

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. I: Miscibility, Curing Behavior, and Volume Shrinkage

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ABSTRACT: The effects of chemical structure and molecular weight of three series of thermoplastic polyurethane-based (PU) low-profile additives (LPA) on the miscibility of styrene (ST)/unsaturated polyester (UP) resin/LPA ternary systems prior to reaction were investigated by using the Flory-Huggins theory and group contribution methods. The reaction kinetics during the cure at 110°C and the cured sample morphology were also studied by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively. The phase-separation characteristics of ST/UP/LPA systems during the cure, as revealed by the cured-sample morphology, and the DSC reaction-rate profile, could be generally predicted by the calculated upper critical solution temperature for the uncured ST/UP/LPA systems. Finally, based on the measurements for volume change and microvoid formation, volume shrinkage characteristics for the cured ST/UP/LPA systems have been explored. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 543–557, 2000

Key words: unsaturated polyester resins; low-profile additives; curing; miscibility; polyurethane; volume shrinkage

INTRODUCTION

Unsaturated polyester resins (UP) are usually made from maleic anhydride, saturated dicarboxylic acid, or its anhydride, and glycol by polycondensation reactions. The number of C=C unsaturation in the UP resin generally ranges from

4 to 20, with a corresponding number-average molecular weight of 800 to 5000 for the UP. The UP resins can be copolymerized with styrene monomers (ST) via free radical crosslinking reactions to form a three-dimensional network. However, one of the major problem in the reactive processing of unsaturated polyester molding compounds, such as SMC (sheet molding compound) and BMC (bulk molding compound), is the high polymerization shrinkage. This could lead to many undesirable problems, such as inability to mold to close tolerance, and wavy surface for the molded parts, etc.¹

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For the past 30 years, the SMC and BMC industries have been using the approach of adding specific thermoplastic polymers as low-profile additives (LPA) in the unsaturated polyester resins (UP) to reduce or even eliminate the polymerization shrinkage during the cure process.^{1,2} Depending on the chemical composition and structure of UP resins and LPA employed, differing degrees of drift in styrene/UP/LPA composition as a result of phase separation during the cure would occur for the styrene/UP/LPA system.³⁻⁶ This could greatly affect the physical and mechanical properties of cured samples. Therefore, the miscibility studies of ST/UP/LPA systems would be indispensable to compound design in SMC and BMC industries.

The objective of this work is to investigate the effects of chemical structure and molecular weight of thermoplastic polyurethane-based LPA on the miscibility and the curing behavior of ST/UP/LPA systems. Three series of LPA including five different LPAs have been synthesized. Using an integrated approach of static ternary phase characteristics of the uncured ST/UP/LPA as predicted from the Flory-Huggins theory, curing kinetics and cured sample morphology, in-depth elucidation of the phase separation characteristics of ST/UP/LPA systems during the cure is given. Based on the measurements for volume change and microvoid formation, volume shrinkage characteristics for the cured ST/UP/LPA systems are also discussed.

EXPERIMENTAL

Synthesis of PU-Based LPA

2,4-Tolylene diisocyanate (2,4-TDI, Janssen Chimica) and varied polyhydroxy materials, including polycaprolactone diol (PCL, Aldrich), polyester diol (self-synthesized⁷ poly(diethylene adipate) diol, PDEA), and polyether diol (poly(propylene glycol) diol, PPG, Aldrich), were first reacted to make the hydroxyl-terminated PU prepolymers in a five-neck 2-L glass vessel reactor by solution polymerizations in styrene, where an isothermal temperature ranging from 55 to 80°C, a nitrogen sparge rate of 50 mL/min, and a stirring speed of 300 rpm were employed. Subsequently, excess maleic anhydride (MA, Acros) was added to make the carboxyl-terminated thermoplastic PU-based LPAs isothermally.^{7,8} The raw materials used and reaction temperature histo-

ries for the two reaction steps in the synthesis of the five LPAs, namely PCL1-PU, PCL2-PU, PDEA1-PU, PDEA2-PU, and PPG1-PU, are summarized in Table I, while the properties of the LPAs synthesized are summarized in Table II.

UP Resins

The UP resins were made from MA and 1,2-propylene glycol (PG, Acros), with and without modification by a saturated dibasic aromatic anhydride, such as phthalic anhydride (PA, Acros), by polycondensation reactions in the bulk phase.^{6,9} Two UP resins, designated as MA-PG and MA-PG-PA, were synthesized, where the molar ratio of PA to MA was chosen to be 1:2. The molecular characteristics of the UP resins are summarized in Table III.

Preparation of ST/UP/LPA Solutions

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 (TBPB, Aldrich).

Phase Characteristics

To study the compatibility of ST/UP/LPA systems prior to reaction, 20 g of sample solutions were prepared in 100 mL separatory glass cylinders, which were placed in a constant-temperature water bath at 30°C. The phase separation time was recorded and the mixture of each layer was separated and weighed.

Cure Kinetics

For the cure kinetic study, 6–10 mg sample solution was placed in a hermetic aluminum sample pan. The isothermal reaction rate profile at 110°C was measured by a DuPont 9000 differential scanning calorimeter, and the final conversion of total C=C bonds at 110°C was calculated.¹⁰

Morphology

In the morphological study, the fractured surface of the sample, which was cured at 110°C for 1 h, followed by a postcure at 150°C for another 1 h in a stainless steel mold with inner trough dimensions of 17 × 1.7 × 0.42 cm, was observed by SEM (Hitachi S-550) at 1000×.

Table I Raw Materials Used and Reaction Temperature Histories in the Synthesis of PU-Based LPA

LPA Codes	Diisocyanate	Diol	M_n	NCO/OH ^a	MA ^b	Catalyst (wt %)	Inhibitor (ppm)	Solvent (wt %)	Temp. History (°C) (Duration Time in Hours)
PCL1-PU	2,4-TDI	polycaprolactone	1250	0.875	0.0625	DBTDL ^c (0.2)	HQ ^d (300)	Styrene (50)	55(2)-55(2) ^e
PCL2-PU	2,4-TDI	polycaprolactone	2000	0.933	0.010	DBTDL (0.2)	HQ (300)	Styrene (50)	55(2)-55(2)
PDEA1-PU	2,4-TDI	poly(diethylene adipate)	1890	0.86	0.035	DBTDL (0.2)	HQ (300)	Styrene (60)	80(2)-80(2)
PDEA2-PU	2,4-TDI	poly(diethylene adipate)	4890	0.85	0.015	DBTDL (0.2)	HQ (300)	Styrene (60)	80(2)-80(2)
PPG1-PU	2,4-TDI	poly(propylene glycol)	2000	0.85	0.015	DBTDL (0.2)	HQ (300)	Styrene (60)	70(2)-75(3)

^a Equivalent ratio; ^b by equivalent with respect to —OH groups; ^c DBTDL denotes dibutyltin dilaurate (Janssen Chimica); ^d HQ denotes hydroquinone; ^e The first step of reaction was carried out at 55°C for 2 h, and the second step of reaction was conducted at 55°C for another 2 h.

