

Interpenetrating polymer network of polyurethane and unsaturated polyester: mechanical properties

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Interpenetrating polymer networks (IPNs) of polyurethane (PU) and unsaturated polyester (UP) were prepared in this study. The mechanical properties of the IPNs were determined to relate to their structure. In order to improve the mechanical properties of the resultant IPNs, it was found that the $-OH$ group present in the UP should be employed to react with some isocyanate-terminated PU prepolymer. Thus, the PU and UP were, in fact, interpenetrated with each other and chemically bonded through a grafting reaction to form the graft-IPN. The tensile strength of the IPNs was increased to a maximum value and then decreased as the PU content increased. The Izod impact strength and fracture energy of the IPNs increased more or less with an increase of the PU content, depending on the types, chain length of polyols used in the PU and the degree of the grafting reaction between PU and UP.

1. Introduction

Unsaturated polyester resin (UP) is widely used for coating, moulding and glass fibre reinforced plastic (FRP) composite [1-3]. Its usage arises from low viscosity, good processing capability and outstanding physical behaviour. Because the applications of UP are gradually increasing, the studies on curing kinetics, toughening techniques, effects of initiators, cross-linking agents and catalysts on the properties have been performed in recent years [4-8]. A mathematical model was proposed for the curing behaviour of the sheet moulding compound [8].

After the interpenetrating polymer network (IPN) structure was proposed in 1969 [9], it was proposed to use PU elastomer to modify UP with IPN structure [10-12]. The mechanical properties of the resultant PU/UP IPN were found to be worse than the primary UP polymer. It was explained that the reaction rates of UP (by free radical mechanism) and PU (by condensation mechanism) differed and therefore resulted in an imperfect network structure of PU/UP system and decreased its mechanical properties [13, 14].

Polyether-type polyurethane (PU (PPG)) and polyester-type polyurethane (PU(PBA)) with different molecular weights were used to modify UP as a copolymer or a graft-IPN structure through bulk and simultaneous polymerization. The tensile strength, impact strength and fracture energy were measured to investigate the dependence of these mechanical properties on the change of the PU content in the composition. The reaction between the $-OH$ group of UP and the $-NCO$ group of PU prepolymer were taken into consideration for this study. The effect of this linkage structure between PU and UP was investigated and will be discussed in this paper.

2. Experimental procedure

2.1. Material

The materials used and their designations in this study are listed in Table 1. Unsaturated polyester resin (UP) with 38 wt % styrene monomer was kept in a refrigerator below $10^{\circ}C$. Polyols (PPG 400, 700, 1000; PBA 500, 700, 1000, 2000), chain extender (1,4-BD or DEA) and cross-linking agent (TMP or TEA) were degassed overnight under vacuum and at $80^{\circ}C$ before they were used. The 1,4-BD/TMP mixture with equivalent weight ratio of 4/1 was employed.

2.2. Determination of the $-OH$ group in UP

The $-NCO$ content of pure MDI was first titrated, then excess MDI at W_1 g, was added into W_2 g UP at room temperature and mixed vigorously in the flask. The reaction was continued for 24 h to make sure a complete reaction occurred, the residual $-NCO$ content was titrated and the equivalent of $-OH$ group in UP can be determined through calculations.

2.3. Preparation of PU/UP copolymer and graft-IPN

PU prepolymers were prepared by the reaction of polyols and MDI. The equivalent ratio of MDI/polyol was set at 2/1. Reactions were carried out in a reaction kettle at $60^{\circ}C$ for 5 h under dry nitrogen.

