Effects of Poly(vinyl acetate) and Poly(vinyl chloride-*co*-vinyl acetate) Low-Profile Additives on Properties of Cured Unsaturated Polyester Resins. II. Glass-Transition Temperatures and Mechanical Properties

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ABSTRACT: Three series of self-synthesized poly(vinyl acetate)-based low-profile additives (LPAs), including poly-(vinyl acetate), poly(vinyl chloride-*co*-vinyl acetate), and poly(vinyl chloride-*co*-vinyl acetate-*co*-maleic anhydride), with different chemical structures and molecular weights were studied. Their effects on the glass-transition temperatures and mechanical properties for thermoset polymer blends made from styrene, unsaturated polyester, and LPAs were investigated by an integrated approach of the static phase characteristics, cured sample morphology, reaction kinetics, and property measurements. Based on Takayanagi mechanical models, the factors that control the glass-transition temperature in each phase region of the cured samples and the mechanical properties are discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3347–3357, 2003

Key words: resins; glass-transition temperatures; mechanical properties; poly(vinyl acetate)

INTRODUCTION

Adding specific thermoplastic polymers as low-profile additives (LPAs) in unsaturated polyester (UP) resins can lead to the reduction or even elimination of polymerization shrinkage during the cure process.[1,2] In part I of this study,[3] the chemical structures and molecular weights of poly(vinyl acetate) (PVAc)-based LPAs were demonstrated to be intimately connected with the miscibility, curing behavior, and cured sample morphology for styrene (St)/UP/LPA systems. Because of a drift in the St/UP/LPA composition as a result of phase separation during the cure of the St/UP/LPA system,[4–7] it is of interest to study how the glass-transition temperatures and mechanical properties of ultimately cured samples are affected by the chemical structure and molecular weight of the PVAc-based LPA.

The objective of this work is to investigate the effects of the chemical structures and molecular weights of three series of PVAc-based LPAs on the glass-transition temperatures and mechanical properties for St/UP/LPA systems. Using an integrated approach combining the static ternary phase characteristics of St/UP/LPA at 25°C, the morphology, the reaction kinetics, and property measurements, an in-depth elucidation of the experimental results is given.

EXPERIMENTAL

Materials

Suspension polymerizations were used to synthesize PVAc-based LPAs with different chemical structures and molecular weights. The detailed procedures of the synthesis can be found elsewhere.[3] The three series of LPAs used in this study, PVAc, vinyl chloride-VAc copolymer (VC-VAc), and VC-VAc-maleic anhydride terpolymer (VC-VAc-MA), are summarized in Table I.

The UP resin[7] was made from MA, 1,2-propylene glycol (PG), and phthalic anhydride with a molar ratio (MR) of 0.63:1.01:0.367. The acid and hydroxyl numbers were found to be 28.0 and 28.2, respectively, by end-group titration, which gives a number-average molecular weight (M_n) of 2000 g/mol. On average, the calculated number of C=C bonds in each polyester molecule was 6.79.

For the sample solution, 10 wt % LPA was added, and the MR of St/polyester C=C bonds was fixed at 2/1. The reaction was initiated using 1 wt % *tert*-butyl perbenzoate.

TABLE I
Low-Profile Additives (LPAs) Used in Study

LPA codes	Monomer	Molar compos.[a]	M_n[b]	M_w[b]	PD[b]	T_g (°C)[c]
PVAc1S	VAc	—	23,000	53,000	2.30	24.1
PVAc2S	VAc	—	83,000	131,000	1.58	23.6
PVAc3S	VAc	—	109,000	166,000	1.52	20.4
VC-VAc1S	VC, VAc	0.85:0.15	34,000	54,000	1.59	56.8
VC-VAc2S	VC, VAc	0.858:0.142	39,000	61,000	1.56	61.0
VC-VAc3S	VC, VAc	0.878:0.122	50,000	75,000	1.50	63.0
VC-VAc4S	VC, VAc	0.874:0.126	71,000	93,000	1.31	65.4
VC-VAc-MA1S	VC, VAc, MA	0.829:0.159:0.011	60,000	81,000	1.35	67.5

[a] Determined by ^{1}H-N MR.
[b] Determined by GPC (g/mol).
[c] Determined by DSC.

Instrumentation and procedures

The sample solutions were degased in a vacuum oven at 50°C for 5 min. Then they were slowly poured into stainless steel rectangular molds, which had inner trough dimensions of $17 \times 1.7 \times 0.42$ cm^3, 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 1 h.

For the measurements of the glass-transition temperatures, dynamic mechanical analysis (DMA) measurements were carried out between −150 and 250°C at 5°C/min and a fixed frequency of 1 Hz. A DuPont 983 dynamic mechanical analyzer was used for the measurements, and rectangular specimens measuring $5 \times 1 \times 0.2$ cm^3 were employed.

In the mechanical tests, dumbbell-shaped specimens (ASTM D638-82a, type V) were used to deter-

mine the tensile properties of low-shrink polyester matrices as measured on a Micro 350 universal testing machine (Testometric Co.) at a constant crosshead speed of 1.0 mm/min. An Izod impact test was also carried out (ASTM D-256-81, method A) with an impact tester (Frank model 53568 pendulum impact tester).

RESULTS AND DISCUSSION

Compatibility of St/UP/LPA systems

The molecular polarities of the UP resin and LPA were calculated by using the Debye equation and group contribution methods in part I of this series,[3] and the results are summarized in Table II. In general, the higher the polarity difference per unit volume between UP and LPA, the lower the compatibility for the

TABLE II
Calculated Molar Volumes and Dipole Moments for UP or LPA, Phase Separation Time for St/UP/LPA
Uncured Systems at 25°C, and Final Conversions of Total C=C Bonds as Measured by DSC
for St/UP/LPA Systems Cured at 110°C

	μ[a]	V[b]	μ'[c]	$\mu'_{UP} - \mu'_{LPA}$	t_p^d	δ[e]	α[f]
UP resin							
MA-PG-PA	3.13	1389	0.084		—	23.38	91.8
LPA							
PVAc1S	10.63	17810	0.080	0.004	∞[g]	21.60	82.5
PVAc2S	20.18	64280	0.080	0.004	∞	21.60	84.0
PVAc3S	23.13	84410	0.080	0.004	∞	21.60	73.0
VC-VAc1S	10.48	22060	0.071	0.013	∞	22.35	72.4
VC-VAc2S	11.20	25790	0.070	0.014	∞	22.36	72.9
VC-VAc3S	12.72	32100	0.071	0.013	5[h]	22.39	—
VC-VAc4S	15.43	47590	0.071	0.013	3[i]	22.38	—
VC-VAc-MA1S	14.42	39390	0.073	0.011	∞	22.52	80.0

