에폭시/우레탄 블렌드의 경화거동과 기계적 계면특성에 관한 연구

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Cure Behaviors and Mechanical Interfacial Properties of Epoxy/Polyurethane Blends

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Key Words : DGEBA, polyurethane, anionic initiator, cure behaviors, mechanical interfacial properties

ABSTRACT

In this work, the blend of diglycidylether of bisphenol A (DGEBA) and modified polyurethane (PU) was prepared and characterized in the cure behaviors and mechanical interfacial properties. The N-benzylpyrazinium hexafluoroantimonate was used as a cationic initiator for cure, and the content of PU was varied within 0~20 phr. The cure behaviors and mechanical interfacial properties were studied by DSC, near-IR, and the critical stress intensity actor (K_{IC}) measurements. Also thermal stabilities were carried out by TMA and TGA analyses. As a result, the cure activation energy (E_a) and the conversion (α) were slightly increased with increasing the PU content, and a maximum value was found at 10 phr PU. The mechanical interfacial properties measured from K_{IC} showed a similar behaviors with the results of conversion. These results were probably due to the increase of the hydrogen bonding between the hydroxyl groups of DGEBA and isocyanate groups in PU.

1. INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fiber composites due to their high modulus and thermal stability. However the highly crosslinked nature of cured epoxy produces an undesirable characteristic, that is, cured epoxies are brittle and show poor resistance to crack growth[1,2].

To enhance their toughness, the modification of epoxy systems by introducing a rubber phase into epoxy networks has been largely studied. In general, an effective improvement in toughness of elastomer-toughened epoxy resins can be achieved when the rubber particles are dispered at the microlevel[3,4]. However, toughness improvements in most elastomer-modified epoxy systems usually result in a significant decrease in the modulus and the glass transition temperature (T_g) of the cured epoxy resins[5].

Thermoplastic polyurethane (PU), because of its high tensile strength, chemical resitance, good processability, and mechanical properties, is being used in many technical applications due to its low stability to the thermoxidative processes[6].

The objective of this work is to study the effect of different weight percentages of PU on the cure behaviors and mechanical interfacial properties of the diglycidyl ether of bisphernol A (DGEBA)/PU blend systems.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

In the system studied, the epoxy resin was the diglycidylether of bisphenol A (YD-128, supplied by Kukdo Chemical Co. of Korea). The epoxide equivalent weight of DGEBA was 185~190 g/eq and its density was 1.16 g/mL at 25 ℃. The polyurethane (PU) supplied by SK Chemicals, and BPH as an initiator was synthesized in our laboratory[7]. The purity and the chemical structure of the product was confirmed by elemental analysis, Fourier transform IR (FTIR), and ^{1}H NMR as shown in Table 1. The DGEBA, PU, and BPH structures are show in Figure 1.

The epoxy resin was heated to melt at 50 ℃ for 30 min in the beaker. After the epoxy resin was melted, the PU was added into the beaker. The content of PU was varied within 0, 5, 10, 15, and 20 phr to neat epoxy. Samples were then degassed in a vacuum oven at 80 ℃. After BPH was added to the mixture, the reactants were homogenized by a stirrer. DGEBA/PU mixture was poured into a stainless mold and the dimensions of a mold were $15 \times 15 \times 0.6$ cm^3. The mixture was degassed in a vacuum oven at 60 ℃ for 10 min before being poured into the mold and cured at 180 ℃ for 2 h and 200 ℃ for 1 h in a convection oven.
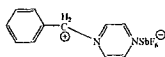
2.2. Cure behaviors

The cure kinetics was evaluated by the measurement of cure activation energy (E_a) with dynamic DSC (Perkin-Elmer DSC-6) method. The samples were placed in aluminum sample pans. The curing process was monitored by DSC between room temperature and 400 ℃ at a heating rate of 10 ℃/min under a nitrogen atmosphere.
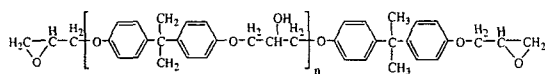
(a) DGEBA
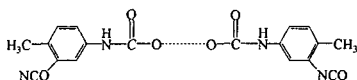
(b) PU

(c) BPH

Figure 1. Chemical structures of DGEBA, PU, and BPH. analysis of BPH.