For preparation of PU/UP copolymers and graft-IPNs, suitable amounts of PU prepolymer and UP were mixed with 0.5 wt % cobalt catalyst (based on UP). The mixture was vigorously stirred for 0.5 min and then degassed. One wt % MEKPO was added as initiator. The mixture was agitated and degassed

TABLE I Material and source

Designation	Description	Source
UP	Unsaturated polyester containing 38 wt % styrene monomer. Mw = 2000 viscosity: 300–500 c.p.s.	CHANG CHUN Co.
PPG400	Poly-(oxypropylene) glycol Mw = 400	CHIUN GLONG Co.
PPG700	Poly-(oxypropylene) glycol Mw = 700	CHIUN GLONG Co.
PPG1000	Poly-(oxypropylene) glycol Mw = 1000	CHIUN GLONG Co.
PBA500	Poly-(tetramethylene adipate) glycol. Mw = 500	TAI GIN Co.
PBA700	Poly-(tetramethylene adipate) glycol. Mw = 700	TAI GIN Co.
PBA1000	Poly-(tetramethylene adipate) glycol. Mw = 1000	TAI GIN Co.
PBA2000	Poly-(tetramethylene adipate) glycol. Mw = 2000	TAI GIN Co.
MDI	4,4' Diphenyl methane diisocyanate	
1,4-BD	1,4 butanediol	HAYASHI PURE CHEM Co.
TMP	Trimethylol propane	HAYASHI PURE CHEM Co.
MDEA	Methyl diethanol amine	MERCK CHEM. Co.
TEA	Triethanol amine	MERCK CHEM. Co.
MEKPO	Methyl ethyl ketone peroxide	CHANG CHUN Co.
–	Cobalt-naphthanate	CHANG CHUN Co.

again and casted onto an aluminium mould at 70 °C and pressed under 140 kg cm⁻² pressure for 2 h. Finally, the samples were post-cured at 90 °C for 8 h. Samples were removed and kept in a desiccator at a relative humidity of 50% for at least 3 days before their properties were determined. For preparation of PU/UP graft-IPNs, the process was similar to that described above except that an excess of PU prepolymer was added at first and then suitable amounts of chain extender and cross-linking agent for PU must be added for complete reaction.

2.4. Testing method

Infrared analysis (IR) was carried out on infrared spectrophotometer (Hitachi 273-30). The reaction mixture was directly coated onto a KBr pellet and covered with another KBr pellet. IR measurements were carried out in the wave number range 400–4000 cm⁻¹ to identify the reaction between the –NCO group of PU prepolymer and the –OH group of UP resin.

Stress–strain tests were performed by using an Instron TM-SM universal test unit according to ASTM–1708–79 procedure at a crosshead rate of 10 mm min⁻¹.

The Izod impact test was carried out according to ASTM–D256 procedure. The specimen dimensions were 6 cm × 1.2 cm × 0.8 cm with a 45° notch.

The fracture energy, J_{IC} was measured using Compact-Tension Specimen (CTS). The J_{IC} value can be calculated as follows:

$$J_{IC} = (A/Bb)f(\alpha/w)$$

where A and w are area under load, crack length and specimen width, B and b are specimen thickness and initial uncracked ligament ($b = w - a$), a is crack length $f(\alpha/w) = 2(1 + \alpha)/(1 + \alpha)$, and $\alpha = [(2a/b) + 2(2a/b) + 2] - (2a/b + 1)$. In this experiment, $a = 1.2$, $b = 1.2$, $\alpha/w = 0.5$, $f(\alpha/w) = 2.265$. A sharp pre-crack was made with a razor blade before the test, the specimen were tested on a screw driven Instron machine at a crosshead rate of 0.5 cm min⁻¹.

3. Result and discussion

3.1. Infrared spectra analysis

Infrared spectra (IR) for the mixture of polyurethane (PU) prepolymer and unsaturated polyester (UP) at the initial and final stage through the reaction period are illustrated in Fig. 1. It can be observed that the IR absorption peaks of isocyanate group (–NCO) at 2270 cm⁻¹ and hydroxyl group (–OH) at 3540 cm⁻¹ reduce from the initial stage to the final stage of the reaction. This is evidence that the hydroxyl-terminated group in UP had reacted with the –NCO group in PU prepolymers. Therefore, as the –NCO content in PU prepolymers is below stoichiometric equivalent of the –OH group in UP, the copolymer of PU/UP will be formed. Whereas the excess of PU prepolymer present in the mixture, the grafted interpenetrating polymer network (graft-IPN) will be formed through the addition of suitable amounts of PU chain extender (or cross-linking agent) and catalyst of UP resin.

