

Effects of thermoplastic additives on mechanical properties and glass transition temperatures for styrene-crosslinked low-shrink polyester matrices

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The effects of four low-profile additives (LPA), namely poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), thermoplastic polyurethane (PU), and polystyrene (PS), and molar ratio of styrene to polyester C=C bonds, on the mechanical properties and glass transition temperatures (T_g) for styrene-crosslinked low-shrink polyester matrices were investigated by an integrated approach of static phase characteristics–cured sample morphology–reaction conversion–properties measurements. Experimental results showed that both mechanical properties and T_g in the major continuous phase of styrene-crosslinked polyester would be generally decreased with increasing LPA content, while T_g in the minor co-continuous or dispersed phase of styrene-crosslinked polyester would show the reverse trend. Also, there usually existed an optimal molar ratio of styrene to polyester C=C bonds at MR 2/1, either below or above which would cause inferior mechanical properties and lower T_g in the major continuous phase. Based on the Takayanagi mechanical models, factors which control the mechanical properties and T_g have been explored. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: low-profile additives; mechanical properties; glass transition temperatures)

INTRODUCTION

Adding specific thermoplastic polymers as low profile additives (LPA) in the unsaturated polyester resins (UP) during the formulation of SMC (sheet moulding compound) and BMC (bulk moulding compound) is a well known industrial technology. Such thermoset polymer blends, essentially made from UP, styrene monomer and LPA, would lead to a reduction or even elimination of the polymerization shrinkage during the cure process. A Class A smooth surface for the moulded part could then result^{1–5}.

Depending on the difference in polarity (or solubility parameter) between LPA and unreacted UP, some LPAs, such as thermoplastic polyurethane (PU) and poly(vinyl acetate) (PVAc), are usually compatible with UP (a reasonably polar prepolymer), while others, such as poly(methyl methacrylate) (PMMA) and polystyrene (PS), are not. When a common solvent, such as styrene, is added to form a ternary styrene/UP/LPA system, the LPA and UP usually cannot coexist in a homogeneous phase especially for the PMMA and PS systems. The static ternary phase characteristics prior to reaction depend on the chemical nature and the molecular weight of the UP and LPA chosen, the molar ratio of styrene to UP C=C bonds, and the mixing temperature^{6–8}. However, during the cure of the styrene/UP/LPA system, whether compatible or incompatible at 25°C prior to reaction, the increase in molecular weights of

the reacting species via crosslinking reactions would invariably enhance the phase separation due to the decrease in entropy of mixing, and could result in a considerably different cured sample morphology for the fracture surface from that of the neat UP resin system (with no LPA) with a flake-like microstructure^{5–7,9,10}. Two common microstructures have been observed, including the one with isolated domains dispersed in a flake-like structure (e.g. the PMMA and PS systems), and the other one with a co-continuous globule microstructure (e.g. the PU and PVAc systems). Detailed microstructure would also rely on the chemical structure of UP resins⁴, the LPA concentration^{5,7,10} and the molar ratio of styrene to polyester C=C bonds^{9,10}.

The effects of LPA on the mechanical properties and glass transition temperatures (T_g) for styrene-crosslinked polyester matrices have been studied by several researchers^{10–12}. All of these researchers explained their experimental results essentially based on the cured sample morphology and the microvoid formation^{13,14}, while other factors such as the crosslinking densities of the ultimately cured sample in both the continuous and dispersed phases were disregarded. The objective of this work is to study the effects of four LPAs, namely PVAc, thermoplastic PU, PMMA, and PS, their concentrations, and the molar ratio of styrene to polyester C=C bonds on the mechanical properties and T_g for the styrene-crosslinked polyester matrices. By an integrated approach of static ternary phase characteristics of styrene/UP/LPA at 25°C, morphology, reaction conversion, and property measurements, in-depth elucidation of the experimental results is given.

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EXPERIMENTAL

Materials

The unsaturated polyester resin (Eternal Chemical Co.) contained isophthalic acid, fumaric acid, and propylene glycol with a molar ratio of 1:1.81:2.91 by 1H n.m.r. analysis. The acid value and the hydroxyl number of the resin were found to be 23.0 and 27.7 respectively by end-group titration, which gives a number-average molecular weight of 2210 g/mol. On average, the calculated number of C=C bonds in each polyester molecule was 8.13 (equivalent molecular weight per C=C bond 272). Four LPAs including poly(vinyl acetate) (PVAc, LP40A, Union Carbide), poly(methyl methacrylate) (PMMA), thermoplastic polyurethane (PU, LP2030, Olin), and polystyrene (PS) were employed, the number-average molecular weights of which were measured to be 42 000, 34 000, 6500, and 150 000 g/mol respectively by vapour pressure osmometry (VPO). For the sample solution with LPA, 5%, 10%, or 15% by weight of LPA was added, while the molar ratio of styrene to polyester C=C bonds was adjusted to be MR 1/1, 2/1, 3/1, or 6/1. The reaction was initiated by 1% by weight of tert-butyl perbenzoate (TBPB). All the materials were employed as received without further purification.

