

Effects of Chemical Structure of Polyurethane-Based Low-Profile Additives on the Miscibility, Curing Behavior, Volume Shrinkage, Glass Transition Temperatures, and Mechanical Properties for Styrene/Unsaturated Polyester/Low-Profile Additive Ternary Systems. II: Glass Transition Temperatures and Mechanical Properties

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ABSTRACT: The effects of three series of thermoplastic polyurethane-based (PU) low-profile additives (LPA) with different chemical structures and molecular weights on the glass transition temperatures and mechanical properties for thermoset polymer blends made from styrene (ST), unsaturated polyester (UP), and LPA have been investigated by an integrated approach of static phase characteristics-cured sample morphology-reaction conversion-property measurements. The three series of PU used were made from 2,4-tolylene di-isocyanate (2,4-TDI) and varied diols, namely polycaprolactone diol (PCL), poly(diethylene adipate) diol (PDEA), and poly(propylene glycol) diol (PPG), respectively, while the two UP resins employed were synthesized from maleic anhydride (MA) and 1,2-propylene glycol (PG) with and without modification by phthalic anhydride (PA). Based on the Takayanagi mechanical models, factors that control the glass transition temperature in each phase region of cured samples, as identified by the method of thermally stimulated currents (TSC), and mechanical properties will be discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 558–568, 2000

Key words: unsaturated polyester resins; low-profile additives; glass transition temperatures; mechanical properties; Takayanagi model; polyurethane

INTRODUCTION

Adding specific thermoplastic polymers as low-profile additives (LPA) in the unsaturated polyester resins (UP) could lead to a reduction or even elimination of the polymerization shrinkage dur-

ing the cure process.^{1,2} In part 1 of this article,³ the chemical structures of polyurethane (PU)-based LPA were demonstrated to be intimately connected with the miscibility, curing behavior, and cured-sample morphology for styrene (ST)/UP/LPA systems. Due to a drift in ST/UP/LPA composition as a result of phase separation during the cure of the ST/UP/LPA system,^{4–6} it is of interest to further study how the glass transition temperatures and mechanical properties of ultimately cured samples would be affected by the chemical structure of the PU-based LPA.

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Table I PU-Based^a LPAs Used in this Study

LPA Codes	Diol Used	M_n	NCO/OH ^b	MA Added ^c	M_n of PU ^d
PCL1-PU	polycaprolactone	1250	0.875	0.0625	18770
PCL2	polycaprolactone	2000	0.933	0.010	27170
PDEA1	poly(diethylene adipate)	1890	0.86	0.035	2870
PDEA2	poly(diethylene adipate)	4890	0.85	0.015	5040
PPG1	poly(propylene glycol)	2000	0.85	0.015	9750

^a Containing 2,4-TDI.^b Equivalent ratio.^c By equivalent.^d By GPC (g/mol).

The objective of this work is to investigate the effects of chemical structure and molecular weight of three series of thermoplastic polyurethane-based LPA on the glass transition temperatures and mechanical properties for ST/UP/LPA systems. Using an integrated approach of static ternary phase characteristics of ST/UP/LPA at 30°C, morphology, reaction conversion, and property measurements, in depth elucidation of the experimental results is given.

EXPERIMENTAL

Materials

2,4-Tolylene diisocyanate (2,4-TDI) and varied diols were first reacted to make the hydroxyl-terminated PU prepolymers. Subsequently, excess maleic anhydride (MA) was added to make the carboxyl-terminated thermoplastic PU-based LPAs. Detailed procedures can be found elsewhere.³ The five LPAs used in this study are summarized in Table I.

The UP resins⁶ were made from MA and 1,2-propylene glycol (PG) with and without modification by phthalic anhydride (PA). The molecular characteristics of the two UPs are summarized in Table II.

For the sample solution, 10% by weight of LPA was added, while the molar ratio of styrene to polyester C=C bonds was fixed at MR = 2/1. The reaction was initiated by 1% by weight of *tert*-butyl perbenzoate.

Instrumentation and Procedure

The sample solutions were degassed in a vacuum oven at 50°C for 5 min, which were then slowly poured into stainless steel rectangular molds with inner trough dimensions of 17 × 1.7 × 0.42

cm and sealed with gaskets. The sample solutions were cured at 110°C in a thermostated silicon oil bath for 1 h, followed by a postcure at 150°C for another hour.

For the measurements of transition temperatures in each phase region, the sample specimen with a thickness of 1.5–2 mm was polarized at 230°C under an electric field of 500 V/mm over a period of 10–35 min by using a Solomat 91000 TSC/RMA (Thermally Stimulated Currents/Relaxation Map Analysis) apparatus.^{7,8} Thermally stimulated currents were recorded from –150 to 250°C at a heating rate of 7°C/min.

In the mechanical tests, dumbbell-shaped specimens based on ASTM D638-82a, type V were used to determine tensile properties of low-shrink polyester matrices on the Micro 350 universal testing machine (Testometric Co.) at a constant crosshead speed of 1.0 mm/min. The Izod impact test was also carried out based on ASTM D-256-81, method A by using an impact tester (Frank Pendulum Impact Tester 53568 type).

Table II Molecular Characteristics of UP Resins

	MA-PG	MA-PG-PA
Molar ratio of UP composition ^a	1 : 1.09	0.63 : 1.01 : 0.37
AN ^b	28.9	28.0
HN ^b	32.0	28.2
M_n (abs.) ^c	1824	1996
% of isomerization ^d	97	97
No. of C=C bonds per UP	11.21	6.79

^a Measured by ¹H NMR.^b AN and HN denote acid number and hydroxyl number, respectively.^c Calculated by end-group titration methods.^d Transformation from maleate to fumarate as measured by ¹H NMR.