Table II Molecular Weights and Transition Temperatures for the Five PU-Based LPAs

LPA Codes	M_n (GPC)	M_w (GPC)	M_w/M_n	T_g (°C)	T_m (°C)
PCL1-PU	18770	33040	1.76	-40.7	35.9
PCL2-PU	27170	71340	2.63	-30.4	39.2
PDEA1-PU	2870	4910	1.71	-50.3	—
PDEA2-PU	5040	27600	5.48	-51.9	—
PPG1-PU	9750	15100	1.55	-55.2	—

RESULTS AND DISCUSSION

Synthesis of PU-Based LPA

There were two stages of reactions in the synthesis of PU-based LPA (Fig. 1). For the first stage of reaction of 2,4-TDI and excess polyhydroxy materials, the molecular weight of diols employed ranged from 1000 to 5000 g/mol (Table I). Using diol with a molecular weight lower than 1000g/mol could lead to the less chain flexibility of the PU prepolymer to be synthesized, while using diol with a molecular weight higher than 5000 g/mol would result in a relatively high molecular weight of PU prepolymer, which, in turn, could reduce the compatibility of ST/UP/LPA system during the cure reaction and would deteriorate the physical and mechanical properties of molded parts. At the end of the first stage of reaction, the —NCO functional group of 2,4-TDI at 2300 cm^{-1} was found⁷ to disappear as measured by FTIR.

Table III 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.

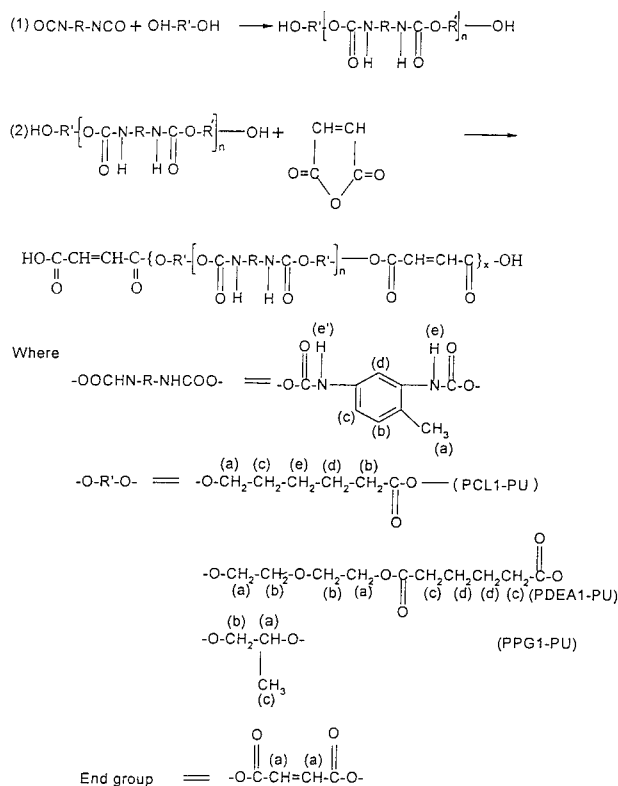


Figure 1 Schemes of the two-stage synthesis of PU-based LPA. Different proton environments as identified from the $^1\text{H-NMR}$ for the three series of PU-based LPAs are also indicated.

For the second-stage reaction of the hydroxyl-terminated prepolymers and excess maleic anhydride, the carboxyl-terminated thermoplastic PU-based LPAs with unsaturated C=C bonds were obtained. On one hand, the terminal carboxylic acid groups introduced in the LPA could react with the thickening agent, such as MgO, during the thickening¹¹ process in the preparation of

polyester molding compounds, and hence, the phase separation of LPA from the molding compound could be prevented prior to cure reaction. On the other hand, the unsaturated C=C bonds in the LPA would allow the chemical reaction to occur between LPA and UP resins via free radical crosslinking during the cure reaction, and the global phase separation of LPA from the reaction mixture could then be avoided.

Characterization of LPA

The chemical shifts as identified by $^1\text{H-NMR}$ for the five PU-based LPAs are summarized in Table IV. The chemical shift of 3.5–3.7 δ could be assigned to the H proton in the —NHCOO— group. The urethane linkage —NHCOO— due to the reaction of 2,4-TDI and diol would encounter appreciable steric hindrance caused by the adjacent neighboring aromatic ring structure so that the strength of intermolecular hydrogen bonding exerted by —NHCOO— could be diminished, leading to a lower chemical shift than expected for the H proton in the —NHCOO—. For the five PU-based LPAs, $^{13}\text{C-NMR}$ results⁷ all showed a chemical shift at 153 δ , which is a characteristic signal due to the C nucleus in the —NHCOO— group, and the structure of PU could be further confirmed.

The number-average molecular weight, M_n , for the five PU-based LPAs fell in the range of 2800–28,000, while the polydispersity (PD) generally ranged from 1.55 to 2.63, except PDEA2-PU with a PD of 5.48 (Table II).

DSC results showed that the PCL-PU synthesized is a crystalline polymer with a melting temperature around 35–40°C. Among the three series of PU-based LPAs synthesized, the glass transition temperature T_g (ranging from –30 to

Table IV Chemical Shift (δ) Assignment for the Three Series of PU-Based LPAs as Identified by $^1\text{H NMR}$

Proton Position (Fig. 1)	(a)	(b)	(c)	(d)	(e)
—OOCHN—R—NHCOO—:	2.1–2.2	6.9–7.1	7.1–7.2	7.7–7.8	3.5–3.7 ^a
—O—R'—O—:					
PCL1-PU	4.1	2.3	1.6–1.7	1.5–1.6	1.3–1.4
PDEA1-PU	4.2–4.3	3.6–3.7	2.3	1.6	
PPG1-PU	3.6	3.4	1.1		
—OOC—CH=CH—COO—:	6.3–6.8				
CDCl_3 solvent:	7.3				

^a The peak due to the proton in the urethane linkage —NHCOO— could be overlapped with that due to other proton environments.