INSTRUMENTATION AND PROCEDURE

Phase characteristics

To study the compatibility of four different types of LPA (i.e. PVAc, PMMA, PU, and PS) with the UP solution in styrene prior to reaction (i.e. the uncured UP resin), several sample solutions with known compositions of styrene/UP/LPA were prepared in 10 ml separatory glass cylinders, which were then placed in a constant-temperature bath. After a phase equilibrium was reached, the phase separation time was recorded and the mixture of each layer was separated and weighed. The PU system formed a homogeneous solution after a phase equilibrium. Composition of samples from upper and bottom layers could then be determined by using FTi.r. (Digilab, FTS-40)^{7,15}. The static ternary phase characteristics (i.e. for the unreacted ternary systems) of styrene/UP/LPA at 25°C (i.e. mixing temperature) were obtained.

In the analysis of i.r. spectra, all the absorbances were based on peak areas. The absorbances at 912 cm⁻¹ (styrene), 1650 cm⁻¹ (UP), 1730 cm⁻¹ (UP, PVAc, and PMMA), and 1495 cm⁻¹ (PS and styrene) were employed to calculate the corresponding species concentrations. Where the peaks overlapped, such as at 1730 cm⁻¹ for UP/PVAc and UP/PMMA, and at 1495 cm⁻¹ for PS/styrene, a simple subtraction method was used to separate the individual peaks with the aid of the non-overlapping peaks of UP at 1650 cm⁻¹ and styrene at 912 cm⁻¹ respectively.

Preparation of cured specimens

The sample solutions were degassed in a vacuum oven at 25°C for 3 h, and then slowly poured into two cast-iron rectangular moulds with inner trough dimensions of 9 × 1.5 × 0.3 cm³ and 15 × 2.6 × 0.4 cm³ respectively and sealed with gaskets. The specimens made from the former mould were used for TMA (thermal mechanical analysis), DMA (dynamic mechanical analysis), impact and tensile tests, while those from the latter one for fracture tests. The sample solutions were cured at 110°C in a thermostated silicone oil bath for 1 h, followed by a post-cure at 150°C for another

1 h. Finally, the cured specimens were further modified so as to meet the specifications suggested by the various tests as described below.

Reaction conversion

The cured sample in the mould was removed and broken into several pieces first; 2 mg of the sample was then milled, mixed with 100 mg of KBr, and pressed into a solid disk with 1 cm diameter. A Fourier-transform infrared spectrometer (Digilab, FTS-40) with a resolution of 4 cm⁻¹ in the transmission mode was used for conversion measurements of styrene and polyester C=C bonds after the cure. Detailed calculation procedures have been described elsewhere^{8,15}.

Morphology

In the morphology study, the broken sample pieces mentioned above were soaked in dichloromethane for one day to remove all soluble materials. The undissolved sample was placed on a filter paper and dried at room temperature for one day. The dry sample was then gold-coated for morphological measurement. Hitachi S-520 and S-550 scanning electron microscopes (SEM) with accelerating voltages of 15 and 20 kV were used to observe the fractured surface of each sample at magnifications of 1000 × to 5000 ×.

Mechanical tests

Dumbbell-shaped specimens based on ASTM D638-82a, Type V, were used to determine tensile properties of polyester matrices on the Micro 500 universal testing machine (Testometric Co.) at a constant crosshead speed of 2 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).

Fracture mechanics tests were carried out on sharply notched three-point bend specimens based on ASTM E-399-83-A3 with a crosshead speed of 1 mm/min. The fracture toughness, K_{IC} , and the fracture energy, G_{IC} , were then calculated using the equations:

$$K_{IC} = P_Q S / (BW^{3/2}) f(a/W) \quad (1)$$

$$f(a/W) = 3(a/W)^{1/2} [1.99 - a/W(1 - a/W)(2.15 - 3.93a/W + 2.7a^2/W^2)] / [2(1 + 2a/W)(1 - a/W)^{3/2}] \quad (2)$$

and

$$G_{IC} = K_{IC}^2 (1 - \nu^2) / E \quad (3)$$

where P_Q is maximum load, B is sample thickness, S is support span, W is sample width, a is initial crack length, ν is Poisson's ratio, and E is Young's modulus. Both ν and E values were obtained from tensile tests.

