Physical Properties of Transfer-Molded Polyurethane-Polyester Interpenetrating Polymeric Network

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Synopsis

A series of polyurethane-polyester simultaneous interpenetrating network (SIN) samples were prepared by a laboratory-scale transfer mold. The effect of compound composition and molding conditions on the tensile properties and crystallinity of molded parts was examined by using an Instron tensile tester and a Perkin-Elmer differential scanning calorimeter (DSC). It was found that incomplete polymerization resulted in a poor tensile strength of 80°C-molded SIN. Postcure treatment and higher molding temperature increased the tensile strength of SIN by improving their limiting conversion and possibly the morphology. Results indicated that postcure was more efficient than molding at higher temperature for SIN samples with high polyurethane content. On the other hand, for SIN with higher polyester content, a high molding temperature resulted in better mechanical properties than postcuring the low-temperature molded samples. Both reaction sequence and cross-linking nature of the constituent polymers had a profound effect on the tensile properties of SIN.

INTRODUCTION

Since the first commercialization in 1975, the major development of materials used in the reaction injection molding (RIM) process has been in the polyurethane (PU) area. The generally soft elastomeric polyurethanes, however, are considered inappropriate for such applications as large, structural body panels of automobiles because of their high thermal expansion coefficient and low rigidity. Changing the resin to nylon, epoxy, or polyester is one way to improve the physical properties of RIM products; adding fiberglass as a reinforcing agent is another approach.[1,2]

In this paper, we discuss the feasibility of using an internal reinforcement approach to improve the physical properties of polyurethanes. This is done by introducing a second reactive polymer, an unsaturated polyester in this case, into the urethane reaction system to make up the deficiencies of polyurethane. This approach is essentially an application of interpenetrating polymeric networks (IPN) to the reactive processing of polymers.

By definition,[3] an IPN is a copolymer of two polymers that have been cross-linked or synthesized in the presence of each other. Since there are two components in an IPN, the synthesis of IPN can be classified according to the polymerizations sequence and the polymer structure. There are two types of IPN according to the polymerization sequence. The first is a simultaneous

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interpenetrating network (SIN) formed when reactants of both polymerizations are added to the reactor at the same time. The second is a sequential IPN formed when the two polymerizations are in sequential order. According to the polymer structure, two IPN can be distinguished. A full IPN is obtained when both components are cross-linked (i.e., thermosetting polymers). If there are one linear (i.e., thermoplastic polymer) and one cross-linked component in an IPN, it is called a semi-IPN.

Many IPN and SIN have been studied before[3-6]; a few of them included polyurethane. Yoon et al.[7] reported a series of semi-IPN composed of a polyurethane and a polyacrylate. A PU-PMMA SIN system was studied by Djomo et al.[8] and Morin et al.[9] Hutchinson et al.[10] reported a series of IPN based on polyurethane precursors and polyester precursors. Most of the work concentrated on the product morphology and mechanical properties. The processing aspect has not been studied in detail. Recently, Nguyen and Suh[11,12] reported their work of processing a PU-polyester SIN by the RIM process. In addition to an elastomeric urethane resin, which accounts for two streams in the impingement mixing, a third stream of an unsaturated polyester resin was introduced to the RIM machine. These three streams were mixed simultaneously with a drive pressure up to 100,000 psi and a Reynolds number up to 10,000. Resulting products showed an improvement over the constituent polymers, such as a decrease of heat sag.

In our laboratory, the reaction kinetics of PU-polyester SIN has been studied using a differential scanning calorimeter (DSC).[13] Results showed that the two polymerizations were highly interacted with each other and the reaction profile depended strongly on the compound composition, reaction sequence, type of catalyst, and cross-linking nature of the constituent polymers. In this paper, we further studied the physical properties of transfer-molded PU-polyester SIN and their dependency on molding conditions.

EXPERIMENTAL

Materials

The ingredient of the PU-polyester SIN used in this study are listed in Table I. In the series of PDO-initiated SIN (L/C, C/C, C/L, L/L), the first letter indicates the phase structure of polyurethane and the second letter indicates the phase structure of polyester. C is cross-linked structure; L is linear structure. The series RA, RB, and RC are the MEK-amine-catalyzed SIN samples. The recipe can be divided into two parts, namely, the polyurethane and the unsaturated polyester. The polyurethane chosen for this study consists of a soft segment based on a poly(ϵ-caprolactone diol) (PCP-0240, Union Carbide) and a hard segment based on a liquid form of 4,4'-diphenyl-methane-diisocyanate (MDI) (143-L, Upjohn) chain extended with 1,4-butanediol (BDO, Aldrich Chemical Company). MDI was degassed and demoistured at room temperature for 20 min to remove water and air. The treated MDI solution was then filtered under vacuum. PCP-0240 is a long-chain diol with a number-average molecular weight of 2000 and is a solid at room temperature. A heating plate was used to melt this material. BDO is a low-molecular-weight diol with a viscosity slightly higher than that of water.

