Effect of Reactive Polyurethane on Toughness of Unsaturated Polyester Resin

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ABSTRACT: Unsaturated polyester (UP) resin is one of the major thermosetting resins and is very useful as a matrix resin of composite material for its processibility. UP resin, however, has several shortcomings: it is weak in alkalis, volume shrinkage occurs during the crosslinking reaction of the oligomeric UP resin with a styrene monomer, and it is also brittle. The mechanical properties of UP resin can be enhanced by blending it with various materials. In this study, polyurethane (PU) was used as a modifier to improve the toughness of the UP resin. The effect of the polyol molecular weight as a PU soft segment and the PU contents on the toughness of PU-modified UP resins were studied. A UP/PU polymer network may occur through a reaction between an isocyanate group in the methyl diisocyanate (MDI) and a hydroxyl one in the UP molecules. The maximum toughness was observed at approximately 2 wt % of the PU content. These results can be rationalized by the incorporation of a rubbery PU segment into a brittle UP resin. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 735–740, 2002; DOI 10.1002/app.10169

Key words: unsaturated polyester; polyurethane; polymer network; toughness

INTRODUCTION

Unsaturated polyester (UP) resin is the one of the major thermoset resins that can be easily used in composite processing because of its low viscosity. It has also been used in common composite resins because the curing time and the temperature can be controlled properly according to the amount and kind of additives.[1–4]

UP can be divided into three classes[5]: The first one is *ortho*-phthalic polyester that is produced by a reaction between maleic anhydride and phthalic anhydride with glycols and its cost is less than that of the other two materials. The second is iso-phthalic polyester, which has good mechanical properties and resistance to water and corrosion but is more expensive than are the others. For this reason, it has been used in high-efficiency construction. The last is bisphenolic polyester, which is replaced phthalic acid or anhydride with bisphenol A, and it has excellent water and acid resistance but high cost.

The 5–8% of volume shrinkage of UP is the significant defect during the curing process in addition to weakness in alkalis and brittleness. These problems are solved by blending it with

Table I   Information of Base Polymer, TP-183™

Resin	Type	Styrene Content (%)	Viscosity at 25°C (cps)	Company
Unsaturated polyester	*ortho*-Phthalic	37	784–960	AEKYUNG Chem. Korea

various additives; instantly, the fracture properties of a cured resin improved when blending with reactive liquid rubber[6,7] and the shrinkage of UP crosslinked with styrene is prevented by introduction of a polar low-shrinkage agent: PMMA, PVAc, and PU.[8,9] It has been reported that the thermal properties and elasticity is also advanced by using a polymer network with bismaleimide.[10]

The mechanical properties of UP resin are greatly improved by introducing polyurethane (PU) into the network.[11] Yang and Lee[12] produced an interpenetrating polymer network (IPN) between UP and PU using various compositions and investigated the conversion of it. They explained that there is no effect on the conversion by the change of the IPN composition and initiator. In an IPN, UP has a solvent effect on the PU reaction and, oppositely, PU has a solid effect on the UP reaction.

The two networks are grafted by a reaction between the hydroxyl end group of UP and the isocyanate of PU. This system is the so-called grafted-IPN.[12] Xu and Liu[13] investigated the relations between the toughness and phase-separation behavior of a UP/PU hybrid polymer network (UP/PU IPN). They reported that adequate control of the phase-separation behavior enhances the impact strength and the most effective impact strength is in the case of a ratio of 63/35 of UP and PU content. Ma et al.[14] reported that the tensile strength of an IPN was increased with the UP content and initiator but elongation was decreased after producing an IPN of UP and PU, by investigating the reaction ratio and mechanical properties according to the content of UP and the initiator. They also reported that the peak of tan δ became broad and the T_g shifted to a high temperature. The primary aim of this work was the examination of the influence of the content of PU and polyol used for producing PU on the toughness of the UP/PU network synthesized by introducing rubbery PU into UP.

EXPERIMENTAL

Materials

The UP used in this study was a common TP-183 *ortho*-phthalic resin (AEKYUNG Chem.) with the properties described in Table I. The initiator used for curing UP was methyl ethyl ketone peroxide (AEKYUNG Chem.) of 55% dissolved in dimethyl phthalate. PU was prepared by a reaction between 25% of crude polymeric methyl diisocyanate (MDI) and a difunctional poly(ether polyol) with a molecular weight of 1000, 2000, and 3000 and a trifunctional poly(ether polyol) with a molecular weight of 3000, 4000, and 5000, respectively. The catalyst for synthesizing PU was dibutyltin dilaurate (Aldrich), 25%, dissolved in acetone. The properties of polyisocyanates used in this study are described in Table II.