Table V Values for the Calculation of Dipole Moment and Solubility Parameter for the PCL1-PU Type of LPA as an Example

Index	Units	Constitution	Number	P_{LLi}	R_{LLi}	E_{coh} (J/mol)	V_i (cm ³ /mol)
1		—COOH	2	16	7.21	27630	28.5
2		—CH=CH—	2	8.88	8.88	8620	27.0
3		—COO—	2 + 60.4 × 2 = 122.4	15	6.21	18000	18.0
4		>C=O	1 + 60.4 × 1 = 61.4	10	4.53	17370	10.8
5		—CH ₂ —	5 + 60.4 × 5 = 307	4.65	4.65	4940	16.1
6		—NH—	60.4 × 2 = 120.8	20	4.53	8370	4.5
7		>C ₆ H ₃ —	60.4	24.41	24.41	31940	33.4
8		—CH ₃ (attached to benzene ring)	60.4	5.64	5.47	4710	33.5

−55°C) was the highest for the polycaprolactone type (i.e., PCL-PU), followed by the polyester type (i.e., PDEA-PU), and the polyether type (i.e., PPG-PU). In reference to Figure 1, the numbers of ester linkage in the —O—R'—O— segment for PCL-PU, PDEA-PU, and PPG-PU are 1, 2, and 0, respectively, while the number of ether linkage —O— (a swivel center) are 0, 1, and 0, respectively. Therefore, the more ester linkage —COO— and the less ether linkage —O— (a swivel center) both in the —O—R'—O— segment of the PU-based LPA (Fig. 1) would be favorable for the increase in T_g for PU. (Higher M_n would also be favorable for the increase in T_g as shown in Table II.)

Molecular Polarity of UP Resin and PU-Based LPA

The molecular polarity of UP and LPA can be evaluated in terms of dipole moments, μ , which can be calculated by using the Debye's equation¹² as follows:

$$P_{LL} - R_{LL} = [(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]M/\rho = 4/9 \pi N_A \mu^2 / kT \sim 20.6 \mu^2 \quad (1)$$

or

$$\mu \sim [(P_{LL} - R_{LL})/20.6]^{1/2} \quad (2)$$

where P_{LL} is molar dielectric polarization, R_{LL} is molar refraction, ϵ is dielectric constant, n is refractive index, M is molecular weight, ρ is density, N_A is the Avogadro's number, k is the Boltzmann's constant, and T is the room temperature at 25°C in Kelvin scale (i.e., 298 K).

Because the molecular polarity of the UP resins and the LPAs should be compared on the same basis, the dipole moment per unit volume, μ' , is calculated as below,

$$\mu' = (\mu^2/V)^{1/2} \sim [(P_{LL} - R_{LL})/(20.6V)]^{1/2} \quad (3)$$

where V is the molar volume.

As an calculation example of μ and μ' for the UP resin and LPA, consider the theoretical formula of PCL1-PU (Fig. 1). Because $M_n = 18,770$, the average degree of polymerization could be calculated as $n = 60.4$ (assuming $x = 1$). Based on the group contribution method, the type and number of constitution units for PLC1-PU, and their corresponding P_{LL} , R_{LL} , and V values^{12,13} are displayed in Table V, from which $\Sigma P_{LLi} = 8158.33$, $\Sigma R_{LLi} = 4849.95$, and $\Sigma V_i = 12504.38$. One can then obtain $\mu \sim 12.67$ debye/mol^{1/2} and $\mu' \sim 0.1133$ debye/cm^{3/2} by using eq. (2) and eq. (3), respectively. The calculated μ and μ' for all of the UP resins and LPAs are listed in Table VI.

The calculated dipole moment per unit volume, μ' , was higher for all of the PU-based LPAs than the UP resins. Among the three series of PU-based LPAs, μ' was the highest for the polycaprolactone type (i.e., PCL-PU), followed by the polyester type (i.e., PDEA-PU), and the polyether type (i.e., PPG-PU). For the UP resins, modification of UP by PA with an aromatic ring structure could lead to a decrease of μ' .

Solubility Parameter and Interaction Parameter for ST/UP/LPA Ternary Systems

Assuming that the ST(1)/UP(2)/LPA(3) ternary system is weakly polar, the three pairs of Flory-

Table VI Calculated Values of Dipole Moments per Mol, Molar Volumes, Dipole Moments per Unit Volume, and Solubility Parameters for the LPAs, UP Resins, and Styrene Monomers, and Flory-Huggins Interaction Parameters for ST/UP/LPA Systems

(a)						
	Dipole Moment μ (debye/mol ^{1/2})	Molar Volume V (cm ³ /mol)	Dipole Moment per Unit Volume $\mu/V^{1/2}$ (debye/cm ^{3/2})	δ (J/cm ³) ^{1/2}		
(a) LPA						
PCL1-PU	12.67	12504	0.1133	25.43		
PCL2-PU	15.24	18100	0.1133	25.43		
PDEA1-PU	4.71	1970.1	0.1062	24.74		
PDEA2-PU	6.28	3426.8	0.1072	24.75		
PPG1-PU	7.94	7029.2	0.0948	23.92		
(b) UP resin						
MA-PG	3.15	1319.6	0.0867	23.35		
MA-PG-PA	3.13	1400.0	0.0836	23.94		
(c) monomer styrene						
styrene	0	18.9	0	18.91		
(b)						
	MA-PG Type of UP			MA-PG-PA Type of UP		
	χ_{12}	χ_{23}	χ_{13}	χ_{12}	χ_{23}	χ_{13}
PCL1-PU	0.901	0.197	1.942	1.156	0.101	1.942
PCL2-PU	0.901	0.198	1.945	1.156	0.102	1.945
PDEA1-PU	0.901	0.088	1.555	1.156	0.029	1.555
PDEA2-PU	0.901	0.089	1.561	1.156	0.030	1.561
PPG1-PU	0.901	0.015	1.149	1.156	1.65×10^{-6}	1.149

^a The subscripts 1, 2, and 3 denote styrene, UP, and LPA, respectively.