Table III Calculated T_c (K) for ST/UP/LPA Uncured Systems

LPA	MA-PG Type of UP	MA-PG-PA Type of UP
PCL1-PU	236.9	252.1
PCL2-PU	237.4	252.6
PDEA1-PU	213.4	232.6
PDEA2-PU	216.5	235.9
PPG1-PU	200.4	224.0

RESULTS AND DISCUSSION

Compatibility of Styrene/UP/LPA Systems

The upper critical solution temperatures (UCST or T_c) prior to reactions for the ST/UP/LPA ternary polymer blends have been calculated by using the Flory-Huggins theory and group contribution methods in part 1 of this article,³ and the results are summarized in Table III. For both the MA-PG and the MA-PG-PA types of UP systems, the calculated T_c , all being well below room temperatures, was lower for the sample solution containing the polyester-based PU (i.e., PDEA-PU) than that containing the polycaprolactone-based PU (i.e., PCL-PU), which reveals that the former system would be theoretically more compatible than the latter one. For both systems, adding a higher molecular weight of PU would result in the less compatibility of the system due to a higher calculated T_c . On the other hand, the calculated T_c was the lowest for the sample containing the polyether-based PU (i.e., PPG-PU), yet it is the only system with the phase separation occurring at room temperature prior to reaction.³ This would be attributed to the negligence of exothermic effect caused by the polar interaction between PU and UP resins in the calculation of the Gibb's free energy change of mixing, ΔG_M .

With a fixed PU-based LPA, adding the MA-PG-PA type of UP would lead to a more incompatible ST/UP/LPA ternary system than that of the MA-PG type of UP system, which could be evidenced by a higher calculated T_c for the MA-PG-PA system than the MA-PG system (Table III), and a shorter phase separation time for the ST/MA-PG-PA/PPG1 system than for the ST/MA-PG/PPG1 system³ (500 vs. 800 min).

During the cure at 110°C, the effects of chemical structures of PU-based LPAs and UP resins on the compatibility of ST/UP/LPA systems showed the same trend as those of the uncured

ST/UP/LPA systems, as observed from the SEM micrographs in part 1 of this article.³

Relationship between Morphologies and Mechanical Properties—the Takayanagi Models

For the cured LPA-containing UP resin systems with morphologies as shown in part 1 of this article,³ their mechanical behavior can be approximately represented by the Takayanagi models,^{9–11} where arrays of weak LPA (R) and stiff styrene-crosslinked polyester (P) phases are indicated (see Fig. 1). The subscripts 1, 2, and 3 for P phases are employed due to the distinction of styrene and UP compositions as a result of phase separation during cure, and the quantities λ , φ , ζ , and ν or their indicated multiplications indicate volume fractions of each phase.

For the systems shown in Figure 4(a)–(d) in part 1 of this article, the microgel particles (phase P_1) would be surrounded by a layer of LPA (phase R). Between the LPA-covered microgel particles, there would be some other microgel particles (phase P_2), with different compositions of ST and UP from those in phase P_1 , dispersed in the LPA phase (phase R). Hence, the characteristic globule microstructure may be represented by the P-P-S model, as shown in Figure 1(a), which is a parallel combination of the three elements, i.e., P_1 , R, and P_2 -R in series. In contrast, for the system shown in Figure 4(e) in part 1 of this article, the microstructure consists of a stiff globule continuous phase of styrene-crosslinked polyester (phase P_1) and a weak globule LPA-dispersed phase (i.e., the hole left behind due to the solvent extraction, the globule morphology of which prior to the solvent extraction can also be represented by a P-P-S model). Hence, the upper bound of mechanical behavior for the overall morphology can be represented by a P-(P-P-S) model as shown in Figure 1(b), which is simply a parallel combination of the continuous phase P_1 and the dispersed phase denoted by a (P-P-S) model.

The mechanical properties of cured samples would change with not only the morphology but also the crosslinking density of styrene-crosslinked polyester in the P_1 , P_2 , and P_3 phases, with the major continuous phase P_1 being the dominant one. The latter information would not be easily obtained, but can be inferred from the static phase characteristics of ST/UP/LPA systems at 25°C before curing.⁵