Thermal analysis

Thermal mechanical analysis was made between -50°C and 200°C at 10°C/min by using a Du Pont 943 TMA equipped with a 1090 thermal analysis system, where rectangular specimens measuring 5 × 5 × 2 mm³ were used. In addition, dynamic mechanical measurements were carried out between -150°C and 250°C at 5°C/min and a fixed frequency of 1 Hz by using a Du Pont 983 dynamic mechanical analyzer, where rectangular specimens measuring 5 × 1 × 0.2 cm³ were employed.

Table 1 Compositions of the upper and bottom layers for three unreacted styrene/UP/LPA systems at 25°C, where LPA = 5%, 10%, and 15% by weight, and MR is 2/1, 3/1, and 6/1

Molar ratio (MR of ST/UP C=C)	2/1			3/1			6/1		
	5	10	15	5	10	15	5	10	15
<i>(a) ST/UP/PVAc system</i>									
Phase separation time (min)	∞	180	270	32	45	67	12	25	40
Upper layer (dispersed phase)									
Relative weight (%)		19.8	21.4	6.7	14.0	18.3	7.5	19.9	40.4
ST (wt%)		50.2	47.0	59.5	55.9	50.0	71.5	67.9	65.8
UP (wt%)		14.7	10.9	13.3	11.4	9.6	8.8	7.7	10.6
PVAc (wt%)		35.1	42.1	27.2	32.7	40.4	19.7	24.5	23.7
MR (ST/UP C=C)		9.1	11.6	12.0	13.1	13.9	21.2	23.8	16.7
Bottom layer (continuous phase)									
Relative weight (%)		80.2	78.6	93.3	86.0	81.7	92.5	80.1	59.6
ST (wt%)		35.7	33.7	49.7	46.4	43.9	65.8	60.9	54.8
UP (wt%)		60.5	58.7	46.9	47.3	46.8	30.4	32.7	36.1
PVAc (wt%)		3.8	7.6	3.4	6.3	9.3	3.8	6.4	9.1
MR (ST/UP C=C)		1.57	1.53	2.82	2.61	2.50	5.76	4.96	4.04
<i>(b) ST/UP/PMMA system</i>									
Phase separation time (min)	90	115	130	24	33	45	9	16	25
Upper layer (dispersed phase)									
Relative weight (%)	2.7	22.2	30.5	9.1	23.9	32.4	17.8	30.5	30.0
ST (wt%)	65.7	59.3	49.5	67.7	61.5	51.7	71.4	62.1	52.4
UP (wt%)	11.6	13.5	16.8	9.3	10.4	13.9	7.1	7.5	12.4
PMMA (wt%)	22.7	27.2	33.7	23.0	28.1	34.4	22.5	29.4	35.2
MR (ST/UP C=C)	15.1	11.8	7.9	19.6	15.8	9.9	26.8	22.1	11.3
Bottom layer (continuous phase)									
Relative weight (%)	97.3	77.8	69.3	90.9	76.1	67.6	82.2	69.5	60.9
ST (wt%)	40.0	32.7	30.8	48.6	43.4	41.8	65.3	61.9	63.5
UP (wt%)	55.5	62.2	62.4	48.2	52.3	52.5	33.5	36.6	34.4
PMMA (wt%)	4.5	5.1	6.8	3.2	4.3	5.7	1.2	1.5	2.1
MR (ST/UP C=C)	1.92	1.40	1.31	2.69	2.21	2.12	5.19	4.50	4.91
<i>(c) ST/UP/PS system</i>									
Phase separation time (min)	40	50	60	17	22	30	7	12	20
Upper layer dispersed (phase)									
Relative weight (%)	15.1	28.6	43.0	14.3	32.4	45.4	9.5	36.1	44.7
ST (wt%)	59.7	57.2	57.4	67.7	64.4	60.4	72.2	70.3	64.7
UP (wt%)	13.4	11.3	10.4	15.3	13.3	12.2	10.4	9.1	7.4
PS (wt.)	26.9	31.5	32.2	17.0	22.3	27.5	17.4	20.6	28.0
MR (ST/UP C=C)	11.9	13.6	14.8	11.9	12.9	13.3	18.6	20.7	23.5
Bottom layer (continuous phase)									
Relative weight (%)	84.9	71.4	57.0	85.7	67.6	54.6	90.5	63.9	55.3
ST (wt%)	37.3	31.1	20.8	47.4	39.7	32.3	65.6	57.8	54.8
UP (wt%)	61.6	67.5	77.2	49.6	56.2	63.1	30.7	38.2	40.7
PS (wt.)	1.1	1.4	2.0	3.0	4.1	4.6	3.7	4.0	4.5
MR (ST/UP C=C)	1.61	1.23	0.72	2.54	1.88	1.36	5.69	4.03	3.59