Table II   Properties of Materials for Reactive Polyurethane

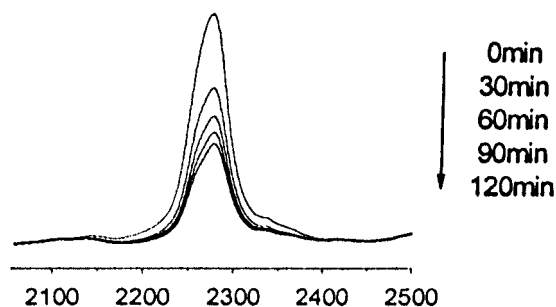| Abbreviation	Trade Name	OH Value (mL KOH g^{-1})	M_w	Functionality	Company
MDI	C-MDI	400	400	2.8	Hankook Polyol
Polyol	PP 1000	113	1000	2	
	PP 2000	56	2000		
	PP 3000	35	3000		
	GP 3000	56	3000	3	
	GP 4000	42	4000		
	GP 5000	31	5000		

Figure 1 Absorbance change of —NCo group for MDI/UP system with reaction time.

UP/PU Network

The preparation of a UP/PU polymeric network is a two-step reaction: UP and MDI were kept at ambient temperature for a sufficient time for the reaction between the hydroxyl end group of UP and the isocyanate of MDI. The curing reaction occurred when an initiator was added at 80°C for 1 h, with subsequently stirring for 60 s. At this time, the isocyanate index was fixed at 2 during the reaction. After the reaction, the UP/PU network was kept at normal temperature for 24 h and tested for its mechanical properties.

Characterization of UP/PU Network

For characterization of the UP/PU polymer network, an FTIR spectrophotometer (Jasco International Co., Jasco FT/IR-620) was used at 2/cm^2 for estimating the degree of the reaction. The change of the viscosity in the reaction time was examined by a rheometer (Parr Physica Co., UDS-200). The rotational test was performed at 100 L/s at ambient temperature using a corn and plate.

Toughness of UP/PU Network

To estimate the toughness of the samples, a universal test machine (Instron Co., M 4465) was used according to ASTM D-638 at a speed of 5 mm/min to test for the tensile strength. The test samples were prepared by casting in a Teflon mold and the mean value of five samples was recorded.

Thermal Properties

By using thermal gravimetry analysis (TGA; Rheometric Co., STA 1500), the presence of the unreacted monomer after the curing reaction was observed at a heating rate of 10°C/min from 25 to 1000°C.

RESULTS AND DISCUSSION

UP/PU Network Formation

The molar ratio of the absorbed molecular species was studied by FTIR using the Beer–Lambert law as shown below:

$$A = \varepsilon c l$$

In this equation, A is the absorbance; ε, the molar extinction efficient; c, the concentration of the absorbed molecular species, and l the thickness of the tested samples. Lee and Yang[15] suggested the degree of the reaction according to the change of the reacted materials' viscosity with the reaction time. Jin and Meyer[16] also elucidated the degree of the reaction according to the decrease of the absorbed peak evaluated by FTIR.

The change of the absorbed peak is shown in Figure 1 according to the time shift. The MDI peak at 2275 cm^{-1} indicates the reaction with the hydroxyl end group of UP because it does not disappear with other functional groups. As the time increases, the peak of the isocyanate of MDI decreased slightly. This phenomenon is caused by the chemical reaction between the isocyanate end group of MDI and the hydroxyl end group of UP.