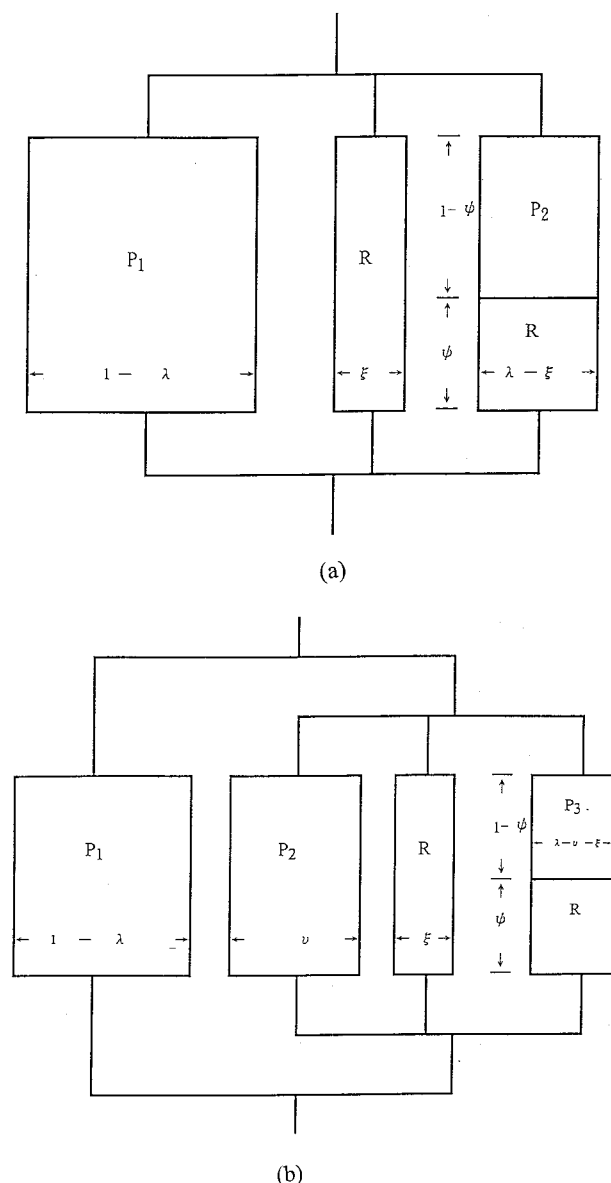


Figure 1 The Takayanagi models for mechanical behavior of cured LPA-containing UP resin systems. (a) Parallel-parallel-series (P-P-S) model, and (b) parallel-parallel-parallel-series [P-(P-P-S)] model. The area of each diagram is proportional to a volume fraction of the phase.

Effects of Drift in Styrene/Polyester Composition During Curing on Cure Conversion

For both the MA-PG and MA-PG-PA types of UP systems, the decreasing order of final conversion would be generally the PDEA-PU system > the PCL-PU system > the PPG1-PU system³ (80–89% vs. 77–85% vs. 69–70%). This reveals that the more compatible ST/UP/LPA system would

lead to a higher final conversion after the cure. As explained in part 1 of this article, this would be due to the molar ratio of styrene consumed to polyester C=C bonds reacted deviating less from (less than) 2 : 1 in the major continuous phase (i.e., phase P₁ in Fig. 1) during curing for the more compatible ST/UP/LPA system, leading to a less compact microgel structure in that phase and, in turn, a higher overall cure conversion.

Transition Temperatures by TSC

For the method of TSC^{7,8} in the determination of transition temperatures, the test conditions, such as polarization temperature, applied electric field, polarization time, and the sample thickness, all play important roles in obtaining the satisfactory results. For an unknown sample, it is usually time consuming to find out the appropriate settings for the above four variables. Therefore, it is more difficult to use for the method of TSC than the dynamic mechanical analysis (DMA) in terms of the setting of test conditions alone. However, the method of TSC is more sensitive in the identification of relaxation motions, including the short-range motions of segments in the main chain and side chain, the long-range motions of segments in the main chain, and the flow behavior of the bulk molecules. This would inevitably lead to the more difficulty in the interpretation of the TSC results compared with that of DMA. In general, the method of TSC is equivalent to the DMA at a test frequency of 10^{-5} to 10^{-6} Hz.

Table IV shows the test conditions for all of the sample specimens as measured by the method of TSC in this study. Under these conditions, the sample specimens were capable of being polarized to a certain extent so that the peak intensity for the thermally stimulated depolarization currents at glass transition temperature and/or melting temperature could be reasonably detected. As a rule of thumb, the polarization temperature selected should be higher than its glass transition temperature by at least 10–20°C, where the mobility of polymer chain segments would be high enough to be easily polarized.

Figure 2 shows the thermally stimulated depolarization current (TSDC or TSC) profile for the cured neat UP resin without LPA. The maximum point in the TSC curve could be identified as the glass transition temperature (T_g) for the major styrene-crosslinked polyester matrix, while the shoulder (or a local maximum peak) could be assigned as the T_g for the minor styrene-crosslinked

Table IV Test Conditions for All of the Sample Specimens Used in this Study by the Method of TSC

UP Type	LPA Code	Polarization Temp. (°C)	Polarization Time (min)	Applied Elec. Field (V/mm)	Sample Thickness (mm)
MA-PG	Neat UP	230	10	500	1.760
MA-PG-PA	Neat UP	230	10	500	1.804
Neat LPA	PCL1-PU	-5	5	200	1.500
	PCL2-PU	45	5	200	1.500
	PDEA1-PU	-5	5	200	1.500
	PDEA2-PU	10	5	200	1.500
	PPG1-PU	-45	5	200	1.500
MA-PG	PCL1-PU	230	15	500	1.502
	PCL2-PU	230	35	500	1.874
	PDEA1-PU	230	10	500	1.684
	PDEA2-PU	230	10	500	1.704
	PPG1-PU	230	10	500	1.940
MA-PG-PA	PCL1-PU	230	35	500	1.710
	PCL2-PU	230	20	500	1.800
	PDEA1-PU	230	10	500	1.635
	PDEA2-PU	230	10	500	1.893
	PPG1-PU	230	10	500	2.011

polyester matrix. As revealed in Figure 2, the T_g s in the major styrene-crosslinked polyester matrices for the MA-PG and MA-PG-PA type of UP resin systems would be 197 and 149.5°C, respectively (see Table V), where the T_g for the former system was higher due to its higher crosslinking density caused by the higher degree of C=C unsaturation in the UP resin (see Table II).