RESULTS AND DISCUSSION

The drift in styrene/polyester composition during the cure-phase characteristics

Table 1 shows the effects of molar ratio of styrene to polyester C=C bonds (MR) and LPA concentration on the static ternary phase characteristics at 25°C for ST/UP/PVAc, ST/UP/PMMA, and ST/UP/PS systems. As MR increased or LPA concentration decreased, the global phase separation time generally became shorter. Increasing LPA concentration would increase the weight fraction of upper layer (i.e. dispersed phase), revealing a higher degree

of phase separation. In terms of both the rate of global phase separation and the degree of phase separation, the phase separation was the most pronounced for the PS systems, followed by PMMA system, and least significant for the PVAc system. (The PU system formed a homogeneous solution after a phase equilibrium.)

After a phase equilibrium at 25°C for ST/UP/LPA systems, the upper layer (i.e. dispersed phase) was dominated by ST and LPA, and the amount of UP was less than 20%; while the bottom layer (i.e. continuous phase) was dominated by UP and ST, and the amount of LPA was less than 10%. The molar ratio of styrene to polyester C=C

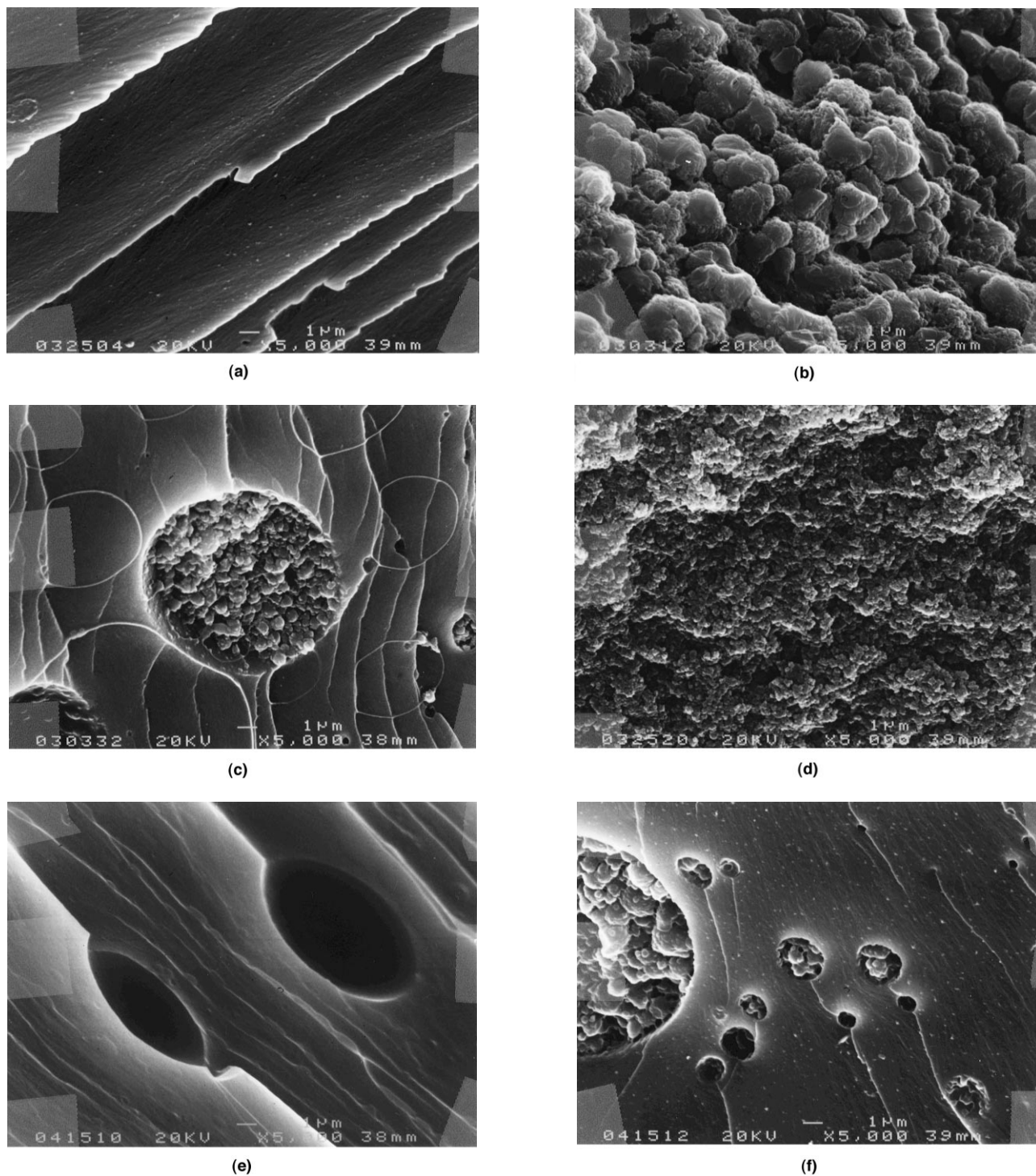