Also, the conversion (a) of this blend system was investigated with near-IR spectroscopy as a function of PU content. The instrument of choice was a Perstorp Analytical Near-IR System 6500 infrared spectrometer equipped with a lead sulfide detector. The spectrometer was operated in the near-IR region from 4000 to 9000 cm^{-1}.

Table 1 Chemical analysis of BPH

		Results
FT-IR (KBr)		3117,1445, 1157, 756, 705, 657 cm^{-1}
^{1}H NMR (acetone-d$_6$)	Peaks for pyridine ring	9.70~9.67, 9.39~9.38 ppm
	Peaks for aromatic ring	7.72~7.52 ppm
	Peaks for – CH$_2$-	6.23 ppm
Elemen tal analysis	Calculated for C$_{11}$H$_{11}$N$_2$SbF$_6$	C 32.6, H 2.9, N 6.7
	Found for C$_{11}$H$_{11}$N$_2$SbF$_6$	C 32.5, H 3.0, N 6.7

2.3. Mechanical interfacial properties

An Instron tester (Model 125) was used to measure mechanical interfacial properties of the DGEBA/PU blend system. The critical stress intensity factor (K_{IC}), one of the fracture toughness parameters, was described by the state of stress in the vicinity of the tip of a crack as functions of the specimen geometry, the crack geometry, and the applied load on the basis of linear elastic fracture mechanics. K_{IC} could be characterized by a single-edge-notched (SEM) beam fracture toughness test (ASTM E399) in three-point bending flexure. The size of the specimens was $6.0 \times 1.2 \times 0.6$ cm^3 and notches were out using a diamond saw, approximately half the depth of the specimen. A span-to-depth ratio of 4:1 and cross-head speed of 1 mm/min were used.

3. RESULTS AND DISCUSSION

3.1 Cure behaviors

Figure 2 shows the dynamic DSC curves at a heating rate of 10 ℃/min for the cure of epoxy with different contents of PU.

It is considered that in the blend system that includes 10 phr of PU, more cure activation energies are required to constitute highly crosslinked network structures.

Figure 3 and 4 show the transmission NIRS of the DGEBA/PU blend system before and after curing in the wave number of 9000~4000 cm^{-1}, and the peak positions of this blend system are summarized in Table 2. In the NIRS, two characteristic peaks of an epoxide ring can be identified at 6064 and 4528 cm^{-1}. As shown in Fig. 3 and 4, the epoxides, the peaks are detected at 4528 cm^{-1}, react

Table 2. Blend Assignment for Chemical Groups from NIR Absorption Spectra of Cure System

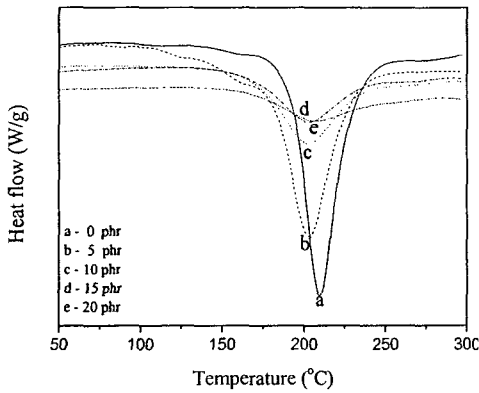| Wavenumber (cm⁻¹)	Chemical group
7,000	-OH overtone and combination bands
6,067	Firsts overtone of terminal (methylene) -CH fundamental stretching vibration
5,990	Phenyl C-H stretching overtone band
5,890	Aromatic CH band
5,240	CH_2, -CH combination band
4,682-4,619	Combination band of the aromatic -CH fundamental stretching
4,530	Conjugated epoxy CH_2 deformation band
4,530	Amine group NH_2

Figure 4. Near-IR spectra of DGEBA/PU after curing.

Figure 2. Dynamic DSC thermograms of DGEBA /PU blends.
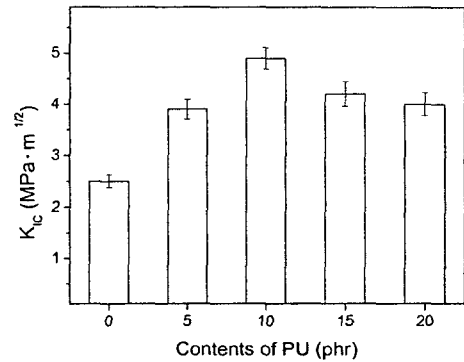
Figure 5. K_{IC} value of DGEBA/PU blends.

during curing.