3.2. Tensile strength

The tensile strength of these copolymers and graft-IPNs of PU/UP is shown in Figs 2–4 with various PU content in the composition. The breaking marks on curves indicate the stoichiometric equivalent of the –NCO group in the PU and of the –OH group in UP for the system. Thus, the PU content below this breaking mark shows a copolymer structure of the system, whereas beyond this mark, it shows a graft-IPN structure. The tensile strength values for the PU/UP system, as in copolymer cases, with the PU based on PPG and PBA are shown in Figs 2 and 3, respectively. They exhibit a similar increasing trend with an increase of PU content to a maximum value and then decrease with further increase of PU content. The shorter chain length of polyols is used in PU, the higher the tensile strength behaves, obviously as the result of the participating strength of PU in the UP main chains. Therefore the polyester-type (PU(PBA)) with short chain length in polyol which has inherently higher strength than the polyether-type (PU(PPG)), is favoured for increasing the tensile strength of the

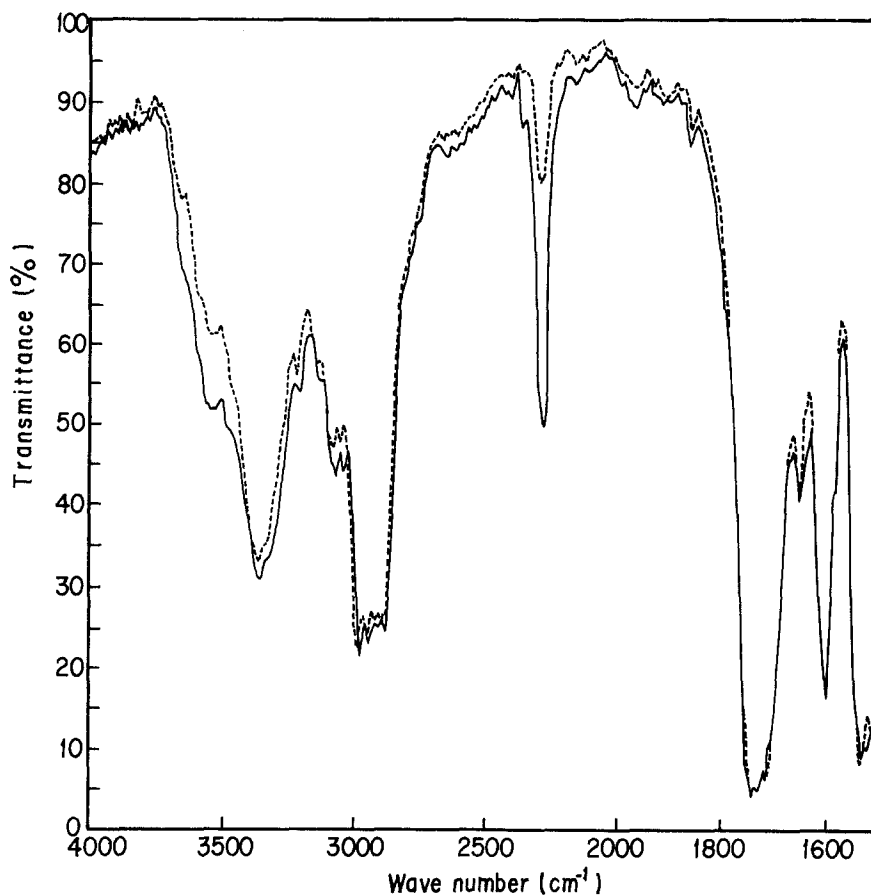


Figure 1 Infrared spectra for mixture of PU(PPG400) prepolymer and UP resin at: (—) initial stage and (---) final stage during reaction.