TABLE I
Recipe Used in This Study

Ingredients	Sample Designation[a] (parts by weight in PU or polyester)						
	L/C	C/C	C/L	L/L	RA	RB	RC
PU in SIN							
MDI (Upjohn 143L)	41	44	44	41	41	41	41
Polyol (UC P0240)	48	—	—	48	48	48	48
Diol (Aldrich BDO)	11	—	—	11	11	11	11
Triol (UC P0310)	—	56	56	—	—	—	—
Catalyst (Lupersol T-12)	0.033	0.033	0.033	0.033	—	—	—
Structure	L	C	C	L	L	L	L
Polyester in SIN							
65% unsaturated polyester in styrene (OCF P340)	67	67	—	—	67	67	67
Styrene	33	33	100	100	33	33	33
PDO	1.38	1.38	1.38	1.38	—	—	—
MEK	—	—	—	—	0.23	0.7	1.15
Amine	—	—	—	—	0.11	0.33	0.55
Structure	C	C	L	L	C	C	C

[a] C = cross-linked structure; L = linear structure.

The combination of the molten PCP-0240 and BDO was degassed for 40 min at 60°C using a heating plate and vacuum to remove water and air. The catalyst, dibutyltin dilaurate (DBTDL-T12, M and T Chemicals), was used as received. The amount of T-12 was 0.033% by volume in MDI for a reasonable reaction time so that the kinetics study by DSC and the sample preparation by transfer molding were possible (the typical catalyst concentration in polyurethane RIM process is 1% by volume). The molar ratio of PCP-0240-MDI-BDO was specified as $1:6:5$, which is typical in the RIM process. For the polyester part, styrene was used as a cross-linking agent for the unsaturated polyester resin (P340, Owens Corning Fiberglas), which is a $1:1$ propylene-maleate polyester combined with 35% by weight of styrene.

Styrene was not freed of inhibitor in all cases. Initiator, t-butyl peroxy-2-ethyl hexanoate (PDO, Lucidol) a diluted high-temperature initiator, was used as received. The molar ratio of styrene to the double bonds of the unsaturated polyester was adjusted to $2:1$.

In the study of reaction sequence effect, initiator PDO was replaced by a combination of methyl ethyl ketone (MEK) and a tertiary amine. The combined reagent is a reduction-oxidation initiator for unsaturated polyester resin. It was used as received without pretreatment. The MEK-amine ratio was set at $1:3:5$ for samples RA, RB, and RC.

In the study of cross-linking effect, a triol was used instead of PCP-0240 and BDO. It has an equivalent molecular weight of 293 (PCP-0310, Union Carbide, hydroxyl number = 191). The molar ratio of triol-MDI was set at $1:1$. The pretreatment of triol was the same as that of diol. Because of the trifunctionality of PCP-0310, its combination with MDI can result in a cross-linked polyurethane. With the introduction of PCP-0310 in the polyurethane reaction and a pure styrene to replace the unsaturated polyester resin, there were four combinations of SIN ranging from full SIN to linear SIN.
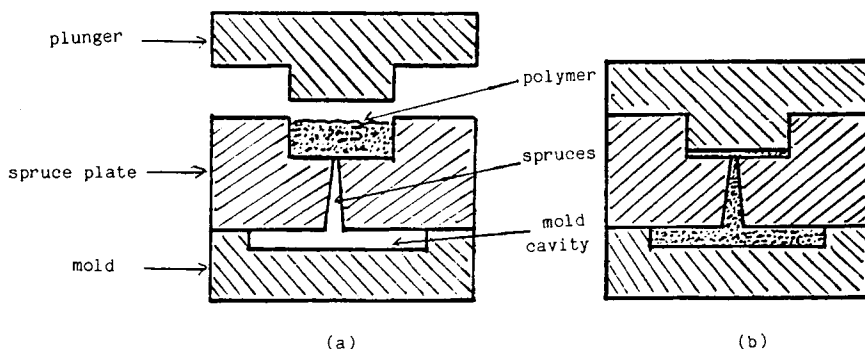
Fig. 1. Schematic of the transfer mold: (a) before molding, (b) after molding.

The ratio of PU to polyester was fixed at 50 : 50 by weight for most SIN prepared. In order to study the effect of compound composition on the mechanical properties of SIN, the ratio of PU-polyester of L/C SIN was varied: 100 : 0, 75 : 25, 50 : 50, 25 : 75, and 0 : 100.