^b A temperature of 298 K was used in the calculations of χ_{ij} .

Huggins interaction parameters, χ_{ij} , for the system, can then be related to the solubility parameters by the following equation,^{14–16}

$$\chi_{ij} = V_r/(RT)(\delta_i - \delta_j)^2 \quad (4)$$

where V_r is the reference molar volume (styrene was taken as the reference species here), δ_i and δ_j are the solubility parameters for species i and j , respectively, R is the gas constant, and T is the absolute temperature. The solubility parameter can be calculated by using group contribution methods,

$$\delta = (\sum E_{\text{coh}}/\sum V_i)^{1/2} \quad (5)$$

where E_{coh} and V_i are the cohesive energy and the molar volume for the constitution unit i of the species, respectively.

As an calculation example for δ , the type and number of constitution units for PLC1-PU, and

their corresponding E_{coh} and V values^{12,13} are displayed in Table V, from which $\sum E_{\text{coh}} = 8083554$, and $\sum V_i = 12504.38$. One can then obtain $\delta = 25.43$ (J/cm³)^{1/2} according to eq. (5). The calculated δ for all of the UP resins, LPAs, and styrene are listed in Table VI.

The calculated solubility parameter, δ , was generally higher for the PU-based LPAs than the UP resin, while the solubility parameter of styrene monomer was lower than those of the PU-based LPA and UP resin. Among the three series of PU-based LPAs, δ was the highest for the polycaprolactone type (i.e., PCL-PU), followed by the polyester type (i.e., PDEA-PU), and the polyether type (i.e., PPG-PU), which showed the same trend as that of μ' .

For ST(1)/UP(2)/LPA(3) ternary systems, the calculated Flory-Huggins interaction parameters, χ_{ij} , based on eq. (4), are listed in Table VI. For a given LPA, modification of UP resin by PA would result in an increase in χ_{12} , revealing an adverse

effect on the compatibility of the ST/UP/LPA ternary system. For a given UP resin, employing the polycaprolactone type of PU (i.e., PCL-PU) would lead to the highest χ_{23} and χ_{13} values, followed by the polyester type of PU system (i.e., PDEA-PU) and the polyether type of PU system (i.e., PPG-PU). Therefore, employing the PCL-PU would be theoretically the least favorable for the compatibility of the ST/UP/LPA ternary system, followed by the PDEA-PU system and the PPG-PU system.

Relationship between Upper Critical Solution Temperature (UCST) and Compatibility of ST/UP/LPA Ternary Systems

The Gibbs free energy change of mixing, $\Delta G'_M$, for a binary polymer blend can be expressed as,^{15,16}

$$\Delta G'_M/RT = v_1/n_1 \ln v_1 + v_2/n_2 \ln v_2 + v_1 v_2 \chi_{\text{blend}} \quad (6)$$

where v_1 and v_2 are volume fractions, n_1 and n_2 are “degrees of polymerization” in terms of a reference volume V_r , and χ_{blend} is a dimensionless interaction parameter. For the ST/UP/LPA ternary system in this study, the miscibility of the system was found to be increased as the mixing temperature was increased. (Styrene monomer is a common solvent for both UP resin and LPA.) Hence, the ST/UP/LPA ternary system would possess an upper critical solution temperature (UCST) instead of a lower critical solution temperature (LCST). In reference to eq. (6), the Gibbs free energy change of mixing, ΔG_M , for the ST/UP/LPA ternary system can then be generalized as,^{16,17}

$$\Delta G_M/RT = [v_1/n_1 \ln v_1 + v_2/n_2 \ln v_2 + v_3/n_3 \ln v_3] + [v_1 v_2 \chi_{12} + v_2 v_3 \chi_{23} + v_1 v_3 \chi_{13}] \quad (7)$$

where the symbols have the same meaning as those of eq. (6), and the subscripts 1, 2, and 3 denote styrene, UP resin, and LPA, respectively. “Windows of miscibility” result when $\Delta G_M < 0$. By setting $\Delta G_M = 0$ in eq. (7), the UCST of the ternary system, T_c , can be solved as,

$$T_c = 298(v_1 v_2 \chi_{12}^0 + v_2 v_3 \chi_{23}^0 + v_1 v_3 \chi_{13}^0) / [- (v_1/n_1 \ln v_1 + v_2/n_2 \ln v_2 + v_3/n_3 \ln v_3)] \quad (8)$$

where χ_{ij}^0 is the interaction parameter at 298 K [Table VI(b)].

According to eq. (8), as χ_{ij}^0 is increased [i.e., the difference of solubility parameter δ_i and δ_j becomes large as revealed by eq. (4)], T_c would be higher, leading to the less compatibility of the ST/UP/LPA ternary system. The calculated T_c for all of the ST/UP/LPA ternary systems along with the volume fractions and “degrees of polymerization” needed to calculate T_c are displayed in Table VII.

Table VII shows that for both the MA-PG and the MA-PG-PA types of UP systems, the calculated T_c was well below room temperature. Also, the calculated T_c 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 (see Table VIII). The discrepancy in the theoretical trend of compatibility would be mainly attributed to the negligence of exothermic effect caused by the polar interaction between PU and UP resins in the calculation of ΔG_M , where the PPG-PU system, due to the lacking of ester linkage in the —O—R'—O— segment as mentioned earlier, would exhibit less polar interaction between PU and UP resins than PCL-PU and PDEA-PU systems.

As mentioned earlier, the calculated molecular polarity per unit volume for the PU-based LPA would be higher than that of the UP resins. Also, it would be higher for the MA-PG type of UP than that of the MA-PG-PA type of UP. Therefore, with a fixed PU-based LPA, the polarity difference (the absolute value) between UP and PU-based LPA per unit volume would be higher for the MA-PG-PA type of UP system than that for the MA-PG system, leading to a more incompatible ST/UP/LPA ternary system for the MA-PG-PA/PU pair than the MA-PG /PU pair. This could be confirmed by a higher calculated T_c for the MA-PG-PA system than the MA-PG system (Table VII), and a shorter phase separation time for the ST/MA-PG-PA/PPG1 system than for the ST/MA-PG/PPG1 system (Table VIII).