Figure 1 SEM micrographs of fractured surfaces for LPA-containing UP resins (MR 2/1) after the cure at 110°C and a post-cure at 150°C: (a) no LPA; (b) 10% PVAc; (c) 10% PMMA; (d) 10% PU; (e) 10% PS; (f) 10% PS with an isothermal curing at 110°C only. Micrographs obtained at 5000 ×

bonds in the upper layer would be greater than that in the original mixture, while the trend would be reversed in the bottom layer. *Table 1* also shows that at a fixed MR, a higher LPA concentration would generally lead to a lower MR in the bottom layer after the phase equilibrium (i.e. much smaller MR than that of the original mixture). On the other hand, at fixed MR and LPA concentration, the less compatible system would generally lead to a lower MR in the bottom layer after the phase equilibrium (i.e. decreasing order of MR followed by PVAc > PMMA > PS system).

On heating from 25°C to 110°C, each of the ST/UP/LPA

ternary systems shown in *Table 1* would appear as a homogeneous single phase prior to reaction, and no global phase separation could be observed. 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 conversion ($\alpha < 1\%$)⁸. Near the gelation point ($\alpha \approx 10\%$)¹⁶, the mass transfer into or out of the continuous phase or the dispersed phase would essentially cease. To a first approximation, the compositions in either phase for