Instrumentation and Experimental Procedure

Transfer Molding

All samples used for the mechanical property test were prepared by a laboratory-scale transfer mold with a single cavity. Figure 1 shows the schematic of such a mold. The spruce plate is 0.25 inch thick, which has four conical spruces with an entrance diameter of 0.25 inch and an exit diameter of 0.05 inch. The spacer directly below the spruce plate is 0.125 inch thick and has a rectangular cavity of 4 × 6 inches. The plunger diameter is 1.5 inch. SIN components were first mixed in a suction flask by a magnetic stirrer until no air bubble was observed. This bubble-free mixture was then transported to the mold cavity through the transfer pot. Once it was in the mold, polymerization was allowed to proceed for 2 h before demolding. For most SIN, the molding temperature was set at 80°C, but for L/C SIN, two molding temperatures were used, 80 and 120°C. Half the 80°C molded L/C samples were further postcured at 120°C for 6 h. The concentrations of catalyst and initiator were chosen in such a way that the mixture would not reach gelation in at least 2 min, which was required for material preparation (i.e., mixing and transfer molding). The transfer molding technology was found successful for the preparation of bubble-free samples.

Tensile Test

Tensile tests were carried out on an Instron tensile testing machine (Model 1137) at −2, 25, and 93°C. Sample specimens were made with a heated die cutter to the dumbbell shape of $5\frac{1}{2}$ inches long and 1 inch wide with a narrow testing section $2\frac{1}{2}$ inches long and $\frac{1}{2}$ inch wide. The thickness of the samples is $\frac{1}{8}$ inch. The specimen was stretched until it failed. The crosshead speed of the tensile tester was set at 0.05 inch/min. Tensile properties were determined from the average value of three to five specimens.
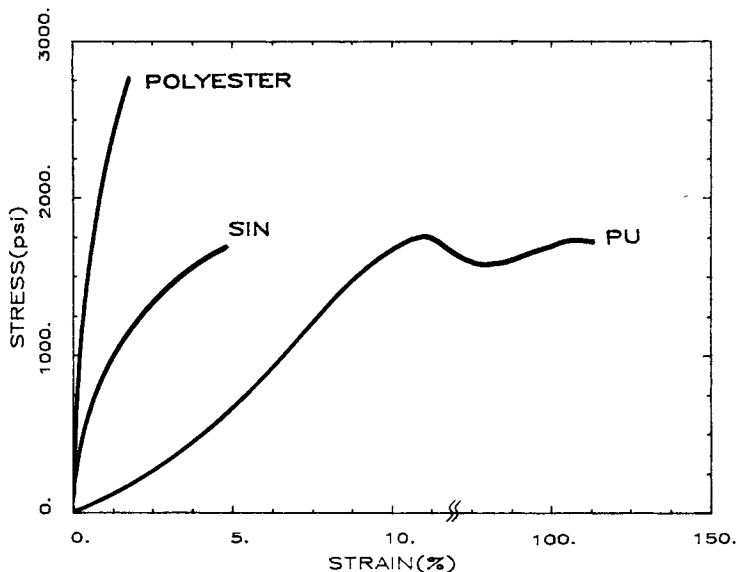
Fig. 2. Typical stress-strain curve of linear PU, polyester, and SIN (L/C sample, PU-polyester = 50 : 50) tested at 25°C. Samples are molded at 80°C and postcured at 120°C for 6 h.

Thermal Analysis

The limiting conversion of molded parts was measured by using a Perkin-Elmer differential scanning calorimeter (DSC-2C). The molded part was cut and weighed in a balance (Mettler, Model-80) with a weight in the range of 10–15 mg. This sample was then transferred to the sample pan of DSC. To check if residual reactivity existed, the reaction exotherm versus temperature was carried out in the scanning mode with temperature increasing from room temperature to 237°C at 20°C/min. Because 237°C is far above the glass transition temperature of either polyurethane or polyester, the completion of polymerization was ensured. A second scanning run was conducted immediately after the first scanning run to determine the baseline. The calculation method of the limiting conversion can be found elsewhere.[14] For SIN, the limiting conversion is based on the polyester reaction only.[13] For PCP-0240-based SIN, the crystallinity of polyurethane phase in the molded samples was also measured using the DSC.

RESULTS AND DISCUSSION

Compositional and Temperature Effects

Figure 2 shows typical stress-strain curves of a PCP-0240-based polyurethane, polyester, and their SIN (L/C sample; PU-polyester = 50 : 50) tested at 25°C. As expected, the rigid polyester has a high tensile modulus and strength but very low elongation, whereas the elastomeric polyurethane shows a much lower tensile strength but a larger elongation. SIN has a stress-strain behavior between those of its constituent polymers.