Then, a number of hydroxyl groups undergo addition reactions with the epoxides, resulting in ring opening and the formation of an increased crosslinking network.

3.2 Mechanical interfacial properties

The degree of adhesion at the interface between PU and matrix can be investigated by the critical stress intensity factor (K_{IC}). The value of K_{IC} is calculated as [9,10]

$$K_{IC} = \frac{P \cdot L}{b \cdot d^{0.5}} \cdot Y \qquad (1)$$

where P is the rupture force, L is the span between the supports, Y is the geometry factor described in ASTM E399, and b and d are the specimen width and thickness, respectively.

Figure 5 shows the mechanical interfacial properties of the DGEBA/PU blend system as a function of PU content. The experimental results show that K_{IC} of the DGEBA/PU blend system are increased with PU content up to 10 phr PU. These results can be attributed to the
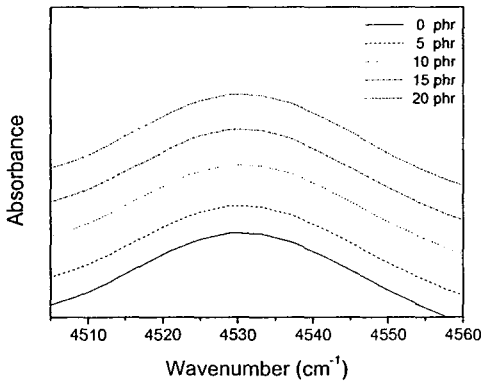

Figure 3. Near-IR spectra of DGEBA/PU before curing.

with the curing agent and make hydroxyl groups produced by ring opening. These characteristic peaks of the epoxy groups decrease considerably in intensity
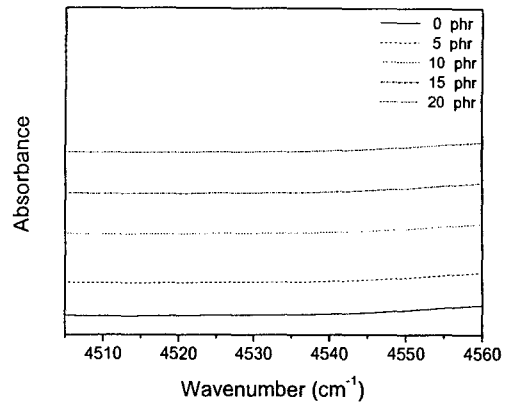
intermolecular interaction, such as hydrogen bonding, in the blends.

The SEM micrograph of neat epoxy resins shows regulative cracks in the fracture surface, indicating a brittle fracture surface, which is accounted for the poor toughness of the neat epoxy resin, as shown in Fig. 6(a). Whereas, the fracture surface of the blends shows a toughness morphology.
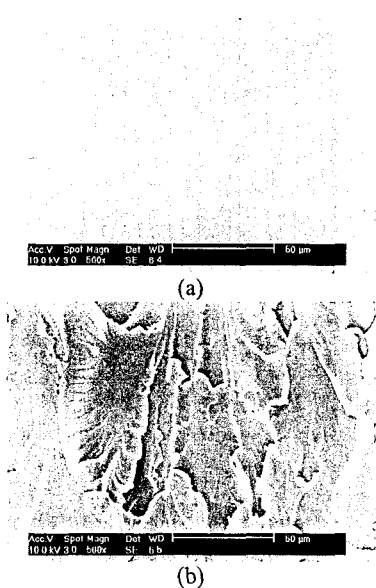

(a)

(b)

Figure 6. SEM images of fracture surfaces, (a) 0 phr, (b) 10 phr.

4. CONCLUSION

In this work, the cure behaviors and mechanical properties of blends of DGEBA/PU were studied using DSC, NIRS, K_{IC}, and SEM.

The cure activation energy (E_a) obtained by dynamic DSC shows maximum value at 10 phr PU content. The mechanical interfacial properties measured in the context of critical stress intensity factor (K_{IC}) also show similar behavior with E_a. These results were probably due to the increase of the hydrogen bonding between the hydroxyl group of DGEBA and isocyanate group in PU.

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