[a] Dipole moment (D/mol$^{1/2}$).
[b] Molar volume (cm^3/mol).
[c] Dipole moment per unit volume [$=(\mu^2/V)^{1/2}$, D/cm$^{3/2}$].
[d] Phase separation time (min) at 25°C.
[e] Solubility parameter [(J/cm^3)$^{1/2}$].
[f] Cure conversion of total C=C bonds (%) for St/UP/LPA systems as measured by DSC at 110°C.
[g] One phase.
[h] 17.0% by weight for the upper layer solution.
[i] 56.4% by weight for the upper layer solution.

St/UP/LPA system at 25°C prior to the reaction. The data in Table II reveal that the sample solution containing PVAc is the most compatible theoretically, followed by the VC-VAc-MA and VC-VAc systems. This is in agreement with the data (Table II) that the VC-VAc system is the only one with phase separation occurring at 25°C prior to the reaction.

During the cure at 110°C, the sample solution containing PVAc was the most compatible, followed by the VC-VAc-MA and VC-VAc systems, as evidenced by scanning electron microscopy (SEM) micrographs and the final conversion of total C=C bonds in part I of this series of articles.[3] In addition, with a fixed LPA, adding a higher molecular weight of LPA can cause lower compatibility of the St/UP/LPA system during the cure at 110°C, as observed from the SEM micrographs.[3]

It should be noted that the miscibility of the St/UP/LPA ternary system at 25°C depends on the chemical nature and molecular weights of the UP and LPA chosen, the MR of St/UP C=C bonds, and the mixing temperature.[4−6] Hence, in this work, at a fixed MR of 2/1 and with various LPAs, the miscibility of the St/UP/LPA ternary system at 25°C was analyzed on the basis of the UP/LPA compatibility, not on the basis of the compatibility of the St/UP binary system as reported in the literature,[4,6] where the chemical structures and compositions of the LPAs employed were fixed rather than varied.

Because the solubility parameter (δ) constitutes a compatibility criterion that is generally accepted for polymeric mixtures and solutions in technological and scientific activities, the calculated δ values for the UP and LPAs based on the cohesive energy (E_{coh}) and the molar volume (V_i) for the constitution unit i of the species, as suggested by Van Krevelen[8] and Fedors,[9] are also listed in Table II. The calculated δ was generally lower for the PVAc and VC-VAc based LPAs than the UP resin, which showed the same trend as that of the dipole moment per unit volume (μ') displayed in Table II. However, among the PVAc, VC-VAc, and VC-VAc-MA types of LPAs, the δ value was the highest for VC-VAc-MA, followed by VC-VAc and PVAc, which showed a different trend than that of μ' (i.e., PVAc > VC-VAc-MA > VC-VAc). This reveals that the analysis of the miscibility of the St/UP/LPA systems in this work would be more pertinent if the concept of μ' was used instead of that of δ.

Relationship between morphologies and mechanical properties: Takayanagi models

For the cured LPA-containing UP resin systems with morphologies as shown in part I of this series,[3] their mechanical behavior can be approximately represented by the Takayanagi models,[10−13] in which arrays of weak LPA (R) and stiff St-crosslinked polyester (P)

(a)

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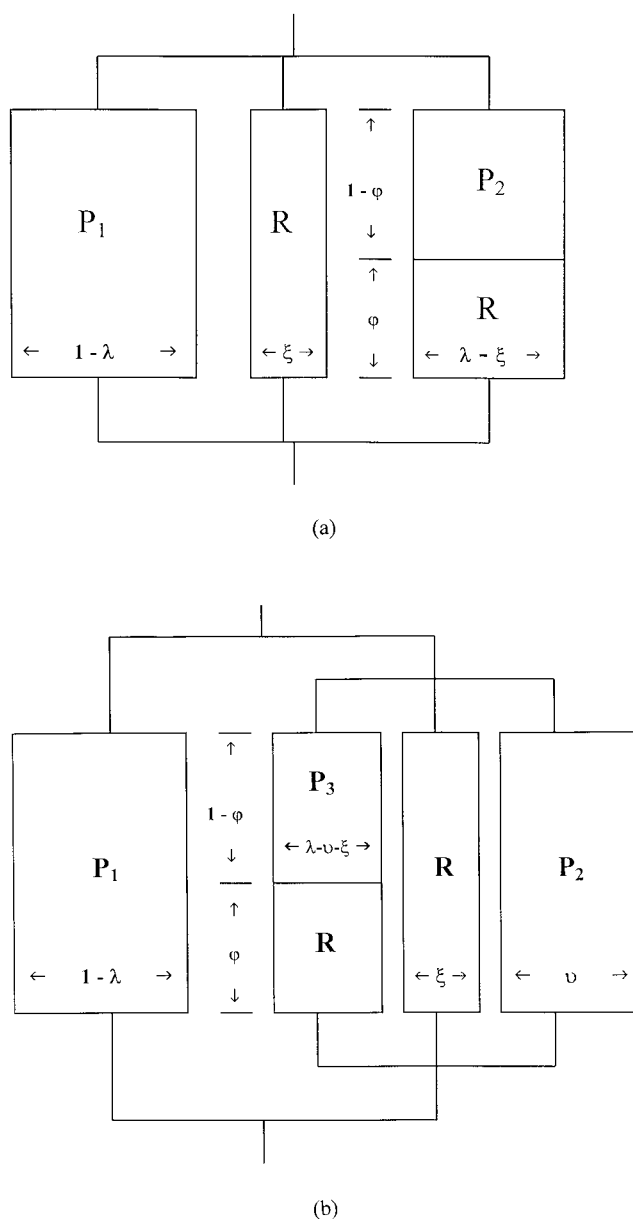
Figure 1 The Takayanagi models for the mechanical behavior of cured LPA-containing UP resin systems: (a) parallel-parallel-series (P-P-S) and (b) parallel-parallel-parallel-series [P-(P-P-S)]. The area of each diagram is proportional to the volume fraction of the phase.

phases are indicated (see Fig. 1). The subscripts 1, 2, and 3 for the P phases are employed for the distinction of St and UP compositions as a result of phase separation during cure; and the quantities λ, ϕ, ξ, and ν or their indicated multiplications indicate the volume fractions of each phase.