Figure 3 shows the TSC profiles for the five PU-based LPAs, where the transition temperatures were identified and are listed in Table V. With the aid of DSC results³ for the transition

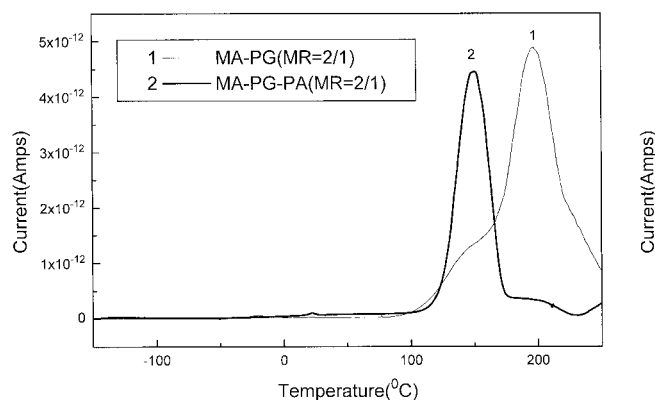


Figure 2 Thermally stimulated current profile of TSC for cured neat UP resin at MR = 2/1 after an isothermal cure at 110°C for 1 h and a postcure at 150°C for another hour. Curve 1: MA-PG type of UP; curve 2: MA-PG-PA type of UP.

temperatures, the melting temperature of PCL2-PU could also be identified. It should be noted that the melting temperature of PCL1-PU could have been identified if the polarization temperature had been set at 45°C instead of -5°C.

Figures 4 and 5 show the TSC profiles for the two cured UP resins containing 10% by wt. of the five PU-based LPAs, respectively. For the 10 ST/UP/LPA systems, the transition temperatures could be identified and are listed in Table VI.

Crosslinking Density Effect and Plasticization Effect on T_g of P Phase

Table VI shows that for the cured sample containing the semicrystalline PCL-PU, the melting point of the PU could be identified by the method of TSC. Two glass transition temperatures of PU phases, one in parallel adjacent to the P phase [i.e., $T_g(R_2)$] and the other in series adjacent to the P phase [i.e., $T_g(R_1)$], could also be identified for the PCL1 and PPG1 systems. The interaction between R_1 and the adjacent P phases would be less than that between R_2 and the adjacent P phases, leading to a lower value of $T_g(R_1)$ than $T_g(R_2)$ (i.e., from -42 to -53 vs. -5°C to 7°C).

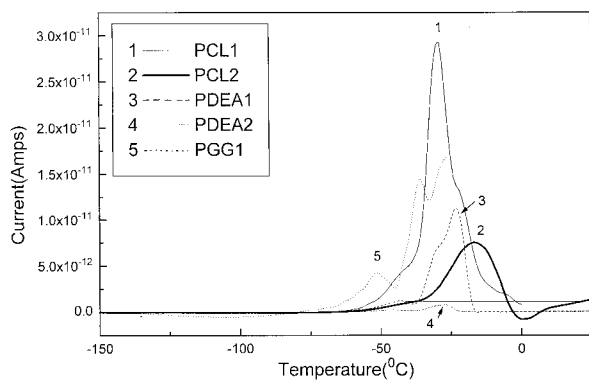
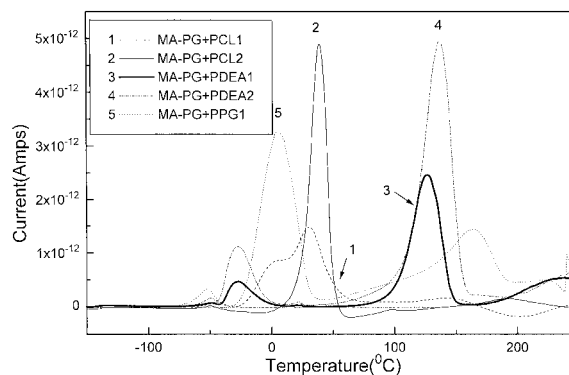
For the MA-PG type of UP systems [Table VI(a)], adding PPG1-PU would lead to the most incompatible ST/UP/LPA cured system, and the interaction of either P_1 or P_2 phase with the R phase would be the most insignificant. The least plasticization effect of R phase on P phase would

Table V Transition Temperatures (°C) for Cured Neat UP Resins and Neat PU-Based LPAs as Determined by the Method of TSC

(a) Neat UP Resins					
UP	MA-PG		MA-PG-PA		
$T_g(P_1)$	197.0		149.5		
$T_g(P_2)$	148.0		192.7		
(b) Neat PU-Based LPAs					
LPA	PCL1	PCL2	PDEA1	PDEA2	PPG1
T_m	—	40.7	—	—	—
$T_{g\alpha}$	-24	-16	—	23.5	-35
$T_{g\beta}$	-30	-40	-23	-28	-51
$T_{g\gamma}$	-40	—	-43	-46	—

result in the highest T_g for either P_1 or P_2 phase among the five cured systems. Similarly, adding PCL-PU would cause a more incompatible cured system when compared with that adding PDEA-PU; hence T_g in the P_1 phase for the former system would be higher. With a fixed PU type, adding a higher molecular weight of PU would cause a more incompatible ST/UP/LPA system (see Figs. 4 and 5 in part 1 of this article), and, in turn, a higher T_g in either the P_1 or P_2 phase.