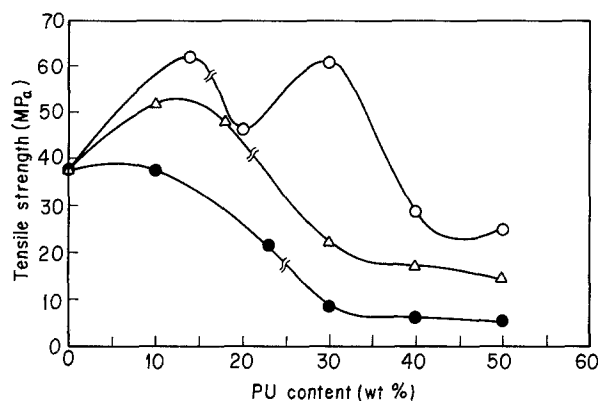


Figure 2 Tensile strength versus PU content plot for: (—○—) PU(PPG400)/UP; (—△—) PU(PPG700)/UP and, (—●—) PU(PPG1000)/UP.

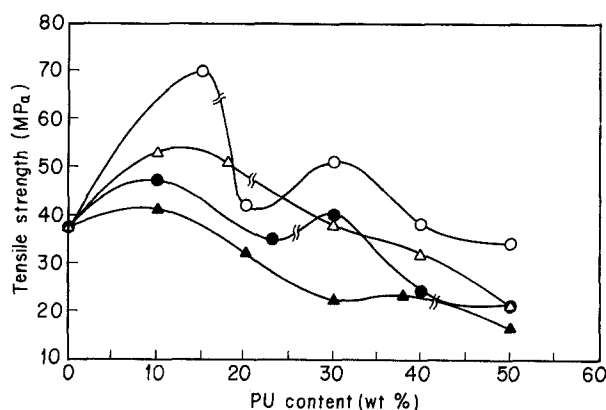


Figure 3 Tensile strength versus PU content plot for: (—○—) PU(PBA500)/UP; (—△—) PU(PBA700)/UP; (—●—) PU(PBA1000)/UP and (—▲—) PU(PBA2000)/UP.

PU/UP copolymer structure. Thus, the formulation of accurate stoichiometric equivalent between the -NCO and -OH groups in the system is expected to have higher tensile strength than that of neglecting the terminated -OH group of the UP in the system, as shown in Fig. 4.

In the graft-IPN cases of PU/UP system, the tensile strength reaches another maximum value as the low molecular weight of polyols (i.e., PPG 400, PBA 500) was employed in the system. The reason for the occurrence of the maximum tensile strength can be explained by the effect of interpenetrating network structure with higher cross-linking density in PU. Hereof, the graft-IPN of PU/UP system possess three bonding

structures. First, the copolymerization between PU and UP. Second, the PU prepolymer which has one -NCO end reacting with chain extender or cross-linking agent, and the other -NCO end reacting with -OH group of UP to form grafting structure. Third, the PU prepolymer reacting only with chain extender and cross-linking agent to form PU network structure. These structures give a intimate bonding and interpenetrating network structure between PU and UP to result in a maximum tensile strength.

If the terminated -OH group at the end of UP was neglected, the incorrect stoichiometric ratio between -OH group and -NCO group (i.e., excess of -OH group) could result in a serious decrease in the tensile

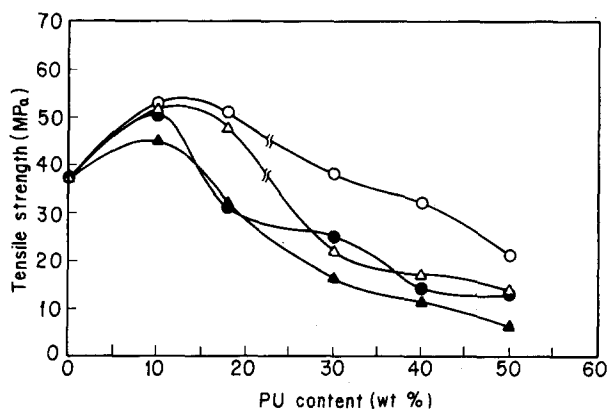


Figure 4 Tensile strength versus PU content plot as neglecting $-OH$ group in UP: (●) PU(PBA700)/UP; (▲) PU(PPG700)/UP, and as counting $-OH$ group in UP: (○) PU(PBA700)/UP, (△) PU(PPG700)/UP in synthesis.