For the PVAc systems shown in figure 1(a–c) in part I of this series, their microgel particles (phase P_1) are surrounded by a layer of LPA (phase R). Between the LPA-covered microgel particles there are some lightly St-crosslinked polyester chains and polystyrene (PS) chains (phase P_2) with different compositions of St and

UP than those in phase P_1, which are dispersed in the LPA phase (phase R). Hence, the characteristic globule microstructure may be represented by the parallel-parallel-series (P-P-S) model [Fig. 1(a)], which is a parallel combination of the three elements (P_1, R, and P_2-R) in series. In contrast, for the VC-VAc and VC-VAc-MA systems shown in figure 1(d–h) in part I of this series,[3] the microstructure consists of a stiff continuous phase of St-crosslinked polyester (phase P_1) and a weak globule LPA-dispersed phase, whose globule morphology 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 parallel-parallel-parallel-series [P-(P-P-S)] model [Fig. 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.

It should be noted that there will be some PS chains in phase P_2 for the cured sample represented by the P-P-S model because Suspene et al.[4] reported that the ^{1}H-NMR results of the solid content in the dichloromethane extract of molded UP resins with or without PVAc or polyurethane as an LPA clearly showed peaks of PS. (The MR of St/polyester C=C bonds was calculated to be 1.65/1 based on a value of 156 g/mol C=C bonds for the typical MA-PG type of UP resin employed in their work.[4]) The amount of uncrosslinked PS was found to be 2–5 wt % of the molding compound. Their explanation is that some St monomers tend to homopolymerize and form uncrosslinked and extractable PS molecules during curing.[4] This is because, at the final stage of curing, the St–St reaction is more favorable than the St–polyester and polyester–polyester reactions, which are due to the high immobility of the polyester chains in the crosslinked network.

The mechanical properties of cured samples may change with not only the morphology but also the crosslinking density of St-crosslinked polyester in the P_1, P_2, and P_3 phases, the major continuous phase P_1 being the dominant one. The latter information would not be easy to obtain, but it can be inferred from the static phase characteristics of St/UP/LPA systems at 25°C before curing.[6]

Cure conversion effects from drift in st/polyester composition during curing

The decreasing order of final conversion for the three systems is generally PVAc > VC-VAc-MA > VC-VAc[3] (82–84 vs. 80 vs. 72–73%, Table II). This reveals that the more compatible St/UP/LPA system may lead to a higher final conversion after the cure. As explained in part I,[3] this is due to the MR of St/polyester C=C bonds deviating less from <2:1 in the major continuous phase (i.e., phase P_1, Fig. 1) during curing for the more compatible St/UP/LPA system, which leads to a

less compact microgel structure in that phase and thus to a higher overall cure conversion.

Crosslinking density effect and plasticization effect on T_g of P phase

Figure 2 shows DMA results for the cured neat UP resins without LPA at varied MRs of St/polyester C=C bonds. Based on the tan δ curve of DMA, the maximum point at higher temperatures ($T_{g1\alpha}$) can be identified as the glass-transition temperature for the overall St-crosslinked polyester matrix whereas the shoulder at lower temperatures ($T_{g1\beta}$) can be identified as the β relaxation temperatures[14] for the polyester segments between the crosslinks alone. We believe that the $T_{g1\beta}$ may also be affected by the motion of the chain segment of the St bridge between the crosslinks.

The T_g values displayed in Table III reveal that, as the MR increases, the $T_{g1\alpha}$ exhibits an increase followed by a decrease; it reaches a maximum at a 2/1 MR ($T_{g1\alpha}$ = 162.4°C), which is a trend similar to those reported in the literature.[15,16] Similarly, the $T_{g1\beta}$ also reaches a maximum at a 2/1 MR ($T_{g1\beta}$ = 115.6°C) in this work. [At a 6/1 MR, $T_{g1\beta}$ cannot be identified, see Fig. 2(d).]

On one hand, the higher the MR, the higher the degree of crosslinking along the polyester chain as evidenced by the higher conversion of polyester C=C bonds,[17] which leads to a favorable effect on the increase of $T_{g1\alpha}$ and $T_{g1\beta}$. On the other hand, the higher the MR, the longer the St bridge between the crosslinks (i.e., the crosslink length of St),[18] resulting in an adverse effect on the increase of $T_{g1\alpha}$ (due to the decrease of toverall crosslinking density) and $T_{g1\beta}$ (due to less restriction for the St bridge to the mobility of the polyester chain segments between the crosslinks). For the St-crosslinked polyester matrix, the crosslinking density reaches an optimum at a 2/1 MR, and below or above that value the crosslinking density is reduced; hence, maximum $T_{g1\alpha}$ and $T_{g1\beta}$ values were observed at a 2/1 MR.