For the less compatible MA-PG-PA type of UP systems [Table VI(b)], the T_g in the P_1 phase was found to be either higher (relatively compatible PDEA and PCL1 systems) or lower (relatively incompatible PCL2 and PPG1 systems) than that of the corresponding MA-PG type of UP system [compare Tables VI(a) and VI(b)]. The former case

**Figure 3** Thermally stimulated current profile of TSC for neat PU-based LPAs. Curve 1: PCL1-PU; curve 2: PCL2-PU; curve 3: PDEA1-PU; curve 4: PDEA2-PU; curve 5: PPG1-PU.**Figure 4** Thermally stimulated current profile of TSC for cured low-shrink MA-PG type of UP resin at MR = 2/1 containing 10% by wt. of varied PU-based LPA after an isothermal cure at 110°C for 1 h and a postcure at 150°C for another h. Curve 1: PCL1-PU system; curve 2: PCL2-PU system; curve 3: PDEA1-PU system; curve 4: PDEA2-PU system; curve 5: PPG1-PU system.

would be again due to the less plasticization effect of R phase on the P_1 phase, while the latter case would result from a much lower crosslinking density in the P_1 phase due to a much more deviation (less than) from a molar ratio (MR) of 2 : 1 for styrene consumed to polyester C=C bonds reacted in the P_1 phase. (The crosslinking density would reach an optimum at an MR of 2 : 1 and lead to a maximum T_g for styrene-crosslinked polyester matrices as reported in the literature.¹²)

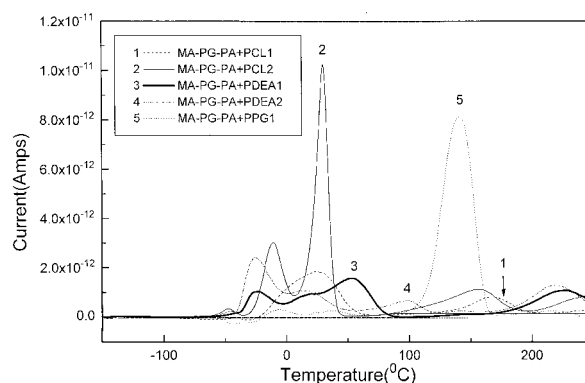
**Figure 5** Thermally stimulated current profile of TSC for cured low-shrink MA-PG-PA type of UP resin at MR = 2/1 containing 10% by wt. of varied PU-based LPA after an isothermal cure at 110°C for 1 h and a postcure at 150°C for another hour. Curve 1: PCL1-PU system; curve 2: PCL2-PU system; curve 3: PDEA1-PU system; curve 4: PDEA2-PU system; curve 5: PPG1-PU system.

Table VI Transition Temperatures (°C) for Cured Samples of ST/UP/LPA Systems as Determined by the Method of TSC

(a) MA-PG Type of UP System					
LPA	PCL1	PCL2	PDEA1	PDEA2	PPG1
Model	P-P-S	P-P-S	P-P-S	P-P-S	P-(P-P-S)
$T_g(P_1)$	140	191	127	137	225
$T_g(P_2)$	90	97	—	—	163
$T_g(P_3)$	—	—	—	—	100
T_m	30	40	—	—	—
$T_{g\alpha}(R_1)$	—	-22	22	23	—
$T_{g\beta}(R_1)$	—	-46	-28	-28	-53
$T_{g\gamma}(R_1)$	-44	—	-49	-50	—
$T_g(R_2)$	5	—	—	—	6

(b) MA-PG-PA Type of UP System					
LPA	PCL1	PCL2	PDEA1	PDEA2	PPG1
Model	P-(P-P-S)	P-(P-P-S)	P-(P-P-S)	P-(P-P-S)	P-(P-P-S)
$T_g(P_1)$	168	156	228	219	221
$T_g(P_2)$	—	—	153	140	141
$T_g(P_3)$	—	—	53	98	38
T_m	25	28	—	—	—
$T_{g\alpha}(R_1)$	—	-11	20	15	—
$T_{g\beta}(R_1)$	—	-48	-25	-26	-52
$T_{g\gamma}(R_1)$	-42	—	-41	-45	—
$T_g(R_2)$	7	—	—	—	-5

In general, the T_g in the P_1 phase would depend upon the relative importance of the two opposing effects, namely, the plasticization effect of the R phase on the P_1 phase and the crosslinking effect of the P_1 phase itself. For the MA-PG-PA type of UP systems, the most compatible PDEA system would generally possess the highest T_g in the P_1 phase. Also, adding a lower molecular weight of PU (with a fixed PU type) would lead to a higher T_g in the P_1 phase [Table VI(b)]. Both are in contrast to that of the MA-PG type of UP systems. Therefore, it is inferred that the crosslinking effect of the P_1 phase would be more significant in determining the T_g of the P_1 phase for the less compatible MA-PG-PA systems, while the plasticization effect of the R phase on the P_1 phase would be more important for the more compatible MA-PG systems.

Reaction-Induced Phase Separation for ST/UP/LPA Systems During Curing

For the ST/UP/LPA system, it should be noted that all of the cured samples listed in Table VI phase separated, despite theoretically calculated

T_c s of the uncured systems (Table III) all being well below room temperatures. This is due to the reaction-induced phase separation during the cure.