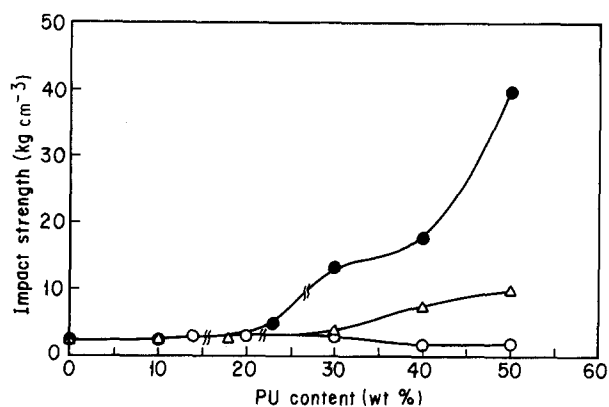


Figure 5 Impact strength versus PU content plot for: (○) PU(PPG400)/UP; (△) PU(PPG700)/UP and, (●) PU(PPG1000)/UP.

strength as shown in Fig. 4. It is because the incorrect stoichiometric ratio leads thereafter to decrease the molecular weight of PU. Besides, there are residual unreacted chain extender and cross-linking agent trapped in the system, which may play a role as plasticizer to decrease the tensile strength.

In general, not only PU(PBA) series containing ester group contributed better compatibility with UP, but the neat PU(PBA) also has higher tensile strength than the PU(PPG). Therefore when the PU content has further been increased beyond the content that provided maximum tensile strength, the reducing rate in tensile strength of PU(PBA)/UP system is less than that of PU(PPG)/UP system as with an increase of PU content.

3.3. Impact strength

The toughening mechanism of impact test and fracture energy measurement should be mentioned before discussing the impact strength of the PU/UP system. The difference between impact test and fracture energy measurement is the shear rate in fracturing process. For high-shear rate fracturing test (i.e., impact test), from previous research [15, 16], the flexibility of molecular chains in continuous phase dominates the toughening mechanism. For low-shear rate fracturing test, suitable amounts of rubber particles distributed in the matrix will terminate a crack and then re-initiate a new crack to absorb the fracture energy. Therefore, phase-separated morphology with suitable amounts of dispersed rubber particles in the matrix dominates the toughening mechanism.

As shown in Figs 5 and 6, both PU(PBA)/UP and PU(PPG)/UP systems have little improvement in impact strength as in copolymer cases. Whereas the impact strength is much improved continuously with the increase of PU content in the graft-IPN cases. This phenomenon occurs because the urethane has been linked to the UP chain structure, which brings the soft characteristic of the PU into the rigid network structure. Thus, the impact strength increases with the increase of PU content resulting from the improved ductility of the matrix. As from the dynamic mechanical analysis for the Graft-IPN cases, the glass trans-

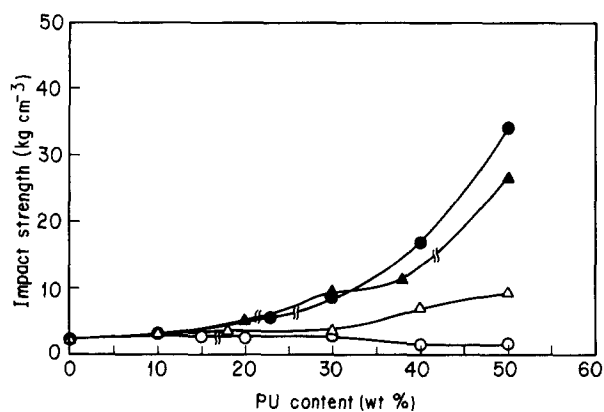


Figure 6 Impact strength versus PU content plot for: (○) PU(PBA500)/UP; (△) PU(PBA700)/UP; (●) PU(PBA1000)/UP and (▲) PU(PBA2000)/UP.