Figure 3 shows the compositional effect on the tensile strength of 80°C molded L/C samples tested at 25°C, along with their limiting conversions
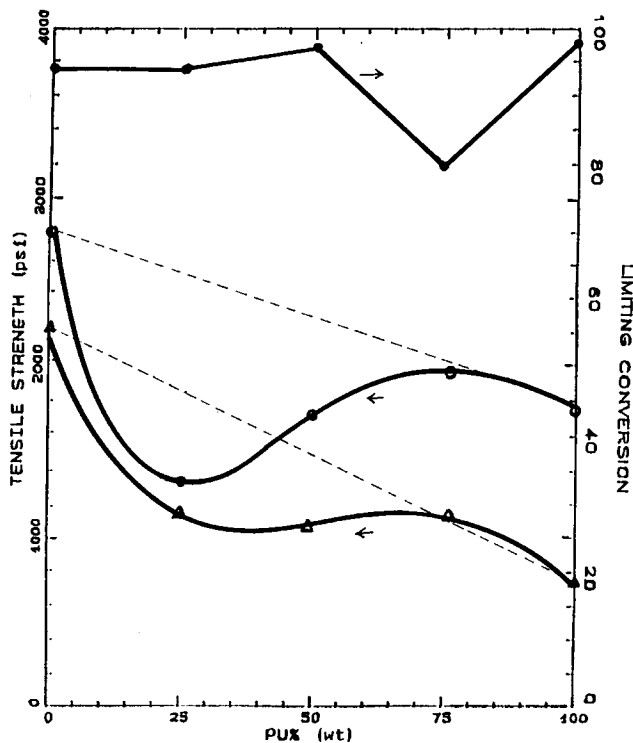
Fig. 3. Tensile strength and limiting conversion of 80°C molded L/C samples before (△) and after (○) postcure. Testing temperature is 25°C.

measured by DSC. The dashed line indicates a relationship based on the additivity rule. The 80°C molded L/C samples show a negative deviation of tensile strength from its linear average. The DSC measurement of residual activity of these samples is very similar to that measured in the thermal kinetic study,[13] which shows that polymerization is incomplete for all samples molded at 80°C. The SIN with 75% polyurethane has the lowest limiting conversion among all samples. To improve the physical properties, the 80°C molded samples were postcured at 120°C for 6 h. In general, improved tensile strength is observed for all samples, as shown in Figure 3, but the negative deviation from linear average still exists. The numerical data are summarized in Table II. The improvement is more significant for samples with a higher polyurethane content. The DSC measurement of crystallinity of polyurethane phase in the molded and postcured L/C samples is shown in Figures 4 and 5. Apparently, the crystallinity structure of the polyurethane phase is composition dependent. Adding polyester to the reaction system sharply reduces the amount of crystallinity. The melting peak of polyurethane crystal shifts to a higher temperature after the postcure treatment.

The results shown in Figures 3 through 5 indicate that the mechanical properties of SIN and their constituent polymers depend on the conversion and morphology of the molded parts. At a molding temperature of 80°C, polymerization cannot reach completion and the final conversion is composition dependent.[15-17] Postcure has an effect of promoting the reaction to a

TABLE II
Tensile Strength and Ultimate Elongation of 80°C Molded and
120°C Postcured L/C Samples Tested at Three Different Temperatures

Temperature (°C)	PU Content				
	0%	25%	50%	75%	100%
	Tensile strength (psi)				
−2	3044	1808	2148	2675	2739
25	2790	1318	1623	1933	1733
93	2509	998	969	1043	640
$\frac{-2}{93}$	1.2	1.8	2.2	2.6	4.3
	Elongation (%)				
−2	1.4	1.9	3.9	21.0	31.0
25	1.8	1.6	4.3	76.5	112.3
93	2.5	4.6	13.2	90.0	164.0
$\frac{-2}{93}$	0.6	0.4	0.3	0.23	0.2

higher conversion, which improves the mechanical properties of the molded parts. It is evident that the tensile strength of postcured samples is higher than that of unpostcured samples for all composition. For SIN and pure polyurethane, the morphological change due to the postcure treatment may also play an important role in the improvement of tensile strength. It is evident that postcure has the effect of shifting the melting peak of the polyurethane phase from a lower temperature to a higher temperature, which implies a more stable crystallinity structure[18] in the polyurethane phase. Accordingly, the increase of tensile strength is also more significant for SIN samples with a higher polyurethane content.
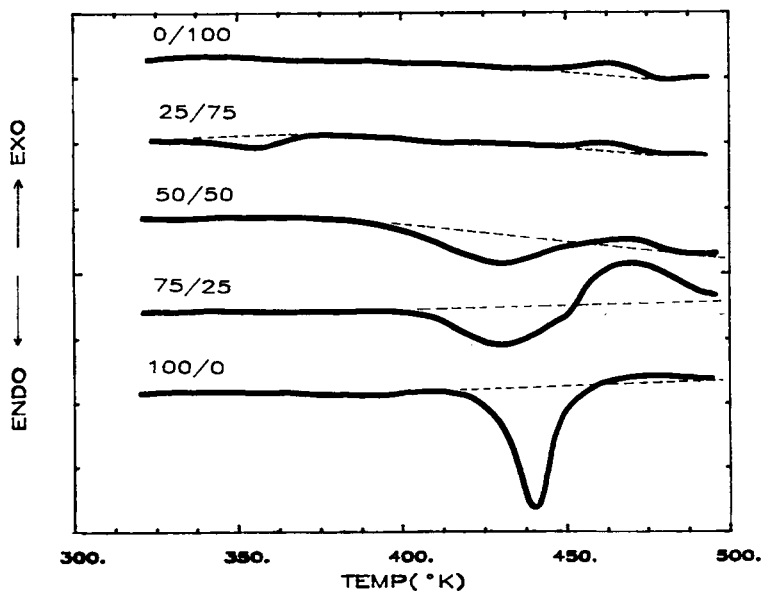