The change of viscosity with time of UP, MDI, and the reacted materials between MDI and UP were observed by a rheometer and are shown in Figure 2. In the case of MDI, there is no remarkable change even in a sufficient reaction time. It seems that this is caused by the volatilization of the styrene monomer used for the diluents. It was observed that the change of viscosity is obvious just at the beginning of the reaction. This proved
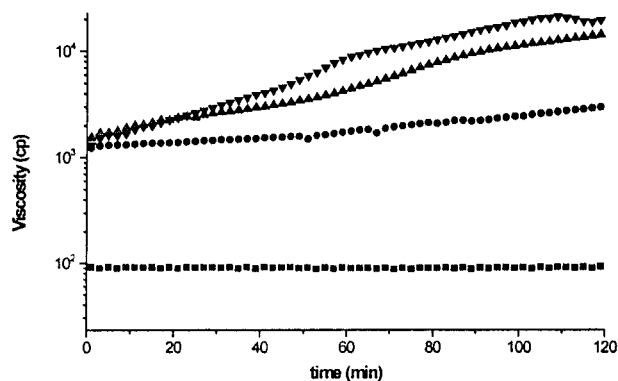

Figure 2 Viscosity behaviors of materials at room temperature: (■) MDI; (●) UP; (▲) MDI?UP = 1/1; (▼) MDI/UP = 2/1.
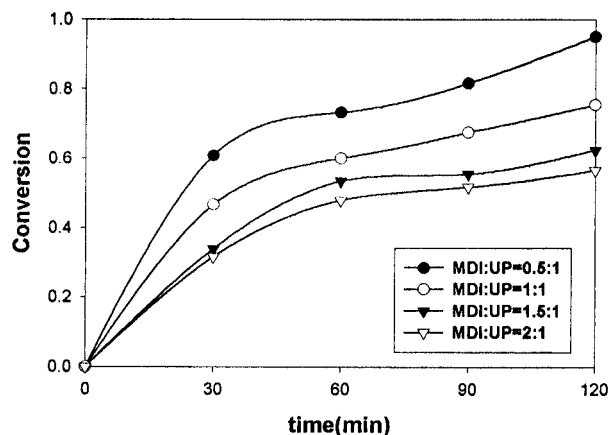
Figure 3 Conversion of different MDI/UP molar ratios.

that the end group of UP was converted into an isocyanate group. The polymerization conversion is determined by the change of the absorbed peak in FTIR characterization.[17,18] The conversion of the respective time is given by

$$X = C_0 - C/C_0$$

where X is the conversion rate; C, the absorbed molecular species; and C_0, the absorbed initial molar ratio of the molecular species. By using the Beer–Lambert law, the conversion according to time is given in Figure 3.

At a decreasing molar ratio of isocyanate, the initial slope increased (Fig. 3). This is caused by the decreasing rate of isocyanate being so fast, because the functional groups related to the reaction are just a few. It is suggested that the conversion, when the molar ratio of MDI and UP of 2/1 is over 50%, is caused by the reaction between the water included in UP and MDI. Also, the conversion that could not reach 100% in the ratios of 0.5/1 and 1/1 was attributed to that MDI could not react with the hydroxyl end group of UP having a high molecular weight. It was observed that the initial reaction rate was very fast as the MDI molar ratio decreased. The polymer network was prepared using a molar ratio of 2/1, which still retained half of the isocyanate content in consideration of the reaction site of polyol with the hydroxyl group when MDI introduced into the end group of UP reacted with polyol.

The UP/PU polymer network was prepared by a curing reaction between polyol and the end group of UP. This reaction was confirmed by the functional group peak of FTIR given in Figure 4.

(A) is UP before the reaction, (B) is UP reacted with MDI, and (C) is MDI/UP reacted with polyol. From spectrum (C), the isocyanate peak at 2275 cm^{-1} caused by UP reacting with MDI disappeared due to the reaction between isocyanate and the hydroxyl group of the polyol. On the other hand, spectrum (A) of 3620 cm^{-1} of the hydroxyl group also disappeared by the reaction with the MDI of isocyanate. So, it can be concluded that the polymer networking reaction was completed.