For the ST/UP/LPA system with a molar ratio of styrene to polyester C=C bonds of 2 : 1 and a 10% by weight of PU-based LPA, almost all the 10 uncured ternary systems exhibited a homogeneous single phase at room temperature except the ST/UP/PPG-PU systems (Table VIII in part 1 of this article). When the mixing temperature was increased to 110°C, even the uncured ST/UP/PPG-PU systems turned out to be a homogeneous single phase. As the cure reaction at 110°C proceeded, the increase in molecular weights of the reacting species via crosslinking reactions could enhance the phase separation (due to the decrease in entropy of mixing), the onset of which would generally occur at very low reaction conversion⁵ ($\alpha < 1\%$). Near the gelation point ($\alpha \sim 10\%$),¹³ the mass transfer into or out of the continuous phase or the dispersed phase would essentially cease. From then on, the morphology for the partially

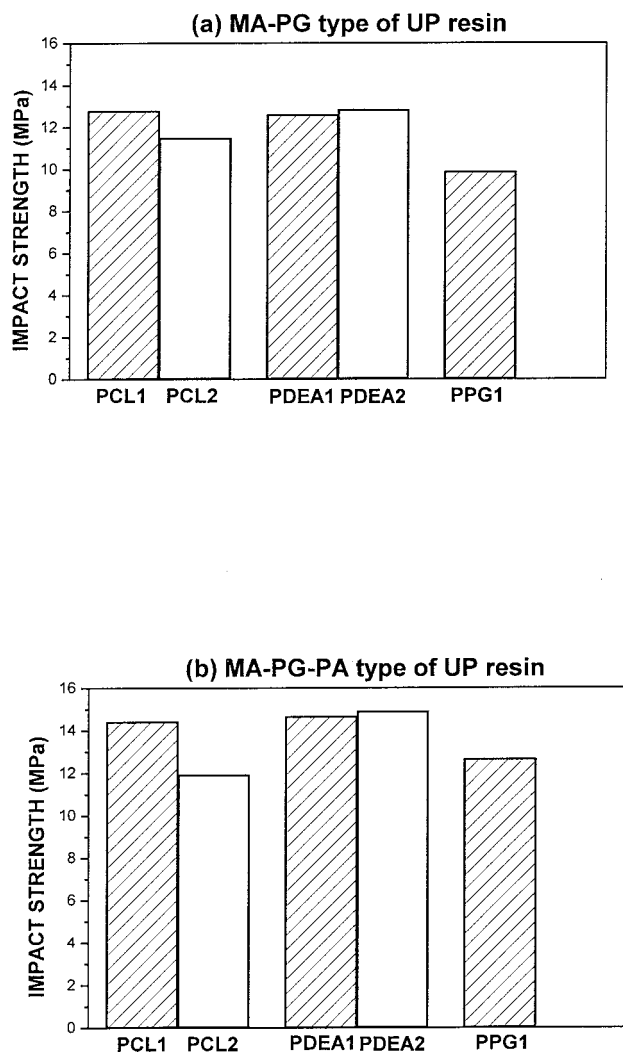


Figure 6 The effects of PU chemical structure and molecular weight on the impact strength of cured UP resins containing 10% PU-based LPA. (a) MA-PG type of UP resin; (b) MA-PG-PA type of UP resin.

cured sample would be virtually unchanged, while the crosslinking density in each phase region would increase with the cure conversion until a limiting conversion (Table IX in part 1 of this article) is reached. A further postcure at 150°C may somewhat enhance the crosslinking density in each phase region, especially that of P_1 phase, where the three-dimensional microgel structures would be the most compact among all the phases.

Effects of PU As an Energy Absorber and Interfacial Adhesion on Impact Strength

Figure 6 shows the effects of PU chemical structure and molecular weight on the impact strength

of cured samples. For the MA-PG type of UP systems [Fig. 6 (a)], the impact strength was generally the largest for the sample containing PDEA-PU, followed by the PCL- and PPG1-containing samples. This would be due to the fact that the better interfacial adhesion between the crosslinked polyester phase and the LPA phase, such as the more compatible systems containing PDEA-PU, would be favorable for the increase of impact strength.

Adding a higher molecular weight of PU (with a fixed PU type) would either increase (relatively compatible PDEA systems with a flake-like microstructure³) or decrease (relatively incompatible PCL system with a globule morphology³) the impact strength. The former could be due to the better energy absorber for the higher molecular weight of PU during the impact test, while the latter would be due to the more pronounced degree of reaction-induced phase separation during the cure, and hence, the worse interfacial adhesion for the system with a higher molecular weight of PU.

The impact strength was higher for the MA-PG-PA system than the MA-PG system [compare Figs. 6 (a) and 6 (b)]. The introduction of a saturated aromatic anhydride in the UP backbone would decrease the degree of C=C unsaturation, and, in turn, diminish the crosslinking density of the cured sample. A higher impact strength could then result. The effects of PU chemical structure and molecular weight on the impact strength exhibited the same trend as that of the MA-PG systems.

Effects of Crosslinking Density and Interfacial Adhesion on Tensile Properties

Based on the iso-strain model in Figures 1(a) and 1(b), tensile strength of the sample would be dominated by $(1-\lambda)\sigma_{P_1}$ provided that the major continuous phase is less brittle than the minor cocontinuous or dispersed phase, and there is sufficient phase P_1 to carry the tensile load even after phases R, P_2 , and P_3 have failed, where $(1-\lambda)$ and σ_{P_1} are the volume fraction and the tensile strength for the stiff P_1 phase, respectively.

Figure 7 shows the effects of PU chemical structure and molecular weight on the tensile strength of cured samples. For the MA-PG type of UP systems [Fig. 7(a)], the tensile strength was the largest for the sample containing PDEA-PU, followed by the PCL- and PPG1-containing samples, which exhibited the same trend as that of impact strength shown in Figure 6(a).

