolymer component. Figure 3 shows SEM micrographs of the epoxy/ABA triblock copolymer blend after 120 min of cure time, at a temperature 140°C. In the case of 10wt% and 20 wt% ABA triblock copolymer systems, it shows that the ABA triblock copolymer-rich phase were dispersed, with a clear boundary of phase, that is to say a sea-island structure. In the epoxy/ABA triblock copolymer (30 wt%) blend, it was comprised of two intertwined continuous ABA triblock copolymer and epoxy domains. This morphology is different from that of the epoxy blends with lower contents of ABA triblock copolymer, the two phase domains are grossly separated. In addition, in these two domains the epoxy component is precipitated in the ABA triblock copolymer domain, and vice versa, the ABA triblock copolymer is precipitated in the epoxy-rich domain, that is co-continuous and interconnected globular structure. In contrast, the two interpenetrating continuous domains of the epoxy/ABA triblock copolymer blend were largely thermoplastic and thermosetting in nature, with no apparent precipitation of one component in the other. So, blends of the epoxy resin with ABA triblock copolymer, with thermoplastic concentrations over 30 wt% will be showed large increases in mechanical properties, especially, impact strength and fracture toughness, as showing by earlier works.[8]

Conclusion

ABA triblock copolymer as a modifier for epoxy resin was synthesized, after that; it was blended with a DGEBA/NMA/catalyst. A study on cure kinetics was carried out for the blend of DNCT system. In the cure process, two major reactions were observed and identified by using a multi-autocatalytic model equation for the cure kinetics. For the concentration of ABA triblock copolymer equal to and higher than 30wt%, at 140°C curing, the co-continuous structure can be achieved.

Acknowledgement

This work was supported by the Brain Korea 21 Project in 2003 and grant (No. R05-2003-000-10513-0) from KOSEF

Reference

1. C. H. Bucknall and A. H. Gilbert, Polymer, 1989, 30, 213

2. D. J. Hourston, J. M. Lane and N. A. MacBeath, *Polymer International*, 1991, 26, 17
3. I. Alig, W. Jenniger, *Journal of Polymer Science Part B*, 1998, 36, 246
4. R. J. Varley, J. H. Hodgkin, D. G. Hawthorne, G P. Simon, D. McCulloch, *Polymer*, 2000, 41, 3425
5. C. C. Su, E. M. Woo, *Polymer*, 1995, 36, 2883
6. Y. Choe, W. Kim, *Mocromol. Res.*, 2002, 10, 259
7. M. Kim, W. Kim, Y. Choe, J. M. Park, and I. S. Park, *Polymer International*, 2002, 51, 1353
8. S. K. Siddhamalli, T. Kyu, *Journal of Applied Polymer Science*, 2000, 77, 1257

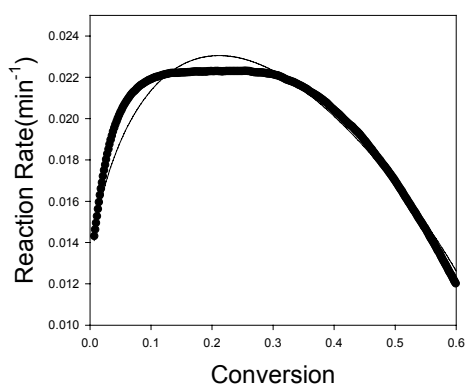


Figure 1. Comparison of experimental data with general autocatalytic cure reaction model predictions : reaction rate, $d\alpha/dt$, versus conversion, a at 120°C, 20 wt% ABA triblock copolymer

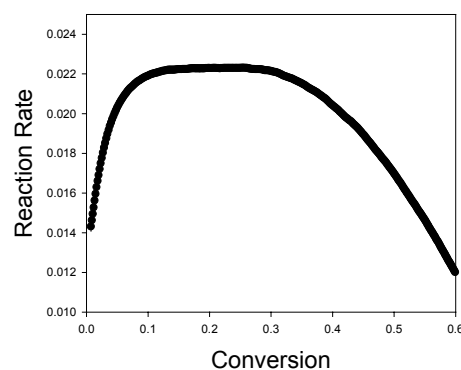


Figure 2. Comparison of experimental data with modified autocatalytic cure reaction model predictions : reaction rate, $d\alpha/dt$, versus conversion, a at 120°C, 20 wt% ABA triblock copolymer

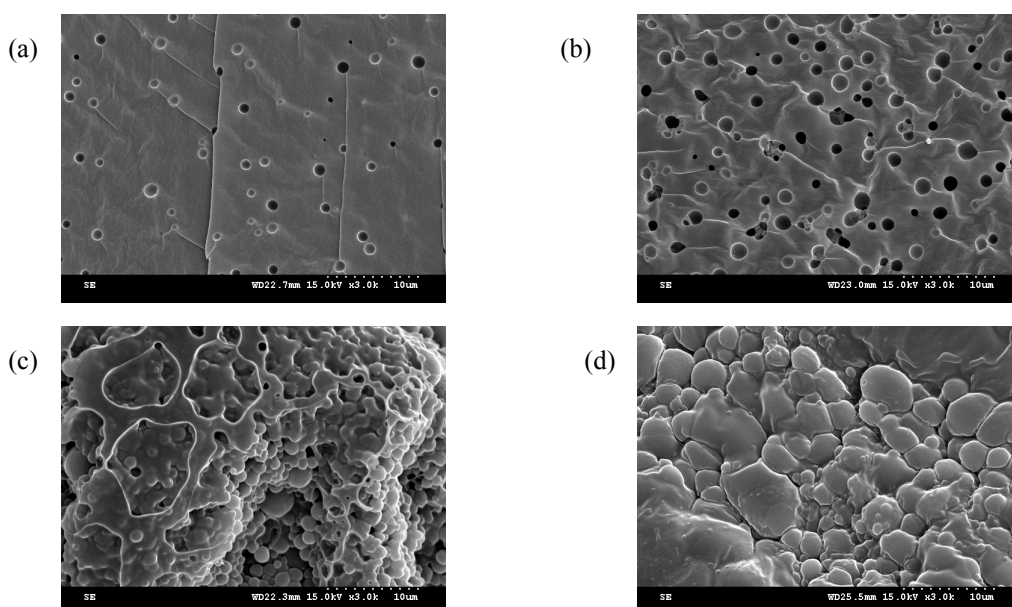


Figure 3. SEM micrographs of methylene chloride etched fracture surfaces for epoxy/ABA triblock copolymer systems : (a) 10 wt% ; (b) 20 wt% ; (c) 30 wt% ; and (d) 40 wt% ABA triblock copolymer systems.