Table VII The Volume Fractions, “Degrees of Polymerization,” and Calculated T_c (K) for ST/UP/LPA Uncured Systems

	(a) Volume Fractions					
	MA-PG Type of UP			MA-PG-PA Type of UP		
	v_1	v_2	v_3	v_1	v_2	v_3
PCL1-PU	0.610	0.316	0.074	0.488	0.433	0.079
PCL2-PU	0.610	0.316	0.074	0.488	0.433	0.079
PDEA1-PU	0.608	0.316	0.076	0.487	0.432	0.081
PDEA2-PU	0.609	0.316	0.075	0.488	0.432	0.080
PPG1-PU	0.606	0.315	0.079	0.485	0.430	0.085

	(b) “Degrees of Polymerization”					
	MA-PG Type of UP			MA-PG-PA Type of UP		
	n_1	n_2	n_3	n_1	n_2	n_3
PCL1-PU	1	11.64	110.27	1	12.35	110.27
PCL2-PU	1	11.64	159.61	1	12.35	159.61
PDEA1-PU	1	11.64	17.37	1	12.35	17.37
PDEA2-PU	1	11.64	30.22	1	12.35	30.22
PPG1-PU	1	11.64	61.99	1	12.35	61.99

LPA	(c) T_c	
	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

Relationship between the Compatibility of ST/UP/LPA Systems, DSC Reaction Rate Profile, and Cured Sample Morphology

During the cure at 110°C, the sample solution containing the polycaprolactone-based PU (i.e., PCL-PU) was also more incompatible than that containing the polyester-based PU (i.e., PDEA-PU). This could be evidenced by the emergence of a shoulder in the DSC rate profile at the later

stage of reaction (see Fig. 2 for the MA-PG systems, and Fig. 3 for the MA-PG-PA systems), which will be explained later on, and the characteristics of larger microgel particles for the fractured surface [compare Fig. 4(a)–(b) and (c)–(d) for the MA-PG systems; Fig. 5(a)–(b) and (c)–(d) for the MA-PG-PA systems] for the former system. In contrast, the sample solution containing the polyether-based PU (i.e., PPG-PU) was the

Table VIII Phase Separation Time for ST/UP/LPA Uncured Systems at 30°C

	PCL1	PCL2	PDEA1	PDEA2	PPG1
MA-PG	∞^a	∞	∞	∞	800 min ^b
MA-PG-PA	∞	∞	∞	∞	500 min ^c

^a One phase.

^b 8% by wt for the upper layer; 92% by wt for the bottom layer.

^c 10% by wt for the upper layer; 90% by wt for the bottom layer.

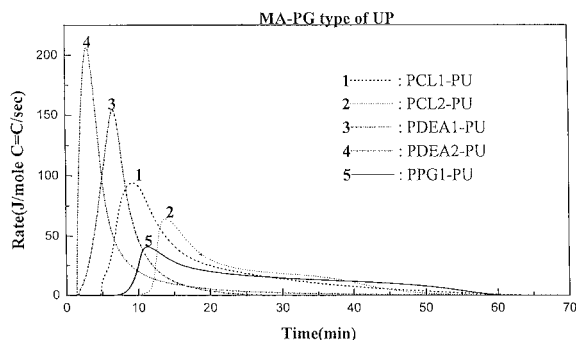


Figure 2 Effects of LPA types on DSC reaction rate profile at 110°C for the MA-PG type of UP systems.

most incompatible during the cure, as evidenced by the DSC rate profile with the longest shoulder and the SEM micrograph with a two-phase microstructure. This could not be predicted by the calculated upper critical solution temperature for the uncured ST/UP/LPA systems, but would agree with the experimental results of compatibility study at room temperature (Table VIII).

As mentioned earlier, with a fixed PU-based LPA, the ST/UP/LPA system would be more incompatible for the MA-PG-PA system than the MA-PG system. This could also be confirmed by the SEM micrograph (compare Figs. 4 and 5), where the MA-PG-PA system apparently exhibited more pronounced phase separation phenomena than the MA-PG system did.

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

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 LPA, 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 ($\alpha \sim 10\%$),¹⁸ the mass transfer into or out of the continuous phase or the dispersed phase would essentially cease. For the ultimately cured sample, the continuous phase would be dominated by UP and ST, while the LPA cocontinuous phase or LPA-dispersed phase would be dominated by ST and LPA.^{5,10,19} In other words, the molar ratio of styrene consumed to polyester C=C bonds reacted in the continuous phase would be smaller than that in the original mixture (i.e., MR = 2/1),

while the trend would be reversed in the LPA cocontinuous phase or LPA-dispersed phase. In reality, the true compositions of the two phases for the cured sample may depend on dynamic phase characteristics, which would be connected with the reaction kinetics and the rate of ongoing phase separation.

For the MA-PG and MA-PG-PA type of UP resin systems, the shoulder at the later stage of reaction rate profile (Figs. 2 and 3) reveals that as cure reaction proceeded, the reaction system could be gradually changing from a single homogeneous phase to two phases. Due to the faster reaction rate between the copolymerization of styrene and polyester C=C bonds than that of self-bonding of styrene monomers,^{20,21} the peak of DSC rate profile would be mainly due to the major continuous phase, in which the molar ratio (MR) of styrene to polyester C=C bonds was smaller than 2:1, while the shoulder of the rate profile at the later stage of reaction would be mainly due to the cocontinuous phase of LPA or LPA-dispersed phase, in which the MR was larger than 2 : 1.

For the MA-PG-PA type of UP resin system (Fig. 3), the DSC rate profile for the PPG1-PU (i.e., polyether type of PU) system exhibited a shoulder and a long tail at the later stage of reaction, which indicates the phase separation during the cure, as mentioned earlier. In contrast, although the rate profiles for the PCL-PU (i.e., polycaprolactone type of PU) and PDEA-PU (i.e., polyester type of PU) systems exhibited a single peak, yet its long tail for the rate profile still revealed the phase separation during the cure for these systems. For a fixed UP resin, the relative magnitude of peak reaction rate in the DSC rate profile could be employed as an index for the degree of phase separation during the cure.