Fig. 4. Scanning DSC results of 80°C molded L/C samples.
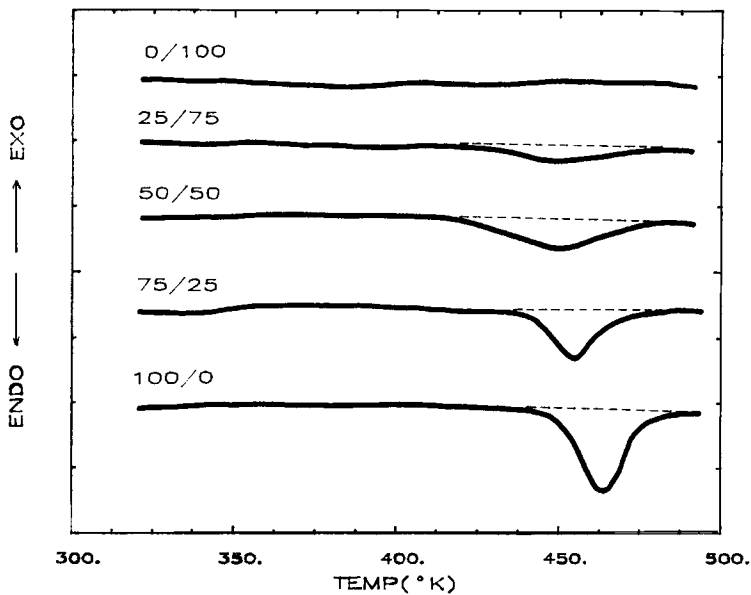
Fig. 5.   Scanning DSC results of 80°C molded L/C samples after postcure treatment.

When the mold temperature was raised to 120°C, the tensile strength was greatly improved. A comparison was made between 80 and 120°C molded L/C samples testes at 25°C, as shown in Figure 6. Unlike the 80°C molded samples, the 120°C molded SIN show a positive deviation of tensile strength from the linear additivity. The higher molding temperature, however, does not greatly affect the tensile strength of the pure polymers. From the previous thermal kinetic study,[13] it is noted that molding temperature has a significant effect on the polymerization rate of SIN. For the PDO-initiated polyester, a temperature of 100°C or higher is required to generate a high reaction rate, but polyurethane polymerization is relatively fast even at low temperatures since the reaction is initiated by mixing. For a PU-polyester SIN reaction at 80°C, the polymerization of urethane resin occurs much earlier than that of polyester. DSC results show that residual activities exist in the 80°C molded samples (see Fig. 3). At 120°C, both polyurethane and polyester reactions occur at almost the same time.[13] DSC results show that all samples reach complete reaction. This seems to suggest that a higher final conversion and simultaneous reactions of polyurethane and polyester are very helpful for increasing the mechanical properties of SIN.

The DSC measurement of crystallinity of 120°C molded L/C samples is shown in Figure 7. Compared with Figures 4 and 5, the higher molding temperature tends to broaden the melting peak of the polyurethane phase but does not shift the melting point to higher temperatures as in the case of postcure treatment.