Toughness

The term 'toughness' can be observed as the total energy of the polymer fracture experiment and also as an area of the stress–strain curve in the tensile test results.[19] Actually, we estimated the relative value of the area for each stress–strain curve for convenience. To improve the toughness, the introduction of low molecular weight or rubbery materials, for example, acrylic rubbers and SBR, into the base resin and chemical modification is also an effective method.[20,21] We used various PUs since polyol and isocyanate are important to determine the structure and mechanical properties of PU resin. Also, it is well known that the chemical structure, molecular weight, OH value, and functionality (f) are greatly affected by the mechanical properties of a resin.[21] In this study, the tensile test was performed to determine the mechanical properties of the UP/PU polymer network. The test specimen was prepared by reaction between polyols of different molecular weights and MDI, each reacted with UP. The effect of the polyols are given in Figures 5 and 6.
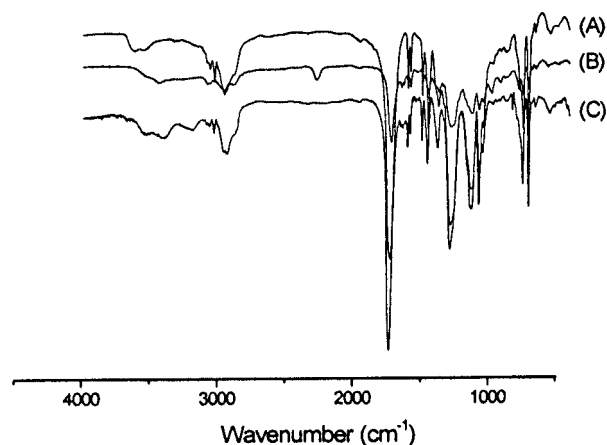

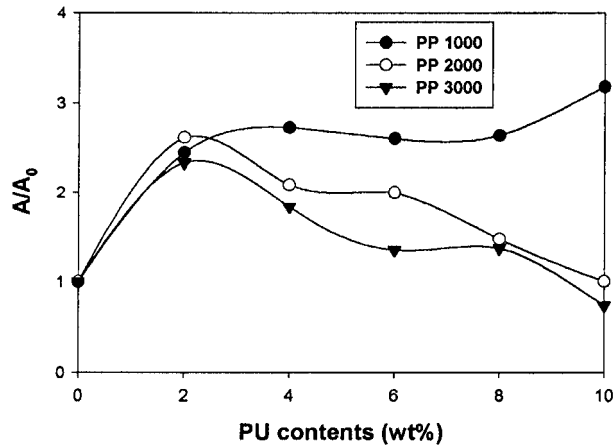**Figure 4** FTIR spectra of samples: (A) UP; (B) MDI/UP; (C) UP/PU system.

Figure 5 Molecular weight effect of difunctional polyol on toughness.

In Figure 5, the area ratio (Ar = A/A_0) is an indication of the relative toughness. The value of A_0 is the area of the stress–strain curve for UP only and A is the area of the stress–strain curves for UP with PU as a modifier. The value of Ar is increased in the case of UP (M_w = 1000) with 2 wt % of PU for all cases, that is, PP 1000, PP 2000, and PP 3000. But it gradually decreased the value of Ar with the addition of PU except for PP 1000. It is elucidated that the most sufficient molar ratio of MDI in polyurethane is 2 wt % when it is reacted with UP resin. Unreacted MDI remains in the system with over 2 wt % of PU contents, which can also react with polyol and form independent PU domains. The mobility of polyol and unreacted MDI was restricted by increasing molecular weight, that is, the reactive site that can
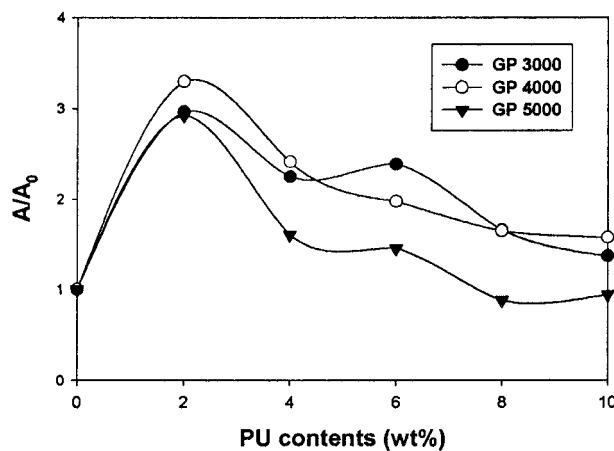

Figure 6 Molecular weight effect of trifunctional polyol on toughness.