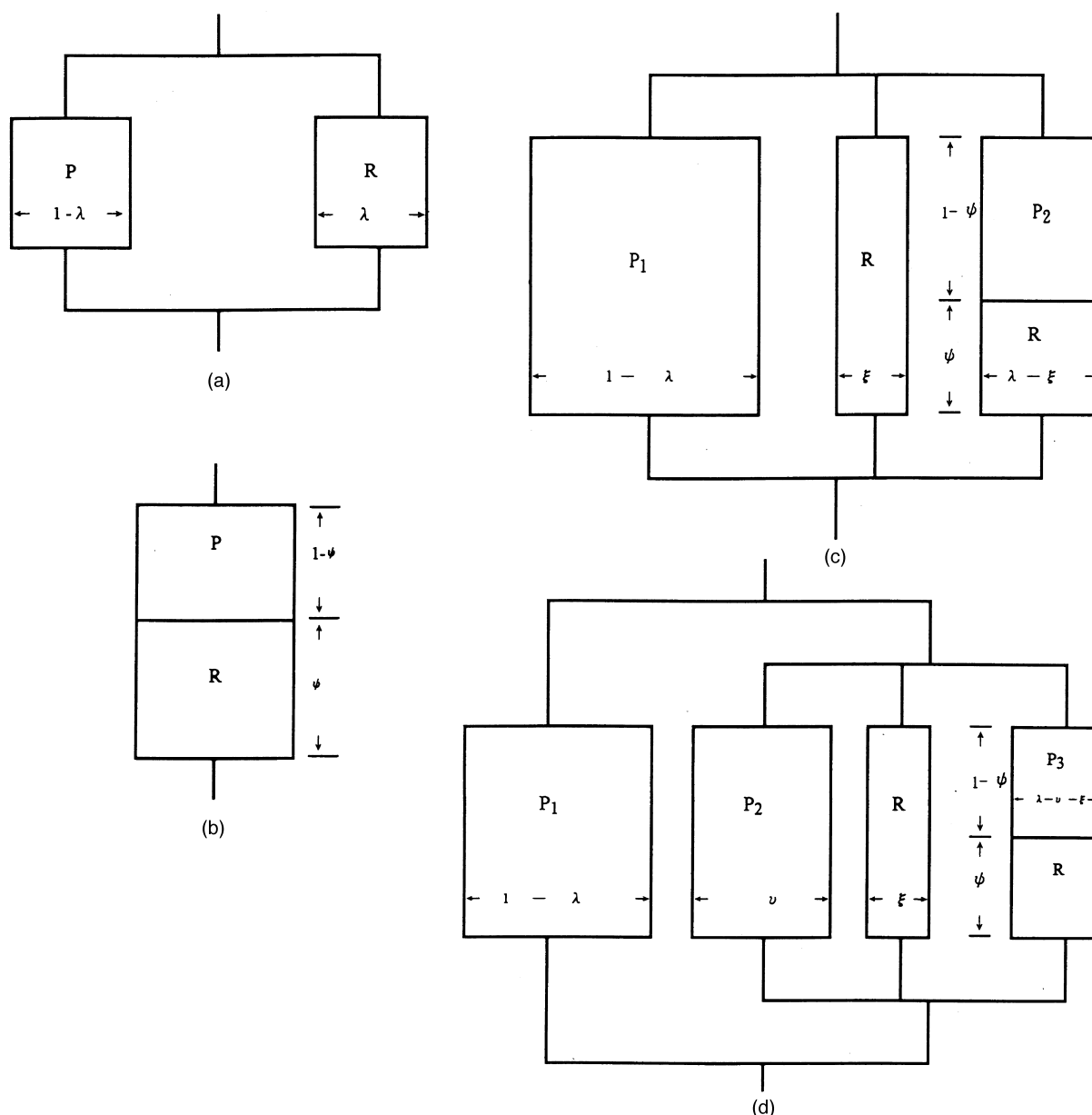


Figure 2 The Takayanagi models for mechanical behaviour of cured LPA-containing UP resin systems: (a) parallel (P) model; (b) series (S) model; (c) parallel-parallel-series (P-P-S) model; (d) parallel-parallel-parallel-series (P-(P-P-S)) model. The area of each diagram is proportional to a volume fraction of the phase

the ultimately cured sample could then be represented, in an average sense, by those based on the static phase characteristics at 25°C as shown in *Table 1*. For instance, the molar ratio of styrene consumed to polyester C=C bonds reacted in the major continuous phase after the cure would be fairly close to the MR in the bottom layer as shown in *Table 1*. This is because the increase in molecular weights of the reacting species via crosslinking reactions would enhance the phase separation in the same direction as the lowering in mixing temperature would. 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 separation.

Relationship between morphologies and mechanical properties – the Takayanagi models

For the cured LPA-containing UP resin systems with morphologies as shown in *Figure 1b–e*, their mechanical

behaviour can be approximately represented by the Takayanagi models^{17–19}, where arrays of weak LPA (R) and stiff styrene-crosslinked polyester (P) phases are indicated (see *Figure 2*). 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 , ψ , ξ , and ν or their indicated multiplications indicate volume fractions of each phase. Four combinations including parallel (P), series (S), parallel-parallel-series (P-P-S), and parallel-parallel-parallel-series (P-(P-P-S)) models are shown in *Figure 2*. For the parallel element, an iso-strain condition exists when the element is subjected to a longitudinal stress, while for the series element, an iso-stress condition results.

Figure 2a apparently represents the case that the phase P and the phase R form a co-continuous phase morphology. It may also denote the upper bound behaviour of a relatively stiff material consisting of a stiff continuous phase P and a weak dispersed phase R. On the other hand, *Figure 2b*

Table 2 Summary of final conversions by FTIR for UP resins cured at 110°C and post-cured at 150°C: (a) effects of molar ratios of styrene to polyester C=C bonds (MR) and (b) effects of LPA types and concentrations at MR 2/1