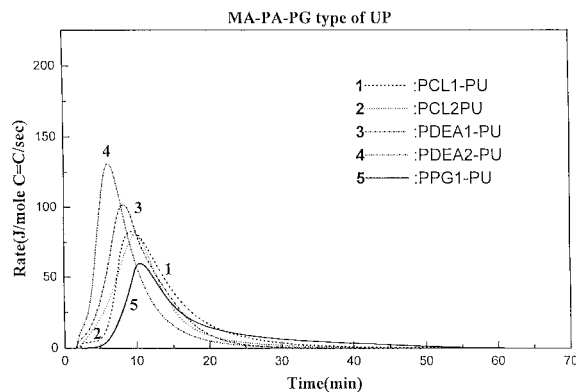


Figure 3 Effects of LPA types on DSC reaction rate profile at 110°C for the MA-PG-PA type of UP systems.

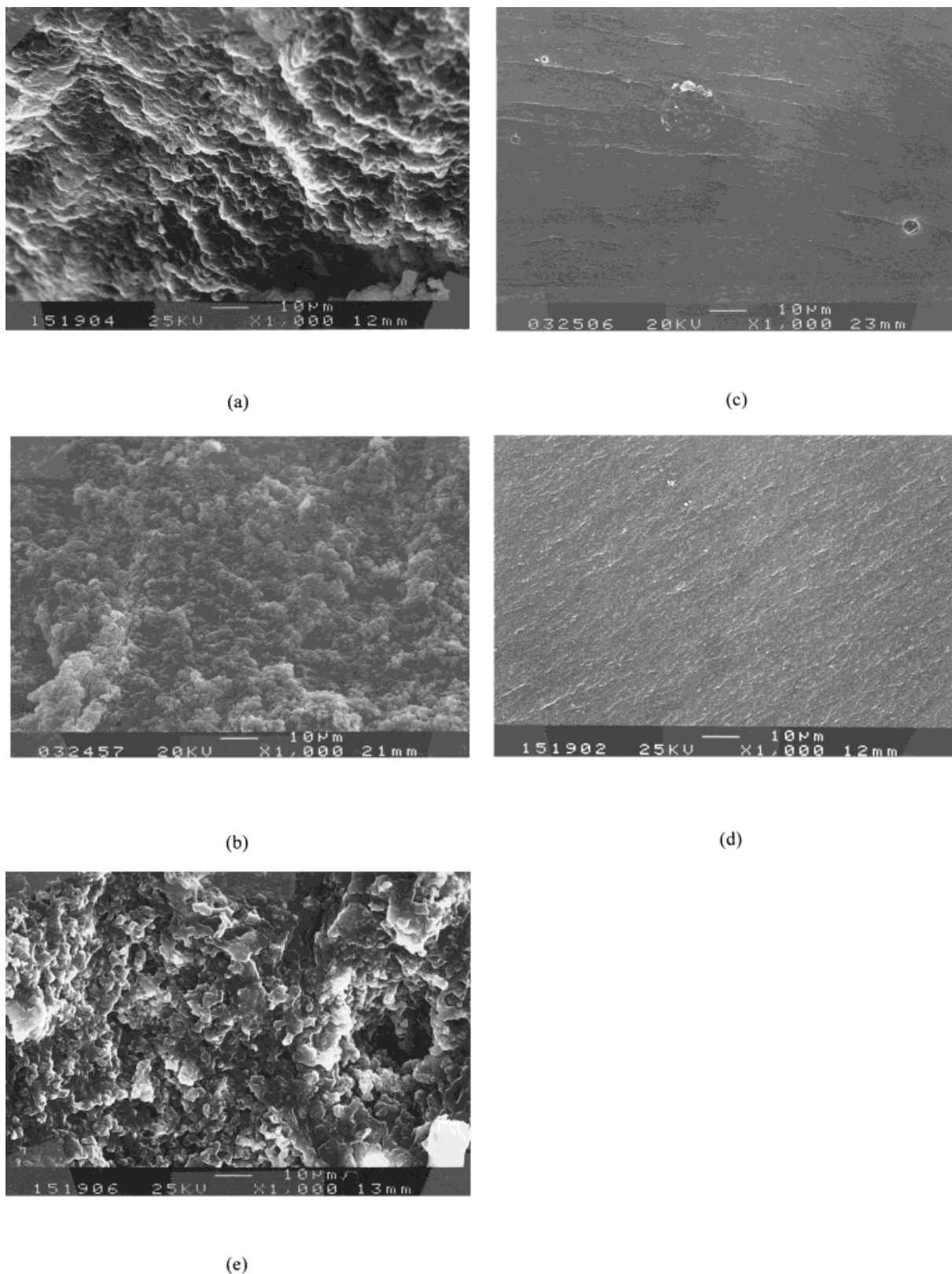
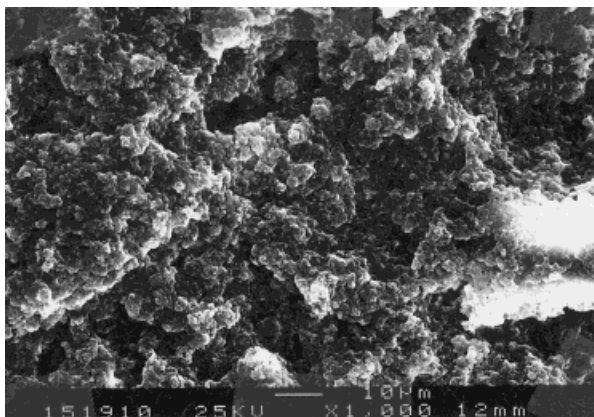
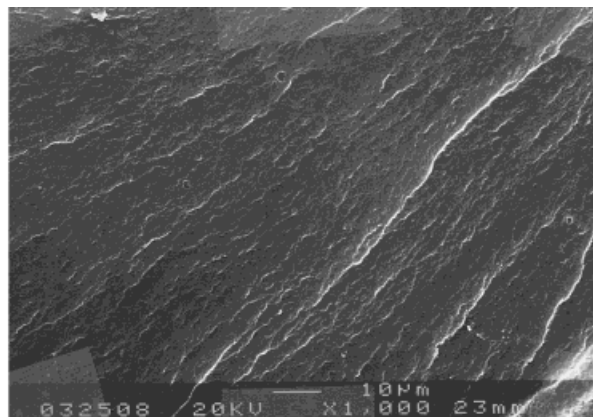


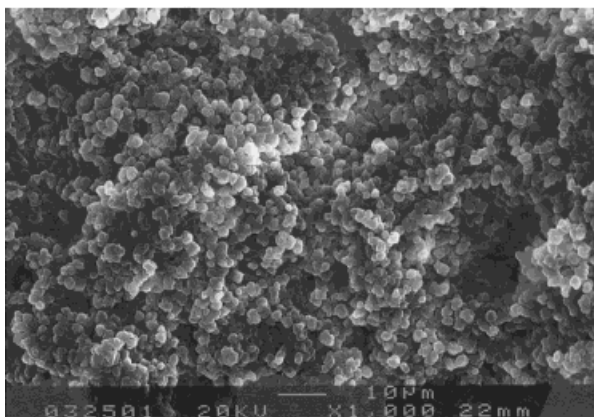
Figure 4 Effects of LPA types on the cured sample morphology under SEM for the MA-PG type of UP systems. (a) PCL1-PU, (b) PCL2-PU, (c) PDEA1-PU, (d) PDEA2-PU, and (e) PPG1-PU.