Thermal stability is a very important consideration for polymeric materials used in the automobile industry. To explore this property, the tensile strength of 80°C molded and 120°C postcured L/C samples was measured under three different temperatures of −2, 25, 93°C. Figure 8 and Table II summarize the
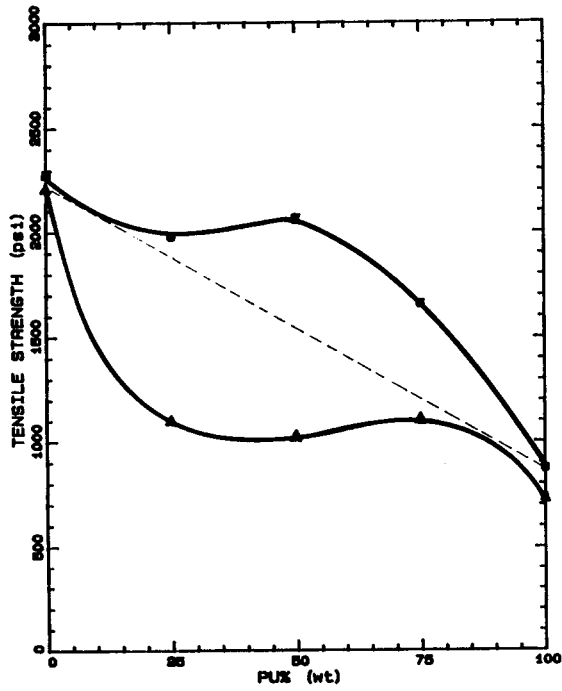
Fig. 6.   Comparison of tensile strength of 80°C (△) and 120°C (□) molded L/C samples. Test temperature is 25°C.
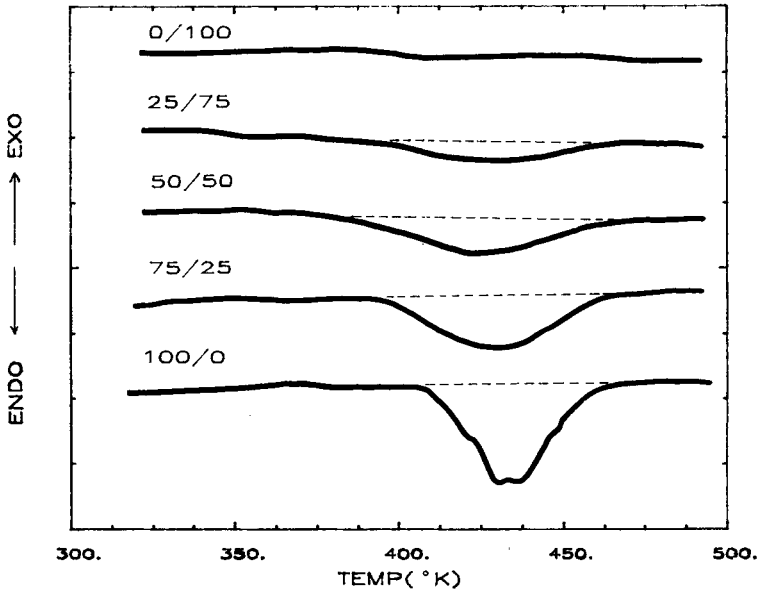

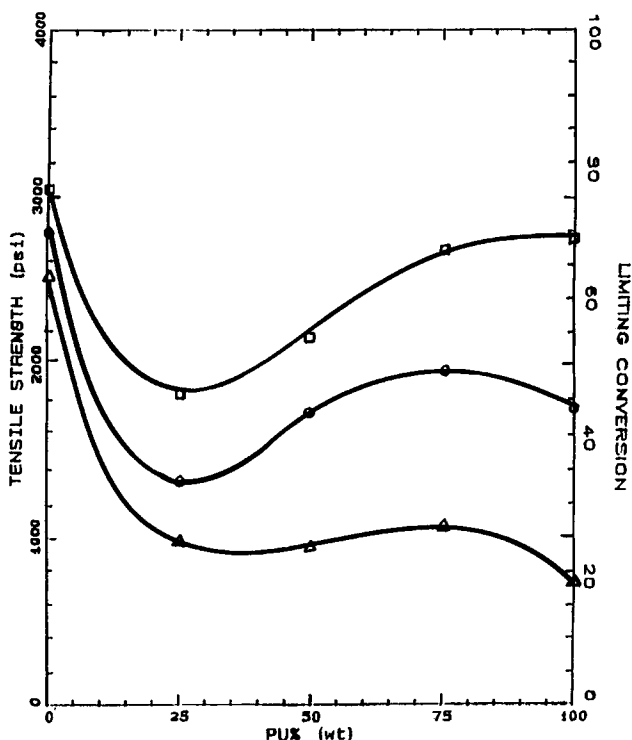Fig. 7.   Scanning DSC results of 120°C molded L/C samples.

Fig. 8. Tensile strength of 80°C molded, 120°C postcured L/C samples tested at −2°C (□), 25°C (○), and 93°C (△).

results. The temperature of 93°C was chosen because it is located in the middle of the glass transition temperature of the polyurethane hard domain (70–80°C) and the glass transition temperature of unsaturated polyester (near 110°C). When the testing temperature was increased from −2 to 93°C, the tensile strength of polyurethane dropped from 2739 to 640 psi, whereas much less difference was observed with the polyester sample. This is because the linear polyurethane is soft and elastomeric in nature and the highly cross-linked polyester is extremely rigid. In general, increasing temperature decreased the tensile strength of all SIN. SIN with high polyurethane content show more reduction in tensile strength than those with low polyurethane content. Ultimate elongation of SIN also shows an intermediate value between those of the constituent polymers. The ratio of tensile strength at −2°C to that at 93°C can be used as a measure of temperature sensitivity. As shown in Table II, the ratio ranges from 1.2 for pure polyester to 4.3 for pure polyurethane. SIN have values between these two extremes.