(a)	Molar ratio (MR)	1/1	2/1	3/1	6/1
	Neat UP resins				
	α_E^a	65.2	77.6	89.6	91.3
	α_S	87.7	90.8	100.0	100.0
	α_{TOT}	76.4	86.4	97.4	98.8
	UP + 5% PVAc				
	α_E	67.3	76.9	92.4	94.6
	α_S	87.9	92.4	100.0	100.0
	α_{TOT}	77.6	87.3	98.1	99.2
	UP + 10% PVAc				
	α_E	65.9	79.1	90.7	89.8
	α_S	82.4	82.3	99.2	100.0
	α_{TOT}	74.1	81.3	97.1	98.5
	UP + 5% PMMA				
	α_E	64.3	76.3	86.6	89.9
	α_S	85.7	88.8	99.0	100.0
	α_{TOT}	75.0	84.6	95.9	98.6
	UP + 10% PMMA				
	α_E	63.7	74.9	85.3	88.5
	α_S	83.9	86.6	96.4	99.8
	α_{TOT}	73.8	82.7	93.7	98.2
(b)	LPA concentration	Neat UP resins	5% LPA	10% LPA	15% LPA
	UP + PVAc (MR 2/1)				
	α_E	77.6	76.9	79.1	80.5
	α_S	90.8	92.4	82.3	80.8
	α_{TOT}	86.4	87.3	81.3	80.7
	UP + PMMA (MR 2/1)				
	α_E	77.6	76.3	74.9	73.6
	α_S	90.8	88.8	86.6	85.9
	α_{TOT}	86.4	84.6	82.7	81.8
	UP + PU (MR 2/1)				
	α_E	77.6	77.8	80.0	80.4
	α_S	90.8	88.7	87.9	87.3
	α_{TOT}	86.4	85.1	85.3	85.0
	UP + PS (MR 2/1)				
	α_E	77.6	75.4	74.9	73.8
	α_S	90.8	87.6	86.3	84.6
	α_{TOT}	86.4	83.5	82.5	81.0

α_E (%) is polyester vinylene conversion, α_S (%) is styrene conversion, and α_{TOT} (%) is total conversion of C=C bonds

denotes the lower bound behaviour of a relatively weak material consisting of a weak continuous phase R and a stiff discontinuous phase P. For the PVAc and PU systems (*Figure 1b* and *d*), 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 2c*, which is a parallel combination of the three elements, i.e. P_1 , R, and P_2 -R in series. In contrast, for the PMMA and PS systems (*Figure 1c* and *e*), the microstructure consists of a flake-like stiff continuous phase of styrene-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 behaviour for the overall morphology can be represented by a P-(P-P-S)

model as shown in *Figure 2d*, 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 as demonstrated earlier.

Morphology

Figure 1 shows the effects of LPA on the morphological change of cured samples. For the neat UP resin system, a flake-like microstructure was observed (*Figure 1a*). Adding PVAc or PU in the neat UP resins, a co-continuous globule microstructure, consisting of a crosslinked UP phase (i.e. globules or microgel particles) and LPA phase, would result

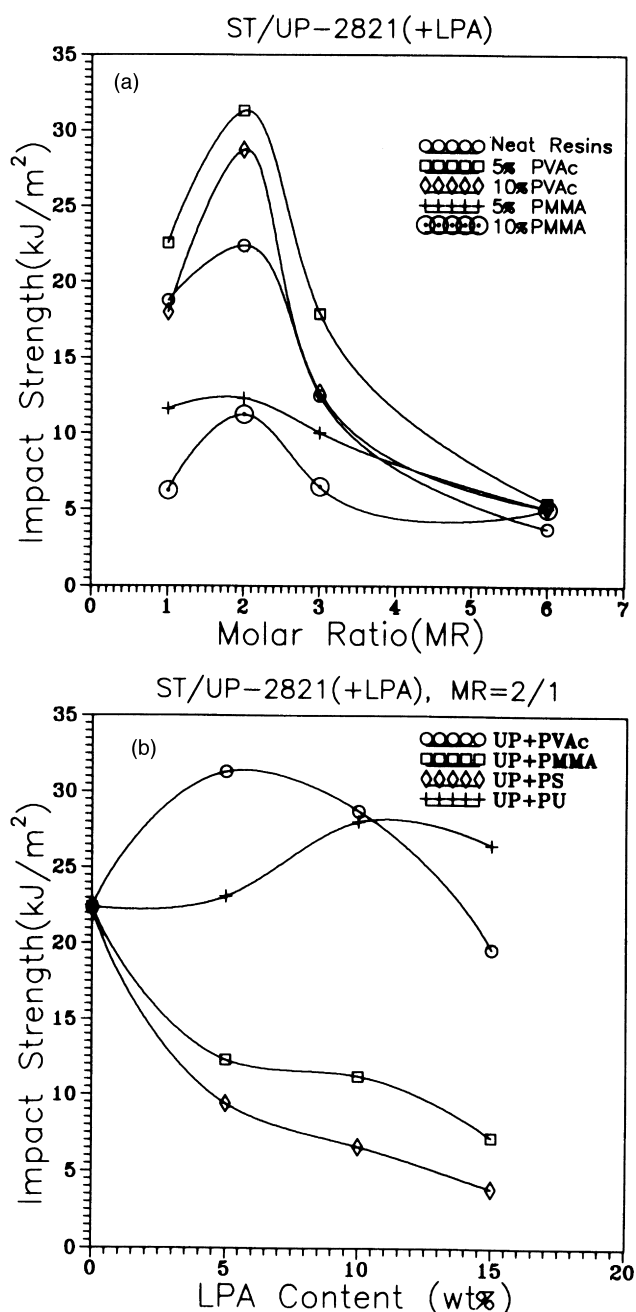


Figure 3 (a) The effects of styrene to polyester C=C bonds (MR) on impact strength of cured UP resins. (b) The effects of LPA type and concentration on impact strength of cured UP resins at MR 2/1