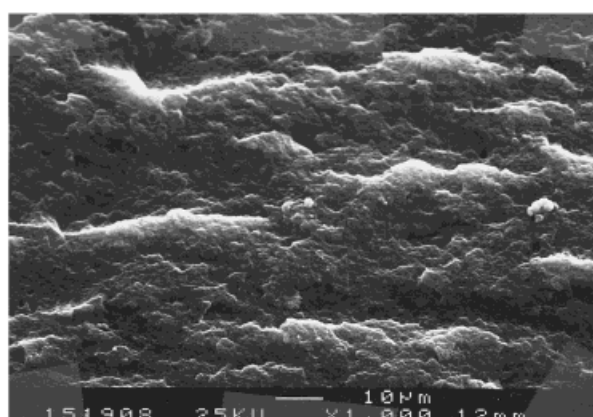
(a)



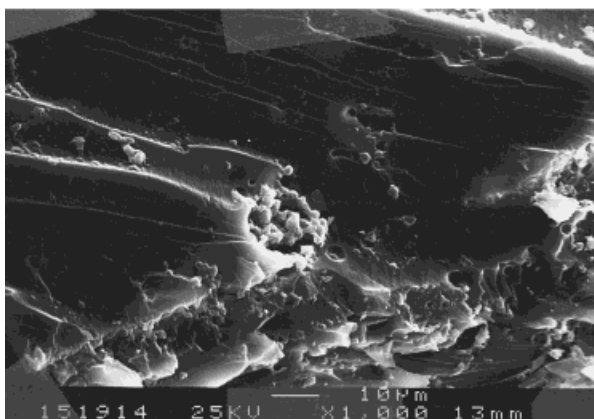
(c)



(b)



(d)



(e)

Figure 5 Effects of LPA types on the cured sample morphology under SEM for the MA-PG-PA type of UP systems. (a) PCL1-PU, (b) PCL2-PU, (c) PDEA1-PU, (d) PDEA2-PU, and (e) PPG1-PU.

Table IX Final Conversion of Total C=C Bonds (%) Measured by DSC for Isothermal Reactions at 110°C

	PCL1	PCL2	PDEA1	PDEA2	PPG1
MA-PG	77	83	88	80.3	69
MA-PG-PA	85	78	89	82.8	70

For both MA-PG and MA-PG-PA systems, the reaction rate at the peak of the DSC rate profile was greater for the PDEA-PU (i.e., polyester type of PU) systems than for the PCL-PU (i.e., polycaprolactone type of PU) systems. This indicates that the degree of phase separation during the cure would be less pronounced for the former systems so that the styrene monomer diffusing from the major continuous phase to the cocontinuous phase of LPA or the LPA-dispersed phase was less. As a result, the molar ratio of styrene consumed to polyester C=C bonds reacted would be deviating less from (less than) 2 : 1 in the major continuous phase during curing for the former system, and a higher reaction rate at the peak of the rate profile at 110°C could arise. (Our previous research²² shows that for styrene/UP reactions, the peak reaction rate would reach a maximum at MR = 2/1, either below or above which could decrease the peak reaction rate.) Because the higher the peak reaction rate the more compatible of the ST/UP/LPA system during cure would be, the sample solution containing the polyester type of PU would be the most compatible, followed by that containing the polycaprolactone type of PU and that containing the polyether type of PU (see Fig. 4 for MA-PG systems and Fig. 5 for MA-PG-PA systems).

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 system (Table IX). This reveals that the more compatible ST/UP/LPA system would lead to a higher final conversion after the cure. 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 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. (Our previous research^{10,19} shows that the higher the molar ratio, the higher the final conversion due to the better swelling effect of styrene on microgel structures.)

Effects of LPA on Volume Shrinkage Control

Table X shows the effect of PU-based LPA on fractional volume shrinkage measured by density methods.²³ The fractional volume shrinkage of the neat UP resin²⁴ was lower for the MA-PG-PA system than for the PA-PG system ($\Delta V/V_0 = -8.69\%$ vs. -10.02%) due to the higher Young's modulus, and, in turn, the more resistance to the polymerization shrinkage for the former system. Adding a PU-based LPA could generally reduce the volume shrinkage²⁵ for both UP systems, and the performance of volume shrinkage control for ST/UP/LPA systems would depend on the UP resin structures, LPA types, and LPA molecular weights.

Table X shows that with a fixed PU-based LPA, the more compatible MA-PG ternary system during the cure would exhibit a lower volume shrinkage than the MA-PG-PA system. However, for both MA-PG and MA-PG-PA type of UP resin systems, the volume shrinkage was the lowest for the least compatible PPG-PU system during the cure, while it was the highest for the most compatible PDEA-PU system. The performance of volume shrinkage control for the less compatible

Table X Fractional Volume Shrinkage Data (%) for ST/UP/LPA Systems After Isothermal Cure at 110°C

	No LPA	PCL1	PCL2	PDEA1	PDEA2	PPG1
MA-PG	-10.02	-3.52	-4.49	-8.31	-8.28	-3.52
MA-PG-PA	-8.69	-7.27	-5.25	-9.64	-9.03	-4.01

Table XI Relative Volume Fraction of Microcracks and Microvoids (%) for Samples of ST/UP/LPA Systems after the Isothermal Cure at 110°C

	PCL1	PCL2	PDEA1	PDEA2	PPG1
MA-PG	20.61	26.51	13.46	12.64	19.55
MA-PG-PA	15.92	23.82	12.88	10.41	18.32

PCL-PU system was better than that of the most compatible PDEA-PU system, but was generally worse than that of the least compatible PPG-PU system. Also, with fixed PU-based LPA and UP resin, the less compatibility of the ST/UP/LPA ternary system caused by adding a higher molecular weight of PU would generally lead to a lower volume shrinkage (except the ST/MA-PG/PCL-PU system).