Figure 3 shows the DMA results for the cured UP resins containing 10 wt % LPA. We propose a P-P-S model [Fig. 1(a)] for the more compatible PVAc systems and a P-(P-P-S) model [Fig. 1(b)] for the less compatible VC-VAc and VC-VAc-MA systems. For the T_g values listed in Table III for the St/UP/LPA cured systems, $T_{g1\alpha}$ is the glass-transition temperature for the major continuous phase of the St-crosslinked polyester (i.e., phase P_1, Fig. 1), $T_{g1\beta}$ (°C) is the β relaxation temperature for the polyester segments between the crosslinks in mainly the densely St-crosslinked polyester phase [i.e., phase P_1, Fig. 1(a); phases P_1 and P_2, Fig. 1(b)], T_{g2} is the glass-transition temperature for either the LPA cocontinuous phase [i.e., phase P_2, Fig. 1(a)] or the major microgel particle phase within the LPA-dispersed phase [i.e., phase P_2,
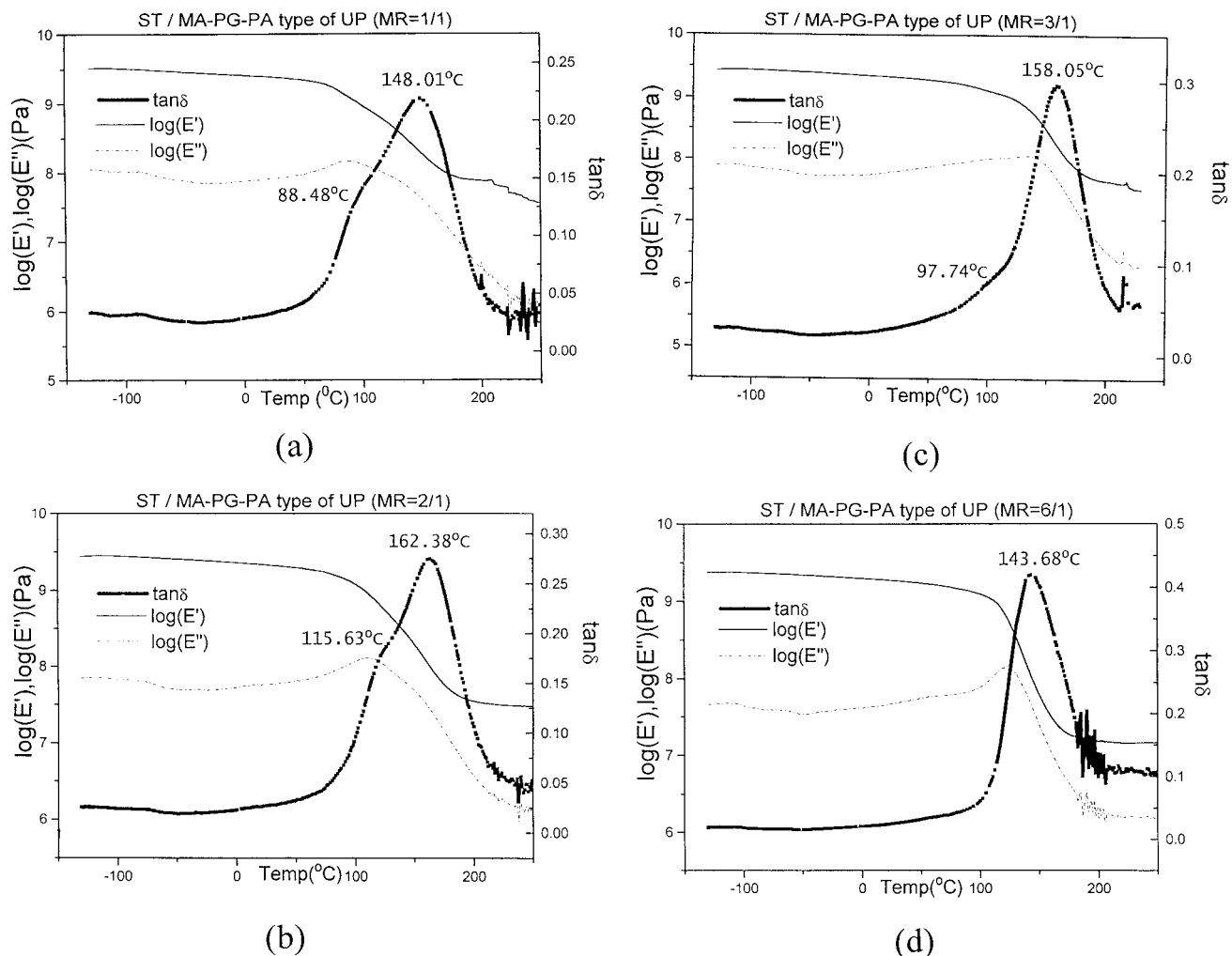
Figure 2 The storage modulus (E'), loss modulus (E''), and tan δ versus the temperature for cured neat UP resins at various molar ratios (MR) of St/polyester C=C bonds as studied by DMA: (a) 1/1, (b) 2/1, (c) 3/1, and (d) 6/1.

Fig. 1(b)], T_{g3} is the glass-transition temperature for the LPA cocontinuous phase within the LPA-dispersed phase [i.e., phase P$_3$, Fig. 1(b)], and T_{gR} is the glass-transition temperature of the R phase. For the PVAc systems represented by a P-P-S model, the value of T_{g2} cannot be clearly identified by DMA, which may be superposed with $T_{g1\beta}$. In contrast, for the VC-VAc and VC-VAc-MA systems represented by a P-(P-P-S) model, T_{g2} and T_{g3} values cannot be identified unambiguously; the former may be overlapped with $T_{g1\alpha}$ and the latter may be overlapped with $T_{g1\beta}$. This is because the T_{g2} in the P-(P-P-S) model and the T_{g3} in the P-(P-P-S) model (or the T_{g2} in the P-P-S model) are inferred to be 140–160°C, which is the same level as $T_{g1\alpha}$ for neat cured UP resin at MRs of 2/1 to 6/1 (Table III) due to the phase separation during the cure, and 100–110°C (T_g for PS and lightly St-crosslinked polyester chains), respectively.

As shown in Table III, for the more compatible PVAc systems, the $T_{g1\alpha}$, $T_{g1\beta}$, and T_{gR} values were 161–164, 100–104, and 66–72°C, respectively; for the

less compatible VC-VAc and VC-VAc-MA systems, the $T_{g1\alpha}$, $T_{g1\beta}$, and T_{gR} were 151–165, 106–119, and 76–84°C, respectively. The $T_{g1\alpha}$ value was generally higher for the more compatible PVAc systems than for the less compatible VC-VAc and VC-VAc-MA systems, whereas the trend was reversed for $T_{g1\beta}$. Because of the molecular mixing between the LPA and the St-crosslinked polyester chains, the T_{gR} was increased as compared with the T_g of independent LPA (i.e., T_{gLPA}, Table I). The degree of increase for the T_g of LPA, ΔT_{gR} ($=T_{gR} - T_{gLPA}$), was much more enhanced for the more compatible PVAc systems than for the less compatible VC-VAc systems (45–47 vs. 16–23°C, see Table III), which is due to the higher extent of molecular mixing between the chains for the former systems.