ition temperature (T_g), shifts toward a lower temperature. It is also evident that the flexibility of matrix increases, and therefore results in the improvement of impact strength. At the same time, for the PU(PPG)/UP system, phase separation occurs gradually with the increase of PU content from scanning electron microscopy (SEM). Thus, it is concluded that the rubber particles are composed of almost neat PU(PPG) and the matrix of UP with some portion of PU(PPG). On the other hand, the better compatibility between PU(PPG) and the rigid styrene chain in UP also contributes effectively to the toughening of PU(PPG)/UP system. Thus, the effectively toughened and strong linkage of rubber particles linked to the matrix leads to the higher impact strength of PU(PPG)/UP system.

Because the polyester-type PU is considered to have higher compatibility with the similar ester-group dominated matrix in UP rather than with the rigid styrene chain, the PU(PBA)/UP system appears consequently a continuous one-phased system. This also shows that the flexibility of the system is increased with an increase of PU content. Hence, the high impact strength, as shown in Fig. 6, is predictable with the toughening mechanism which was mentioned before.

When the PU/UP was synthesized without considering the presence of the -OH group at the end of UP, the impact strength, as shown in Fig. 7, can not be enhanced with introduction of PU into UP structure. This phenomenon has resulted from the low molecular weight of PU formed with excess -OH-terminated and therefore resulted in loss of strength of the matrix.

3.4. Fracture energy

As mentioned before, the separated phase morphology, with sufficient rubber particles dispersing in the matrix, will have higher fracture energy. From Fig. 8, the fracture energy of PU(PPG)/UP system increases with the increase of PU content. The PU(PPG 700)/UP has exceptionally higher fracture energy than the others. The morphology from SEM is illustrated as many rubber particles dispersing in the matrix of the PU(PPG 700)/UP system. Hence, at low-shear rate fracturing, the crack propagation is stopped by the rubber particles. The fracture energy is consumed by the deformation and/or breaking of the rubber particles and the consequent re-initiation of a new crack in the matrix. For the PU(PBA)/UP system it has been mentioned before that one-phased morphology has resulted. Thus, the fracture energy for the PU(PBA)/UP system is mainly contributed to by

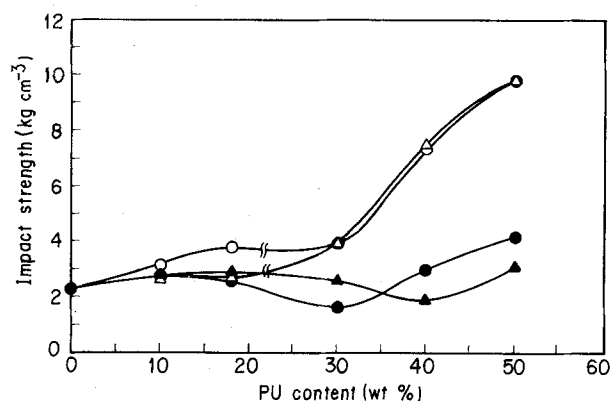


Figure 7 Impact strength versus PU content plot as neglecting -OH group in UP: (●) PU(PBA700)/UP; (▲) PU(PPG700)/UP, and as counting -OH group in UP: (○) PU(PBA700)/UP; (△) PU(PPG700)/UP in synthesis.

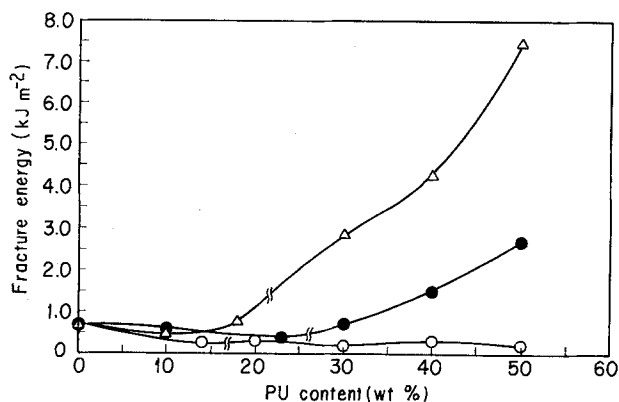


Figure 8 Fracture energy versus PU content plot for: (○) PU(PPG400)/UP; (△) PU(PPG700)/UP and (●) PU(PPG1000)/UP.