Sequential Effect

The two polymerizations in SIN do not necessarily occur at the same time. The actual polymerization sequence depends on the molding temperature and catalyst used in each constituent polymer. All 80°C molded SIN samples discussed so far have been in the sequence that polyurethane reacted first and

	Sample designation			
	L/C	RA	RB	RC
Tensile strength (psi)	1050	2344.5	1489.1	1440
Ultimate elongation (%)	4.26	7.59	5.58	4.18
Limiting conversion (%)	96.7	97.2	95.3	78.2

[a] PU-polyester = 50 : 50; testing temperature is 25°C.

polyester reacted later by employing a high-temperature peroxide initiator, PDO, which required a long period of induction time at 80°C.

To study the effect of the reaction sequence, a combination of MEK and tertiary amine was used to substitute for PDO in the polyester reaction. The combined initiator is a reduction-oxidation (redox) initiator that may start the free radical polymerization at low temperatures. The ingredients of the polyurethane phase remained the same, but without the catalyst T-12, because tertiary amine is also known to be a weak catalyst for polyurethane. By changing the amount of this combined initiator, the reaction rates of polyester and polyurethane can be adjusted. The previous thermal kinetic study[13] showed that substantial overlapping occurred between polyurethane reaction and polyester reaction when MEK-amine was employed as the initiator. Increasing the concentration of MEK-amine increased the extent of overlapping. The tensile properties of SIN samples molded at 80°C with different MEK-amine concentration are presented in Table III. The PU-polyester ratio is 50 : 50. For comparison, the tensile properties of a similar SIN initiated by PDO and T-12 are also listed in the same table.

It is found that the PDO-initiated SIN has a lower tensile strength and ultimate elongation than the MEK-amine-initiated SIN. Apparently, the overlapping of polyurethane and polyester reactions by speeding up the polyester reaction enhances the mechanical properties of SIN, which is very similar to molding the PDO-initiated SIN at high temperatures (e.g., 120°C). Among the redox samples, that with the lowest MEK-amine concentration (i.e., sample RA) shows the highest tensile strength and ultimate elongation. This is probably due to the influence of limiting conversion, as shown in Table III. The effect of the reaction sequence on the crystallinity of the polyurethane phase is shown in Figure 9. It seems that the overlapping of polyurethane and polyester reactions reduces the degree of crystallinity in the polyurethane phase.

The change in tensile properties among different SIN samples may be effected by both polymerization kinetics and sample morphology. Such factors as phase separation, chain interpenetration, crystallinity structure of polyurethane phase, and network structure of polyester phase may all play important roles. Dynamic mechanical test, thermal analysis,[11,12,19] and electron and optical microscopy[18-21] have been used to study IPN morphology.
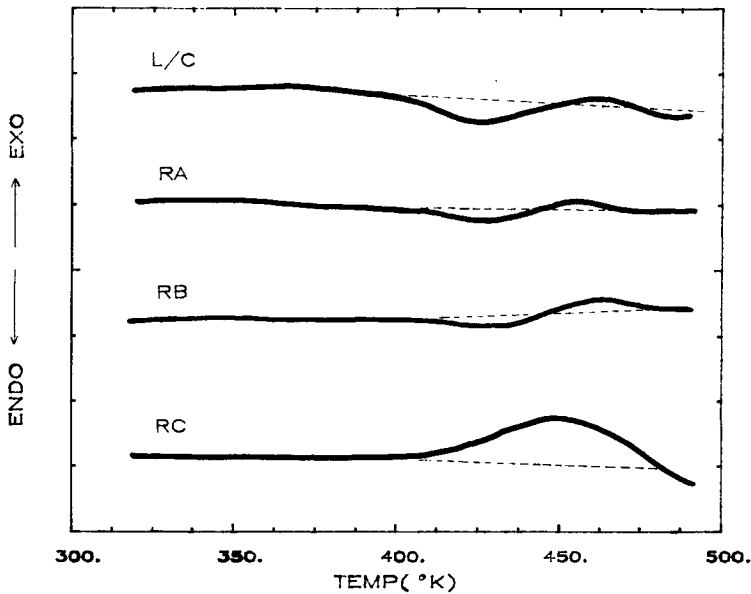
Fig. 9. Scanning DSC results of 80°C molded L/C samples with different initiator combination (PU-polyester = 50:50).

These techniques are currently being tried in our laboratory. The results are expected to provide a clearer picture of the interactions among compound composition, processing conditions, product morphology, and mechanical properties.