For the more compatible St/UP/LPA cured system, such as the PVAc system, the MR of St/polyester C=C bonds would deviate less from <2:1 in the major continuous phase P$_1$, leading to a higher crosslinking density in that phase as mentioned earlier. The better

TABLE III
Glass-Transition Temperatures of Fully Cured St/UP/LPA Systems Based on tan δ by DMA

LPA	MR	Model	$T_{g1\alpha}$	$T_{g1\beta}$	T_{g2}	T_{g3}	T_{gR}	ΔT_{gR}
Neat UP resin	1/1		148.0	88.5				
	2/1		162.4	115.6				
	3/1		158.1	97.7				
	6/1		143.7	—				
LPA								
PVAc1S	2/1	P-P-S	161.3	100.7	—		69.2	45.1
PVAc2S	2/1	P-P-S	163.7	—	—		71.3	47.7
PVAc3S	2/1	P-P-S	162.7	103.4	—	—	66.5	46.1
VC-VAc1S	2/1	P-(P-P-S)	164.3	107.7	—	—	76.1	19.3
VC-VAc2S	2/1	P-(P-P-S)	152.5	106.8	—	—	84.0	23.0
VC-VAc3S	2/1	P-(P-P-S)	151.8	117.2	—	—	80.3	17.3
VC-VAc4S	2/1	P-(P-P-S)	152.6	118.3	—	—	81.6	16.2

$T_{g1\alpha}$ (°C), the glass-transition temperature for the overall styrene-crosslinked polyester matrix (for neat UP system) or the T_g for the major continuous phase of styrene-crosslinked polyester (i.e., phase P_1 in Fig. 1 for ST/UP/LPA cured systems). $T_{g1\beta}$ (°C), the β relaxation temperature for the polyester segments between the crosslinks.[14] T_{g2}, the T_g for the LPA cocontinuous phase [i.e., phase P_2 in Fig. 1(a)] or the T_g in the major microgel particle phase within the LPA-dispersed phase [i.e., phase P_2 in Fig. 1 (b)]. See text for details. T_{g3} (°C), the T_g for the LPA cocontinuous phase within the LPA-dispersed phase [i.e., phase P_3 in Fig. 1 (b)]. See text for details. T_{gR}, the T_g for the R phase. ΔT_{gR} (=$T_{gR} - T_{gLPA}$), the degree of increase for the T_g of LPA (i.e., phase R) due to the molecular mixing between LPA and styrene-crosslinked polyester chains, where T_{gLPA} is the T_g of independent LPA as measured by DSC and shown in Table I.

crosslinking density effect of the P_1 phase itself resulted in a higher $T_{g\alpha}$ for the P_1 phase than for the less compatible VC-VAc and VC-VAc-MA systems. On the other hand, the higher MR in the P_1 phase for the more compatible PVAc system may lead to less restriction of the St bridge for the mobility of polyester chain segments between the crosslinks, resulting in a lower $T_{g1\beta}$ than the less compatible VC-VAc and VC-VAc-MA systems.

With a fixed LPA type, adding a higher molecular weight of LPA can cause lower compatibility of the St/UP/LPA system as mentioned earlier, and the MR would deviate more from <2:1 in the major continuous phase P_1. However, for the more compatible PVAc systems, as the molecular weight of the LPA was increased, the $T_{g\alpha}$ in the P_1 phase exhibited an increase, which was followed by a decrease; the trend was reversed for the less compatible VC-VAc and VC-VAc-MA systems (see Table III).

All of these findings are ascribed to the fact that, for a more compatible St/UP/LPA system, the plasticization effect of the R phase on the P_1 phase is more pronounced (i.e., more molecular interaction between P_1 and R phases), and the crosslinking density in the P_1 phase itself is also higher. Considering that the higher plasticization effect is unfavorable for the increase of the T_g in the P_1 phase but the concomitant higher crosslinking effect is favorable, the $T_{g\alpha}$ in the P_1 phase may then depend upon the relative importance of the two opposing effects. Because the crosslinking effect is more significant, a more compatible St/UP/LPA system can lead to a higher $T_{g\alpha}$ in the P_1 phase, whereas the trend may be reversed because the plasticization effect is more important. Apparently, a rel-

atively incompatible ternary system, such as the VC-VAc systems (except the VC-VAc4S system), pertains to the former case (i.e., the crosslinking effect predominates) whereas a relatively compatible ternary system, such as the PVAc system (except the PVAc3S system), is categorized as the latter case (i.e., the plasticization effect predominates).

Reaction-induced phase separation for St/UP/LPA systems during curing

For the St/UP/LPA system with a MR of St/polyester C=C bonds of 2:1 and a 10 wt % PVAc-based LPA, six out of the eight uncured ternary systems exhibited a homogeneous single phase at room temperature, the exceptions being the VC-VAc3S and VC-VAC4S systems (Table II). When the mixing temperature was increased to 110°C, even the uncured St/UP/VC-VAc3S and St/UP/VC-VAc4S systems turned out to be a homogeneous single phase. As the cure reaction at 110°C proceeds, the increase in the molecular weights of the reacting species via crosslinking reactions can enhance phase separation (because of the decrease in the entropy of mixing), the onset of which generally occurring at a very low reaction conversion[6] ($\alpha < 1\%$). In reality, from the start of the copolymerization reaction in the St/UP/LPA (initially miscible) ternary system, it is transformed into a quaternary system with the following components: the growing St/UP copolymer, unreacted St/UP monomers, and the LPA. A qualitative analysis of the phase separation phenomena in the pregel state, using the basic concept of Flory–Huggins (FH) theory,[19–22] would show that the reaction induced phase separation mechanism for

this system is the result of three main contributions: the entropic effect caused by the presence of the St/UP copolymer; the interaction energies quantified from the six binaries FH interaction parameters; and the change of the concentration of each component that participates in the copolymerization reaction (St, UP, and St/UP copolymer), which influences the magnitude of the second and third effects. After macrogelation, the analysis is much more complex because the elastic contribution introduced by the copolymer network must be taken into account.

Near the gelation point ($\alpha \sim 10\%$),[23] the translational diffusion for the large molecules, such as UP and LPA, essentially ceases because the viscosity tends toward infinity. However, diffusion of St, which is a small molecule, and segmental diffusion of UP and LPA can still proceed in the lightly crosslinked, St swollen network. Nevertheless, because the long-range diffusion of St that crosses phase boundaries is considerably curtailed, the compositions in the continuous and LPA-dispersed phases remain virtually unchanged near gelation. From then onward the morphology for the partially cured sample is virtually unchanged, but the crosslinking density in each phase region may increase with the cure conversion until a limiting conversion (Table II) is reached. A further postcure at 150°C may somewhat enhance the crosslinking density in each phase region, especially that of the P_1 phase, where the 3-dimensional microgel structures are the most compact among all the phases.