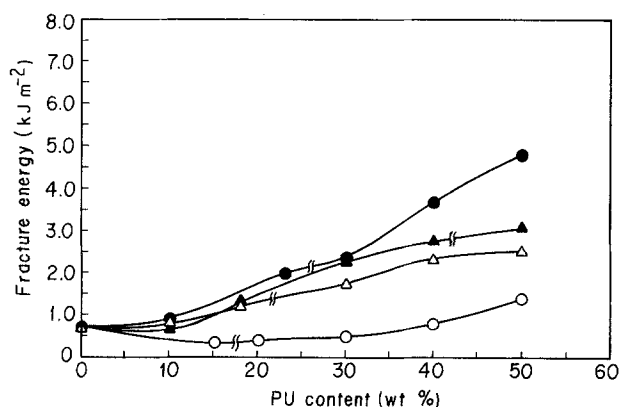


Figure 9 Fracture energy versus PU content plot for: (○) PU(PBA500)/UP; (△) PU(PBA700)/UP; (●) PU(PBA1000)/UP and (▲) PU(PBA2000)/UP.

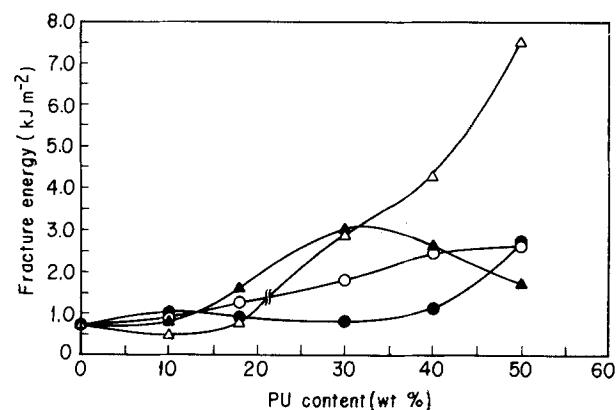


Figure 10 Fracture energy versus PU content plot as neglecting -OH group in UP: (●) PU(PBA700)/UP; (▲) PU(PPG700)/UP, and as counting -OH group in UP: (○) PU(PBA700)/UP; (△) PU(PPG700)/UP in synthesis.

increasing flexibility of the system by introducing the PU into the system.

Because the two-phased morphology is predominant for higher fracture energy at low-shear rate fracturing mechanism, the interfacial bonding force between the matrix and rubber particles becomes a crucial role to perform this fracturing mechanism. As shown in Fig. 10, a great drop in fracture energy with increasing PU content for the two-phased PU(PPG 700)/UP system has been observed due to the neglected linkage of the rubber particles to the matrix, and the result of low molecular weight of the PU.

4. Conclusion

The mechanical properties of UP are significantly improved by introducing PU elastomer into UP network structure. Maximum tensile strength may be observed at certain ratios of PU/UP. It has been as a result of the copolymerization of PU and UP to increase molecular weight and cross-linking density of UP network in the copolymer case. Interpenetrating structure becomes another effect to increase the tensile strength as in graft-IPN case. Impact strength is improved for a one-phased structure with high flexibility of the matrix. The PU (PBA 1000)/UP system is the

most successful case for this study. However, fracture energy is significantly improved for two-phased morphology with a suitable amount of rubber particles distributed in the matrix. The deformation and/or breaking of rubber particles and re-initiation of a new crack consume high fracture energy.

Neglecting the existence of the hydroxyl group in UP will cause incorrect stoichiometric ratio of the $-NCO/-OH$ in the system and decrease the grafting reaction. It seriously decreases the mechanical properties of the PU/UP system because of the decreased molecular weight of PU and residual chain extender trapped in the system as a plasticizer.

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