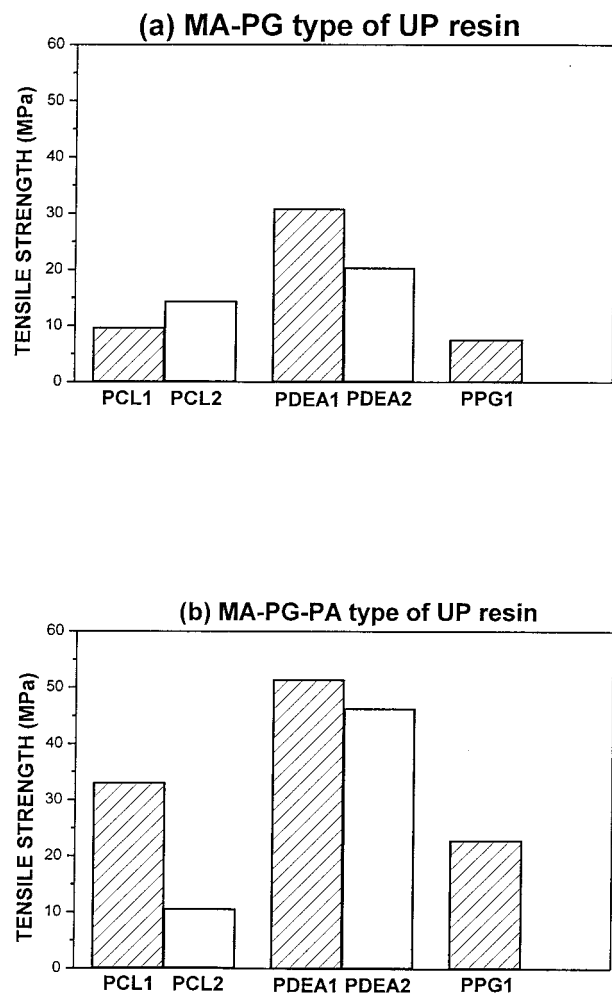


Figure 7 The effects of PU chemical structure and molecular weight on the tensile strength of cured UP resins containing 10% PU-based LPA. (a) MA-PG type of UP resin; (b) MA-PG-PA type of UP resin.

For the most compatible PDEA-containing samples, the molar ratio of styrene consumed to polyester C=C bonds reacted (i.e., crosslinking density) in the continuous phase of crosslinked polyester [i.e., P_1 phase in Fig. 1(a)] would exhibit the smallest negative deviation from 2 : 1, leading to the highest crosslinking density in that phase, and, in turn, the greatest enhancement in tensile strength for the whole sample. Also, the best interfacial adhesion for the PDEA-containing sample could be most beneficial for the increase of tensile strength.

Adding a higher molecular weight of PU (with a fixed PU type) would either decrease (relatively compatible PDEA systems) or increase (relatively incompatible PCL systems) the tensile strength, which showed a reverse trend to that of the im-

pact strength. When the molecular weight of PCL-PU added was increased from 18,000 to 27,000 g/mol, the globule morphology for the cured sample remained [see Figs. 4(a) and 4(b) in part 1 of this article], and the phase separation rate during the cure prior to gelation (gel conversion $\alpha \approx 10\%$) would be slower due to the increase in viscosity, leading to a less negative deviation from MR of 2 : 1 in the major continuous phase. Hence, the crosslinking density in that phase for the PCL2 system would be higher than the PCL1 system, as supported by a higher final conversion for the former system³ (83 vs. 77%), and a higher tensile strength could then result. On the other hand, when the molecular weight of PDEA-PU added was increased from 2800 to 5000 g/mol, although the flake-like microstructure for the cured sample remained [see Figs. 4(c) and 4(d) in part 1 of this article], yet the phase separation during the cure became more conspicuous, resulting in a more negative deviation from MR of 2 : 1 in the major continuous phase, and, in turn, a lower tensile strength.

The tensile strength was generally higher for the MA-PG-PA system than the MA-PG system due to the increase of chain stiffness in the UP skeleton for the former system [compare Figs. 7(a) and 7(b)], the trend of which is the same as that of impact strength. The effects of PU chemical structure on the tensile strength exhibited the same trend as that of the MA-PG systems, while adding a higher molecular weight of PU would lead to a lower tensile strength for both the PCL and PDEA systems. With the more incompatible MA-PG-PA type of UP system, adding a higher molecular weight of PCL-PU (i.e., PCL2) would result in a much more noticeable phase separation [see Figs. 5(a) and 5(b) in part 1 of this article], leading to a more negative deviation from MR of 2 : 1 in the major continuous phase. Hence, the tensile strength for the whole sample would be reduced due to a lower crosslinking density in that phase.

Effects of Network Compactness and Volume Fraction in the Major Continuous Phase on Young's Modulus

Based on the iso-strain model in Figures 1(a) and 1(b), Young's modulus of the sample would be dominated by $(1-\lambda)E_{P_1}$, because moduli of phases R, P_2 , and P_3 multiplied by their corresponding volume fractions would generally be much smaller than that of phase P_1 multiplied by its