Effects of interfacial adhesion on impact strength

Table IV shows the effects of the chemical structure and molecular weight of PVAc-based LPA on the impact strength of cured samples. The impact strength was generally the highest for the more compatible PVAc systems, followed by the less compatible VC-VAc systems. In addition, the VC-VAc-MA system possessed a higher impact strength than the more incompatible VC-VAc system. This is attributable to the fact that the better interfacial adhesion between the major St-crosslinked polyester phase and the LPA-rich phase caused by the more compatible system is favorable for the increase of the impact strength.

For the more compatible PVAc systems, the impact strength was the largest for the sample containing PVAc1S, followed by the PVAc2S- and PVAc3S-containing samples, as expected. (The compatibility was ranked as PVAc1S > PVAc2S > PVAc3S.) In contrast, for the less compatible VC-VAc systems, as the molecular weight of the LPA was increased, the impact strength exhibited a slight increase (i.e., VC-VAc1S, VC-VAc2S, and VC-VAc3S systems), which was followed by a notable decrease (i.e., VC-VAc4S system). Increasing the LPA molecular weight can lead to an increase in both the phase separation time (because of

the increase of the solution viscosity) and the degree of phase separation (because of the decrease of the entropy change in the solution process) prior to gelation during the cure; both of these may affect the interfacial adhesion between the crosslinked polyester phase and the LPA-rich phase, in addition to the dynamic phase characteristics of St/UP/LPA systems, such as the ternary compositions of the phases mentioned in part I of this series.[3] The later phase separation time (or lower phase separation rate) is favorable for the increase of interfacial adhesion between the crosslinked polyester phase and the LPA-rich phase. [See fig. 1(d–g) in part I[3] for the cured sample morphologies, giving special attention to the interface regions.] In contrast, the higher degree of phase separation is unfavorable for interfacial adhesion. For the VC-VAc1S, VC-VAc2S, and VC-VAc3S systems, the favorable effect of the phase separation time would be much more significant than the adverse effect of the degree of phase separation caused by the increase in the LPA molecular weight, which leads to better interfacial adhesion between the crosslinked polyester phase and the LPA-rich phase, and, in turn, leads to higher impact strength. Adding an excessively high molecular weight of LPA, such as the VC-VAc4S system, may greatly enhance the degree of phase separation during the cure, thus reducing the impact strength because of a considerable decrease of the interfacial adhesion.

It should be noted that the dependence of the impact strength on the interfacial adhesion in the cured St/UP/LPA materials cannot be clearly explained by considering only the relation between the time of phase separation, the degree of phase separation, and the molecular weight of the LPA. The relations between the molecular weight of the modifier, the temperature, the mixture viscosity, the interfacial energy, the conversion, and the phase separation degree was analyzed theoretically by Williams et al.[24–26] in an epoxy-amine rubber-modified reactive system, in which a high degree of interrelation and complexity between the phase separation phenomena and the above-mentioned parameters was shown.

Crosslinking density and interfacial adhesion effects on tensile properties

Based on the isostrain model in Figure 1(a,b), the tensile strength of the sample would be dominated by $(1 - \lambda)\sigma_{P1}$, provided that the major continuous phase is less brittle than the minor cocontinuous or dispersed phase and there is sufficient P_1 phase to carry the tensile load even after phases R, P_2, and P_3 have failed. Here $(1 - \lambda)$ and σ_{P1} are the volume fraction and tensile strength for the stiff P_1 phase, respectively.

Table IV shows the effects of the chemical structure and molecular weight of PVAc-based LPA on the tensile strength of cured samples. The tensile strength
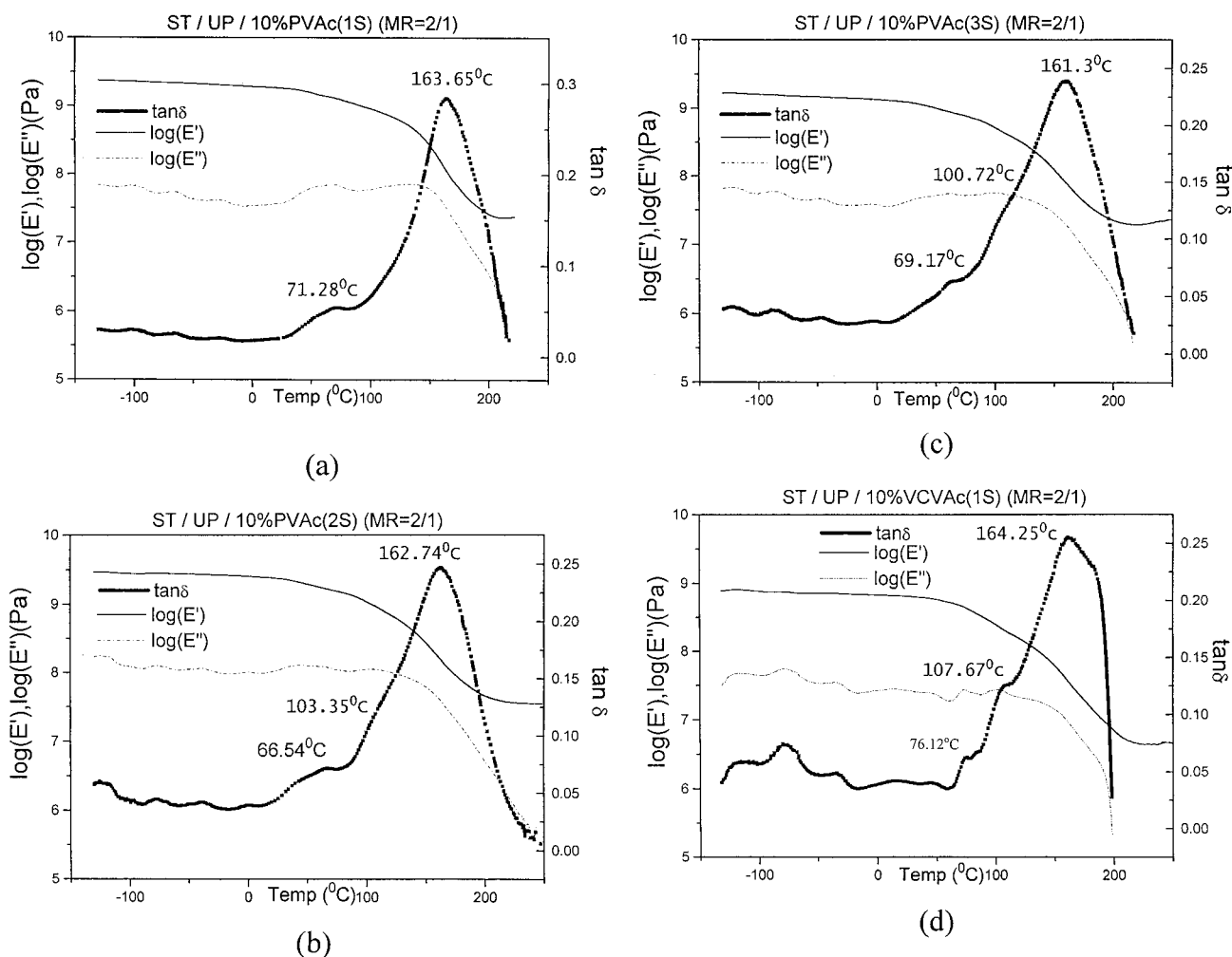
Figure 3 The storage modulus (E'), loss modulus (E''), and tan δ versus the temperature for cured St/UP/LPA systems containing 10% LPA at MR = 2/1 as studied by DMA: (a) PVAc1S, (b) PVAc2S, (c) PVAc3S, (d) VC-VAc1S, (e) VC-VAc2S, (f) VC-VAc3S, and (g) VC-VAc4S.