Cross-linking Effect

Since there are two constituent polymers in a PU-polyester SIN and each polymer can be either linear or cross-linked, the mechanical properties of SIN may depend on the cross-linking nature of the two polymers.[22-24] The cross-linking effect of polyurethane and polyester on the tensile strength of SIN is shown in Table IV, where U_c is PCP-0310-based thermosetting polyurethane and U_l is PCP-0240- and BDO-based linear polyurethane. All samples have a PU-polyester ratio of 50:50. They were molded at 80°C and tested at 25°C. The limiting conversion of molded and postcured samples is also listed in Table IV. The results show that postcure improves the tensile strength of all samples, but to different extents. For cross-linked polyurethane, the increase of tensile strength from 956 to 1828 psi owing to the postcure treatment can be attributed to the increase of polyurethane limiting conversion from 92 to 100%, which not only reduces the residual monomers but also increases the cross-linking density. For linear polyurethane, the postcure treatment only slightly increases the limiting conversion; therefore, the significant increase in tensile strength must be attributed to a change in morphology, such as crystallinity structure and phase separation. For the two polyester-based SIN, the molded C/C sample shows a higher tensile strength than that of L/C sample, which is apparently due to the dual network structure of the C/C sample. Postcure increases the limiting conversion of the

TABLE IV
Effect of Cross-linking on Tensile Strength and Limiting Conversion
of 80°C Molded Samples Before and After Postcure Treatment[a]

Sample designation		80°C molded	Postcured
C/C	σ (psi)[b]	1496	1961
	α (%)[c]	86	~ 100
L/C	σ (psi)	1050	1623
	α (%)	96.7	~ 100
C/L	σ (psi)	954	1528
	α (%)	93	~ 100
L/L	σ (psi)	1280	2080
	α (%)	98.7	~ 100
U_c	σ (psi)	956	1828
	α (%)	92	~ 100
U_l	σ (psi)	730	1733
	α (%)	97.5	~ 100

[a] PU-polyester = 50 : 50; testing temperature is 25°C.
[b] Tensile strength.
[c] Limiting conversion.

C/C sample substantially. Consequently, the tensile strength also greatly increases. For the L/C sample, limiting conversion does not change much by postcure treatment; the morphological change of the polyurethane phase must be the reason for the increased tensile strength. Postcure treatment shows a more significant influence on the tensile strength for the polystyrene-based SIN than for the polyester-based SIN. One may again attribute the influence on the C/L sample to the increase in limiting conversion. For the L/L sample, the substantial increase in tensile strength due to the postcure treatment cannot be attributed to the slight increase in limiting conversion. The results from the thermal analysis of molded and postcured samples shown in Figure 10 again suggest that morphological changes, such as rearrangement of crystallinity structure in the polyurethane phase, must be a main reason of the improvement. Apparently, the linear polystyrene phase is less rigid than the cross-linked polyester phase at the postcure temperature. Thus, postcure treatment is more beneficial for polystyrene-based SIN than for polyester-based SIN.

CONCLUSIONS

Simultaneous interpenetrating network samples consisted of a polyurethane and a polyester were prepared using a laboratory-scale transfer mold. Tensile properties and crystallinity structure were examined using an Instron tensile tester and a Perkin-Elmer DSC.

The results of the present study show that PU-polyester SIN can improve the mechanical properties (e.g., tensile strength) of generally soft polyurethanes, but the processing of SIN is more complicated than that of polyurethanes because of strong interaction between the two polymerizations. At a temperature of 80°C, which is a typical molding temperature of the polyurethane RIM process, incomplete reaction was found in all SIN samples, which resulted in a low tensile strength. This problem can be solved by
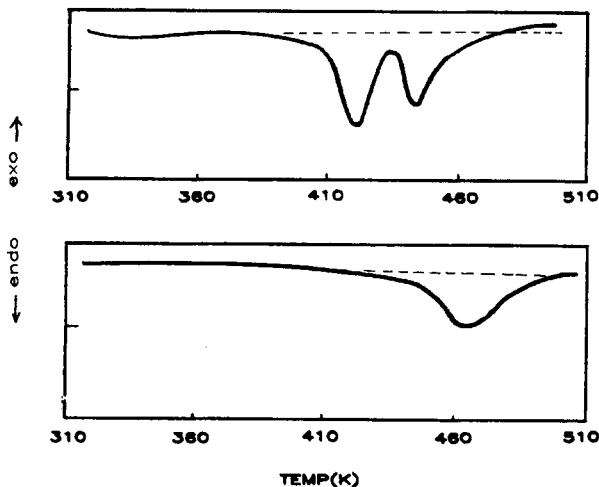
Fig. 10. Scanning DSC results of 80°C molded L/L samples: (a) before postcure, (b) after postcure.

postcure treatment or by using a higher molding temperature. A higher molding temperature is more beneficial for SIN with a higher polyester content, and the postcure treatment is more efficient for SIN with a higher polyurethane content.

Both the reaction sequence and the cross-linking nature of the constituent polymers are important in determining the tensile properties of SIN. It is believed that, in addition to reaction kinetics, morphological characteristics, such as degree of chain interpenetration, network structure, and crystallinity structure, play influential roles in governing the mechanical properties of SIN. Continuous efforts are being made in these areas, which should be able to provide a better understanding of this new class of polymeric materials.

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