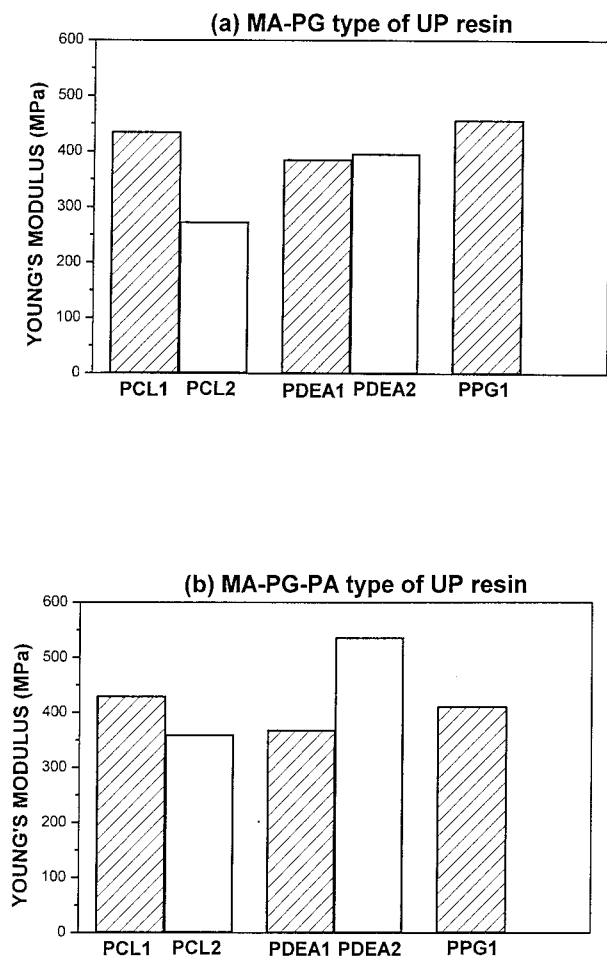


Figure 8 The effects of PU chemical structure and molecular weight on Young's modulus of cured UP resins containing 10% PU-based LPA. (a) MA-PG type of UP resin; (b) MA-PG-PA type of UP resin.

volume fraction [i.e., $(1-\lambda)E_{P_1}$], where E_{P_1} is the Young's modulus of the major continuous phase.

Figure 8 shows the effects of PU chemical structure and molecular weight on Young's modulus of cured samples. For the MA-PG type of UP systems [Fig. 8(a)], Young's modulus was generally the largest for the sample containing PPG1-PU, followed by the PCL- and PDEA-containing samples, which showed a reverse trend to that of tensile strength shown in Figure 7(a). This reveals that a less compatible ST/UP/LPA system could result in a higher Young's modulus after the cure. Because the Young's modulus represents the extent of resistance to deformation for a sample in the initial stage of tensile test, during which the sample would be unbroken, it would be connected with degree of tightness of the network rather than degree of crosslinking of the sample.

For ST/UP/LPA systems, a higher degree of phase separation during the cure would lead to a lower styrene content in the continuous phase of crosslinked polyester [phase P_1 in Figs. 1(a) and 1(b)]. A lower average crosslink length of styrene and a more compact network in that phase would result after the cure, which, in turn, could lead to a higher Young's modulus for the whole sample.

Adding a higher molecular weight of PU (with a fixed PU type) would either increase (relatively compatible PDEA systems) or decrease (relatively incompatible PCL systems) Young's modulus, which exhibited a reverse trend to that of the tensile strength shown in Figure 7(a). This is because while the less negative deviation from MR of 2 : 1 in the major continuous phase due to the reaction-induced phase separation would be favorable for the tensile strength, it would be detrimental to Young's modulus.

For the MA-PG-PA system, Young's modulus would be either higher (PCL2 and PDEA2 systems) or lower (PCL1, PDEA1, and PPG1 systems) than that of the MA-PG system [compare Figs. 8(a) and 8(b)], which is in contrast to the tensile strength shown in Figure 7, where it would be higher for the MA-PG-PA system than the MA-PG system. Apparently, the increase of chain stiffness in the UP backbone for the MA-PG-PA system (in reference to the MA-PG system) alone could not outweigh other potentially adverse effects for the increase of Young's modulus. In general, a more incompatible ST/UP/LPA system, such as the MA-PG-PA system, would lead to a more negative deviation from a molar ratio of 2 : 1, and a lower volume fraction both in the major continuous phase. Experimental results of Young's modulus in Figure 8 imply that for the PCL2 and PDEA2 systems, the former effect, leading to a more compact network therein (i.e., a higher E_{P_1} for the MA-PG-PA system), would be more significant than the latter one, while for the PCL1, PDEA1, and PPG1 systems, the latter effect (i.e., a lower $(1-\lambda)$ for the MA-PG-PA system) would be more pronounced. The effects of PU chemical structure and molecular weight on Young's modulus mostly exhibited the same trend as that of the MA-PG systems. The highest Young's modulus for the PDEA2 system could be due to the best balance between the molar ratio and the volume fraction in the major continuous phase [see Fig. 5(d) in part 1 of this article].

CONCLUSIONS

The effects of thermoplastic polyurethane-based LPA with different chemical structures and molecular weights on the glass transition temperatures and mechanical properties for styrene-crosslinked low-shrink polyester matrices have been investigated by an integrated approach of static phase characteristics-cured sample morphology-reaction conversion-property measurements. Based on the proposed Takayanagi mechanical models, the transition temperatures in each phase region of cured samples in the model could be identified by the method of thermally stimulated currents (TSC). In general, the T_g in the P_1 phase would depend upon the relative importance of the two opposing effects, namely, the plasticization effect of R phase on P_1 phase and the crosslinking effect of P_1 phase itself in terms of the molar ratio of styrene consumed to polyester C=C bonds reacted. A more incompatible ST/UP/LPA system could lead to a lower plasticization effect and a concomitant lower crosslinking effect, the former of which would be favorable for the increase of T_g in the P_1 phase, while the latter of which would be unfavorable.

The mechanical properties have been demonstrated to depend upon the cured sample morphology, the molar ratio of styrene consumed to polyester C=C bonds reacted, and the volume fraction both in the major continuous phase of styrene-crosslinked polyester as a result of phase separation during cure. These three factors would be intimately connected with the compatibility characteristics of ST/UP/LPA systems, and could be controlled by the chemical structure and molecular weight of UP and LPA.

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