was the highest for the most compatible PVAc systems, followed by the less compatible VC-VAc-MA system and the least compatible VC-VAc systems, which exhibited essentially the same trend as the impact strength. For the more compatible St/UP/LPA system, the MR of St/polyester C=C bonds reacting (i.e., crosslinking density) in the continuous phase of the crosslinked polyester [i.e., P_1 phase, Fig. 1(a)] exhibits the smallest negative deviation from 2:1; this leads to a higher crosslinking density in that phase and then to greater enhancement in the tensile strength for the whole sample. In addition, the better interfacial adhesion for the more compatible St/UP/LPA system could aid the increase of the tensile strength.

For the more compatible PVAc systems, the tensile strength was decreased by increasing the molecular weight of the LPA, which is due to the lowering of both the crosslinking density in the P_1 phase and the interfacial adhesion, as expected. However, it was in-

creased by further increasing the molecular weight of tLPA (i.e., PVAc3S system), despite the reduction in both the crosslinking density in the P_1 phase and the interfacial adhesion. Our explanation is that, for the PVAc system with a cocontinuous microstructure [see fig. 1(a–c) in part I[3]), the generally dispersed microvoids,[27,28] which would be generated during the cure at the interface between the LPA-rich and crosslinked UP phases, as well as inside the LPA-rich phase, were found[3] to be more effective than the microvoids localized in the LPA-dispersed phase for the VC-VAc systems with a two-phase microstructure [see fig. 1(d–g) in part I.[3]] Because the microvoids can lead to a crack tip blunting effect[29] of releasing the stress concentration at the crack tip and delaying crack propagation, a noticeable improvement in the tensile strength was observed for the PVAc3S system. (The relative volume fractions of microvoids for the PVAc1S, PVAc2S, and PVAc3S systems were 3.6, 13.9, and 49.0%, respectively.[3]) In contrast to the tensile test, specimens were
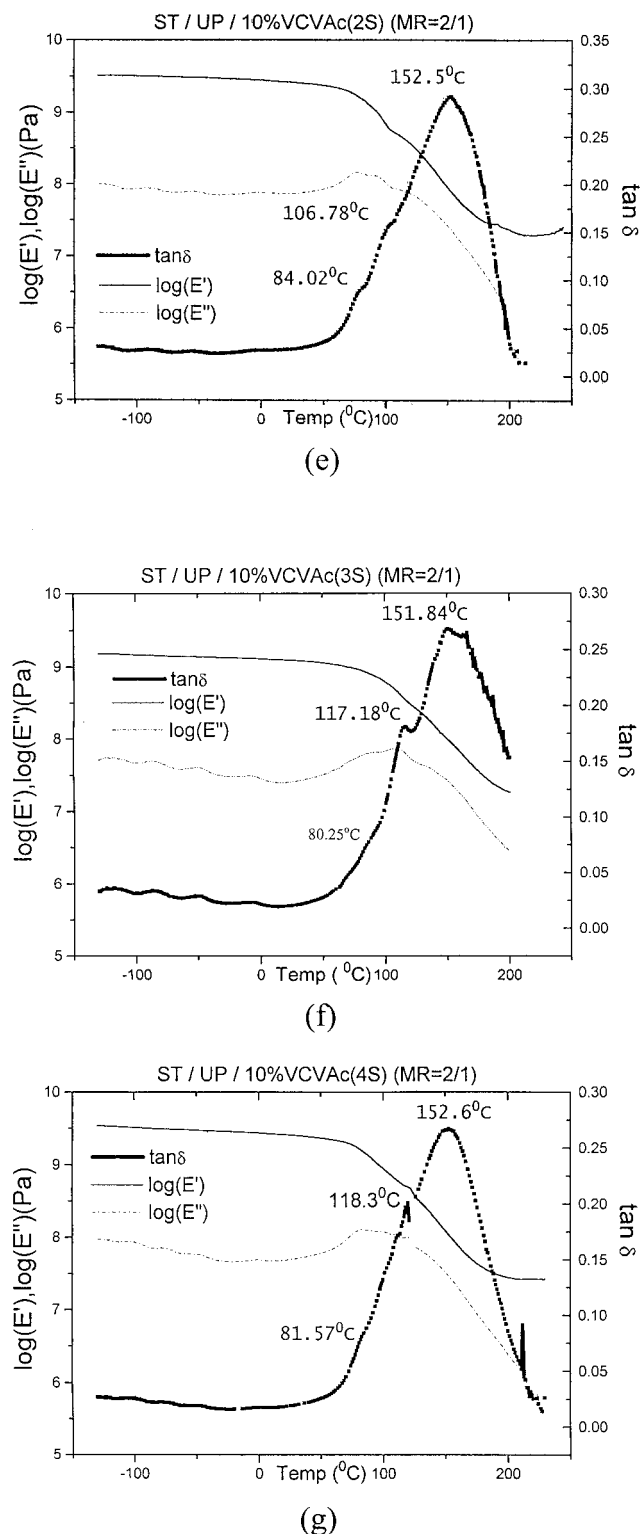
ST / UP / 10%VCVAc(2S) (MR=2/1)

ST / UP / 10%VCVAc(3S) (MR=2/1)

ST / UP / 10%VCVAc(4S) (MR=2/1)

Figure 3 (*Continued from the previous page*)

subjected to a much higher strain rate during the impact test. An excessively high volume fraction of microvoids in the PVAc3S system can cause an adverse effect on the impact strength because the crack would somewhat easily propagate through the plane

voids during impact testing of the specimens, leading to the lowest impact strength among the PVAc systems for the PVAc3S system (Table III).