LPA Mechanism of Volume Shrinkage Control

Pattison et al.^{26,27} have proposed that as the crosslinking of LPA-containing UP resin proceeds, strain due to polymerization shrinkage, develops in the system, particularly at the interface of LPA phase and crosslinked UP phase. This strain could increase to the point that stress cracking propagates through the weak LPA phase, relieving this strain, forming microcracks and/or microvoids, and compensating for the overall volume shrinkage by the microcrack or microvoid space. Recent studies^{3,5,23,28} have also shown that microvoid and/or microcrack formation would occur at the interface between the LPA and crosslinked UP phases as well as inside the LPA phase.

Because the microvoids and microcracks essentially exist in the phase region with a cocontinuous globule microstructure, where the interface generated between the LPA phase and the crosslinked UP phase makes possible the strain relief through stress cracking and the subsequent formation of microvoids and microcracks in the weak LPA phase, the volume fraction of microvoids and microcracks should be greater for the PCL-PU and PPG-PU systems than for the PDEA-PU system, as inferred from the SEM micrographs in Figures 4 and 5 (compare Figs. 4(a), (b), and (e) with 4(c)–(d) for MA-PG system; compare Figs. 5 (a)–(b) with 5(c)–(d) for MA-PG-PA system). Hence, PCL-PU and PPG-PU could generally provide better volume shrinkage control than PDEA-PU.

In this work, the relative volume fraction of microcracking and/or microvoids, v_f , in the mor-

phology sample under an optical microscope (OM) was measured by means of an image analyzer.^{23,25,28} Table XI shows the measured v_f for the ST/UP/LPA systems cured isothermally at 110°C. For both MA-PG and MA-PG-PA systems, v_f was the lowest for the most compatible PDEA-PU system during the cure, while it was higher for the less compatible PCL-PU system and the least compatible PPG-PU system during the cure. However, with a fixed PU-based LPA, v_f was lower for the more incompatible MA-PG-PA system when compared with that for the MA-PG system. Apparently, moderate phase separation between the LPA and crosslinked UP phases during the cure would be indispensable for the microcrack and/or microvoid formation, while either too little or too much phase separation would be unfavorable.

Microvoid Formation vs. Intrinsic Polymerization Shrinkage

With a fixed LPA, experimental results in Tables X and XI support the volume shrinkage mechanism of strain relief through stress cracking, and that greater microcrack and/or microvoid formation would give less volume shrinkage. However, with a fixed UP resin, experimental data in Tables X and XI reveal that the greater microcrack and/or microvoid formation would not necessarily lead to less volume shrinkage. This is attributed to the fact that the overall volume change for the ultimately cured sample (Table X) would be determined not only by the volume compensation due to the microcrack and/or microvoid formation during the cure (Table XI) but also by the intrinsic polymerization shrinkage²³ of the ST/UP/LPA system, which depends on the final cure conversion (Table IX).

Higher cure conversion would enhance the intrinsic polymerization shrinkage effect, which could counterbalance the volume compensation effect due to microcrack and/or microvoid formation. For instance, for the MA-PG system, the volume shrinkage was greater for the PCL2-PU system than for the PCL1-PU system ($\Delta V/V_0$

= -4.49% vs. -3.52% in Table X), which would result from the enhanced intrinsic polymerization effect due to a higher cure conversion ($\alpha = 83\%$ vs. $\alpha = 77\%$ in Table IX) overwhelming the favorable volume compensation effect due to more microvoid formation ($v_f = 26.51\%$ vs. $v_f = 20.61\%$ in Table XI) for the former system. On the other hand, for the PPG-PU system, the relatively low intrinsic polymerization effect ($\alpha = 69\%$ for the MA-PG system and $\alpha = 70\%$ for the MA-PG-PA system) could make up for the somewhat inadequate volume compensation effect ($v_f = 19.55\%$ for the MA-PG system and $v_f = 18.32\%$ for the MA-PG-PA system), leading to the best volume shrinkage control among the systems ($\Delta V/V_0 = -3.52\%$ for the MA-PG system and $\Delta V/V_0 = -4.01\%$ for the MA-PG-PA system).

CONCLUSIONS

The phase-separation characteristics of ST/UP/LPA systems during the cure, as revealed by the cured-sample morphology, and the DSC reaction-rate profile, could be generally predicted by the calculated upper critical solution temperature for the uncured ST/UP/LPA systems based on the Flory-Huggins theory and group contribution methods. For the ST/UP/LPA system, the sample solution containing the polyether-based PU (i.e., PPG-PU) was the least compatible during the cure at 110°C, followed by that containing the polycaprolactone-based PU (i.e., PCL-PU) and that containing the polyester-based PU (i.e., PDEA-PU). The less compatible ternary system could be evidenced by either the emergence of a more conspicuous shoulder in the DSC rate profile at the later stage of reaction or a relatively lower peak reaction rate. Moreover, the final conversion of total C=C bonds after the cure would be lower, and the microgel particles precipitated as observed from the fractured surface would also be larger. With a fixed PU-based LPA, modification of MA-PG type of UP by phthalic anhydride (PA) could result in a less compatible ST/UP/LPA system.

The volume shrinkage control for the ST/UP/LPA systems would be determined not only by the volume compensation due to the microcrack and/or microvoid formation during the cure, which depends on the compatibility of the ST/UP/LPA systems during the cure and the cured sample morphology, but also by the intrinsic polymer-

ization shrinkage of the ST/UP/LPA system, which depends on the final cure conversion. Moderate phase separation between the LPA and crosslinked UP phases during the cure would be indispensable for the microcrack and/or microvoid formation, while either too little or too much phase separation would be unfavorable. With the PU-based LPAs in this work, the performance of volume shrinkage control for ST/UP/LPA system would generally be better by employing an MA-PG type of UP resin, a PCL-PU type (i.e., polycaprolactone type of PU) or a PPG-PU type (i.e., polyether type of PU) of LPA, and a lower molecular weight of LPA ($M_n = 10,000$ – $20,000$ g/mol).

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