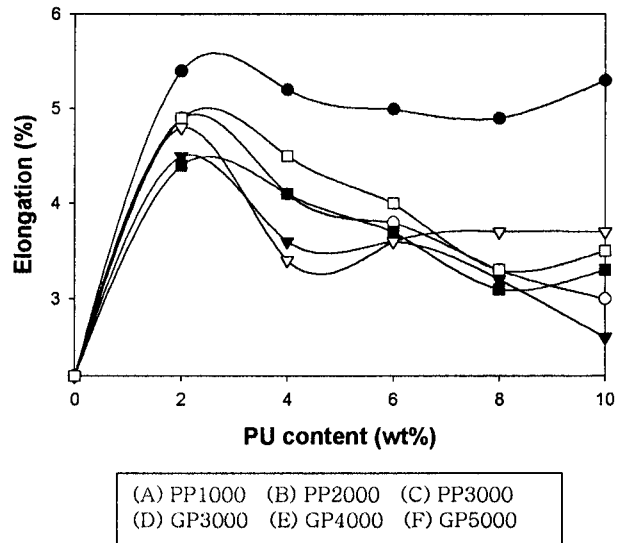(A) PP1000   (B) PP2000   (C) PP3000
(D) GP3000   (E) GP4000   (F) GP5000

Figure 7 Effect of polyol on elongation (%) of UP/PU polymer network.

react with MDI decreased with an increasing molecular weight, so the mechanical properties became worse. It is effective to increase the toughness with PP 1000 for all experimental formulations because of its proper molecular weight.

In Figure 6, similar results are observed as those of Figure 5; the maximum value of Ar was estimated in the case of 2 wt % of PU. Figure 7 implies that the elongation of UP reacted with each PU with different polyols. It was also proved that the elongation was increased obviously in the case of introducing 2 wt % of PU into the resin. This value is over twice as high as for the case of UP. It is elucidated that the elongation has a tendency of toughness (Ar). This behavior was also attributed to the unreacted polyol.

Thermal Analysis

The thermal degradation temperature, the stability, and the chemical composition of the specimen can be evaluated by changes of the sample weight according to the temperature. The TGA results of the specimen are given in Figure 8, which shows the UP/PU system using PP 2000 with both 2 and 10 wt % of PU. The results show that the thermal degradation temperature became lower because of the presence of unreacted monomer; in addition, there is a significant difference in residues. These results are similar to the relative toughness that became lower because of the unreacted polyol effect on the toughness of the UP/PU system when the content of PU is 10 wt %, as mentioned previously.
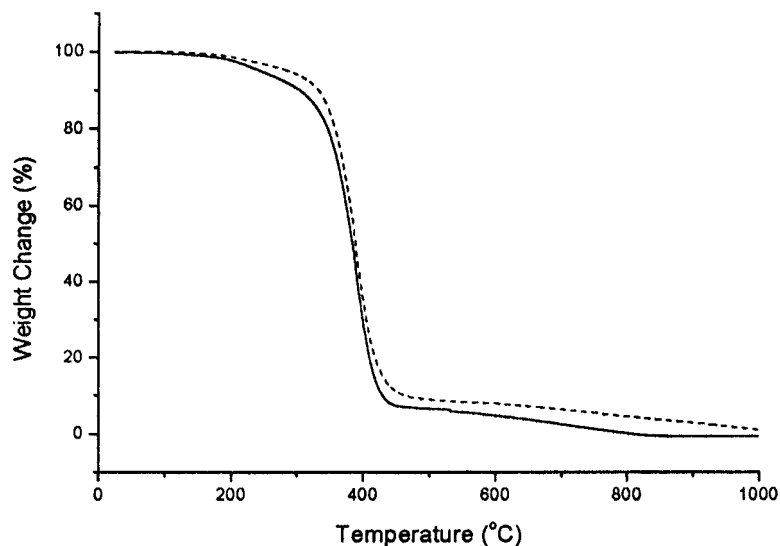
Figure 8 TGA thermograms of PU-toughened system: (—-) PU/UP = 2/98; (—) PU/UP 10/90.

CONCLUSIONS

The introduction of PU into the end group of UP in the polymer network to improve the toughness of UP was investigated. The effect of polyol on the toughness and reactivity of UP and MDI was also studied. The maximum toughness was observed in the case of 2 wt % of PU included; this result was caused by the network formation of UP with PU. Above 2 wt %, the toughness value deteriorated because of the unreacted remains of polyol. In the case of difunctional polyol, polyol cannot participate in the network reaction effectively as the molecular weight increases, so the toughness decreased because the chain mobility decreased. But in the case of trifunctional polyol, it was suggested that toughness was not affected considerably by the molecular weight.

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