In contrast, for the less compatible VC-VAc systems, as the molecular weight of the LPA was increased, the tensile strength exhibited an increase (i.e., VC-VAc1S and VC-VAc2S systems), followed by a decrease (i.e., VC-VAc4S system), which showed the same trend as that of the impact strength. This is because, as the molecular weight of the LPA was increased, the interfacial adhesion between the crosslinked polyester phase and the LPA-rich phase experienced an increase and then a decrease, as explained earlier.

Effects of network compactness and volume fraction in major continuous phase on young's modulus

Based on the isostrain model in Figure 1(a,b), the Young's modulus of the sample is dominated by $(1 - \lambda)E_{P1}$ because the moduli of phases R, P_2, and P_3 multiplied by their corresponding volume fractions is generally much smaller than that of phase P_1 multiplied by its volume fraction [i.e., $(1 - \lambda)E_{P1}$]. The Young's modulus of the major continuous phase is represented by E_{P1}.

Table IV shows the effects of the chemical structure and molecular weight of PVAc-based LPAs on the Young's modulus of cured samples. For the more compatible PVAc systems, the Young's modulus was the largest for the sample containing PVAc3S, followed by the PVAc2S- and PVAc1S-containing samples, which had a reverse trend to that of the tensile strength. In contrast, for the less compatible VC-VAc systems, as the molecular weight of the LPA was increased, the Young's modulus exhibited an increase (i.e., VC-VAc1S and VC-VAc2S systems) and then a decrease (i.e., VC-VAc4S system). The Young's modulus for the VC-VAc-MA1S system was also much higher than that of the VC-VAc4S system. (The molecular weights for VC-VAc-MA1S and VC-VAc4S types of LPAs were close enough for comparison as shown in Table I.) This reveals that a less compatible St/UP/ LPA system can 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 testing, during which the sample is unbroken, it is connected to the degree of tightness of the network rather than the degree of crosslinking of the sample. For St/UP/LPA systems, a higher degree of phase separation during the cure may lead to a lower St content in the continuous phase of the crosslinked polyester [phase P_1, Fig. 1(a,b)]. A lower average crosslink length of St and a more compact network in that phase may result after the cure, which can lead to a higher Young's modulus for the whole sample.

TABLE IV
Impact Strength, Tensile Strength, Ultimate Tensile Strain, and Young's Modulus for St/UP/LPA
Systems after Isothermal Cure at 110°C for 1 h and postcure at 150°C for 1 h

LPA Added	Impact strength (J/m)	Tensile strength (MPa)	Ultimate tensile strain (%)	Young's modulus (MPa)
Neat Resin	—	—	—	—
PVAc1S	14.5 (0.5)	24.4 (0.6)	5.6 (0.1)	322 (7)
PVAc2S	14.1 (0.1)	22.6 (1.3)	5.8 (0.1)	408 (6)
PVAc3S	13.2 (0.1)	28.8 (2.2)	5.9 (0.2)	415 (4)
VC-VAc1S	13.2 (0.3)	16.6 (0.4)	5.0 (0.1)	301 (4)
VC-VAc2S	13.4 (0.2)	17.3 (0.4)	5.3 (0.1)	357 (9)
VC-VAc3S	14.3 (0.9)	—	—	—
VC-VAc4S	10.8 (0.1)	10.6 (0.6)	4.4 (0.3)	192 (4)
VC-VAc-MA1S	14.5 (0.3)	20.9 (1.0)	5.8 (0.1)	330 (4)

The values in parentheses represent the estimated standard errors for the experimental averages.

In general, a more incompatible St/UP/LPA system, such as the VC-VAc systems, may lead to a more negative deviation from a 2:1 MR and a lower volume fraction in the major continuous phase. The experimental results for the Young's modulus in Table IV imply that, for the VC-VAc1S and VC-VAc2S systems, the former effect, which leads to a more compact network therein (i.e., a higher E_{P1}), is more significant than the latter one; whereas, for the VC-VAc4S system, the latter effect [i.e., a lower $(1 - \lambda)$] is more pronounced. In addition, the much lower Young's modulus for the VC-VAc4S system than for the VC-VAc-MA1S system is attributable to a much lower $(1 - \lambda)$, in spite of a higher E_{P1} for the former system [see fig. 1(d–g) in series part I[3]].

CONCLUSIONS

The effects of PVAc-based LPAs with different chemical structures and molecular weights on the glass-transition temperatures and mechanical properties for St-crosslinked low-shrink polyester matrices were investigated by an integrated approach of the static phase characteristics, cured sample morphology, reaction conversion, and property measurements. Based on the proposed Takayanagi mechanical models, all of the transition temperatures in each phase region of the cured samples in the model cannot be identified by DMA. In general, the T_g in the major continuous St-crosslinked polyester phase (i.e., the P_1 phase) may depend upon the relative importance of the two opposing effects, namely, the plasticization effect of the LPA phase (i.e., the R phase) on the P_1 phase and the crosslinking effect of the P_1 phase itself in terms of the MR of St/polyester C=C bonds. A more incompatible St/UP/LPA system can lead to a lower plasticization effect and a concomitant lower crosslinking effect, the former of which is favorable for the increase of the T_g in the P_1 phase and the latter of which is unfavorable.

The mechanical properties were demonstrated to depend upon the cured sample morphology, the in-terfacial adhesion between the LPA-rich and major St-crosslinked polyester phases, the MR of St/polyester C=C bonds, and the volume fraction in the major continuous phase of St-crosslinked polyester as a result of phase separation during cure. These four factors are intimately connected with the compatibility characteristics of St/UP/LPA systems, and they can be controlled by the chemical structure and molecular weight of UPs and LPAs.

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