after the cure (Figure 1b and d). The LPA phase would surround the microgel particles but had been washed off in the extraction procedure. For the PU system, the microdomain of crosslinked UP phase appeared much smaller than that of PVAc system ($< 0.2 \mu\text{m}$ versus $2 \mu\text{m}$) due to the better compatibility between PU and UP resin than between PVAc and UP resin. In contrast, for PMMA or PS as an LPA, a two-phase microstructure, containing a flake-like continuous phase and a globule LPA dispersed phase, would generally arise (Figure 1c and e). However, for the PS system, the microgel particles in the LPA dispersed phase could scarcely be seen, which was unlike the PMMA-containing sample (Figure 1c) and the isothermally cured PS-containing sample at 110°C prior to the post-cure at 150°C (Figure 1f).

The globule features in Figure 1c and f appear to be

similar to those of Figure 1b and d, showing a certain degree of compatibility among phases R, P₂ and P₃. Phase separation is affected by the temperature of mixing (before reaction) and the extent of crosslinking. Since phase separation was the most pronounced for PS, it would show very little compatibility with P₁, P₂ or P₃ after curing at 150°C . The LPA particles would have been dissolved in the solvent after extraction, leaving a 'hole' in the matrix. The microgel structure could hardly be seen.

Increasing either MR or LPA concentration would enhance the degree of phase separation for the cured LPA-containing samples, as evidenced by the more conspicuous microgel particles being observed or the larger area of LPA-dispersed phase domains based on the SEM micrograph of the fracture sample surface¹⁵ (not shown), and vice versa. For instance, at MR 1/1 and PVAc 5 wt% a flake-like microstructure for the cured sample was observed, which would be due to the inadequate segregating effects of both styrene and PVAc on microgel particles^{8,9}.

Cure conversions

Table 2 shows the effects of molar ratio of styrene to polyester C=C bonds (MR) and LPA types and concentrations at MR 2/1 on the final conversion of styrene (α_S), polyester C=C bonds (α_E), and total C=C bonds (α_{TOT}) for the cured samples. As MR increased from 1/1 to 6/1, α_S , α_E , and α_{TOT} all increased [Table 2(a)] as a result of the enhancement of styrene swelling effect on microgel particles⁸. As high as 25% differences in α_E could arise between the samples for MR 1/1 and 6/1. On the other hand, at a fixed MR of 2/1, as LPA concentration increased from 0 to 15%, α_E generally increased for PVAc and PU systems, while it showed a drop for PMMA and PS systems [Table 2(b)]. For all of the four systems, α_S and α_{TOT} generally declined with increasing LPA concentration. However, the differences of α_S , α_E or α_{TOT} between the samples were within 5%.

Impact strength

Figure 3a shows the effects of molar ratio of styrene to polyester C=C bonds (MR) on the impact strength of cured samples containing LPA (PVAc or PMMA) and no LPA. For all of the samples, as MR increased, the impact strength exhibited an increase, followed by a decrease, and reached a maximum at MR 2/1. This is attributed to the fact that on the one hand, increasing MR could enhance the average crosslink length of styrene^{20,21}, through which the vinylene groups either in two adjacent polyester molecules (i.e. intermolecular crosslinking) or in the same polyester molecule (i.e. intramolecular crosslinking) are connected, in the styrene-crosslinked polyester matrix after the cure. An adverse effect on the impact strength would thus arise due to the brittle nature of the polystyrene segment. On the other hand, increasing MR could elevate the final conversion of polyester C=C bonds (i.e. α_E) and hence the degree of crosslinking (see Table 2) of the cured samples, leading to a favourable effect on the impact strength. Hence, the effect of MR on the impact strength shown in Figure 3a would be a result of competition for the two opposing effects, the optimal balance between which would occur at MR 2/1.

Figure 3b shows the effect of LPA concentration (PVAc, PMMA, PS or PU) on the impact strength of cured samples at a fixed MR of 2/1. For the PVAc and PU systems, the impact strength first increased and then decreased with increasing LPA concentration, reaching a maximum at 5%

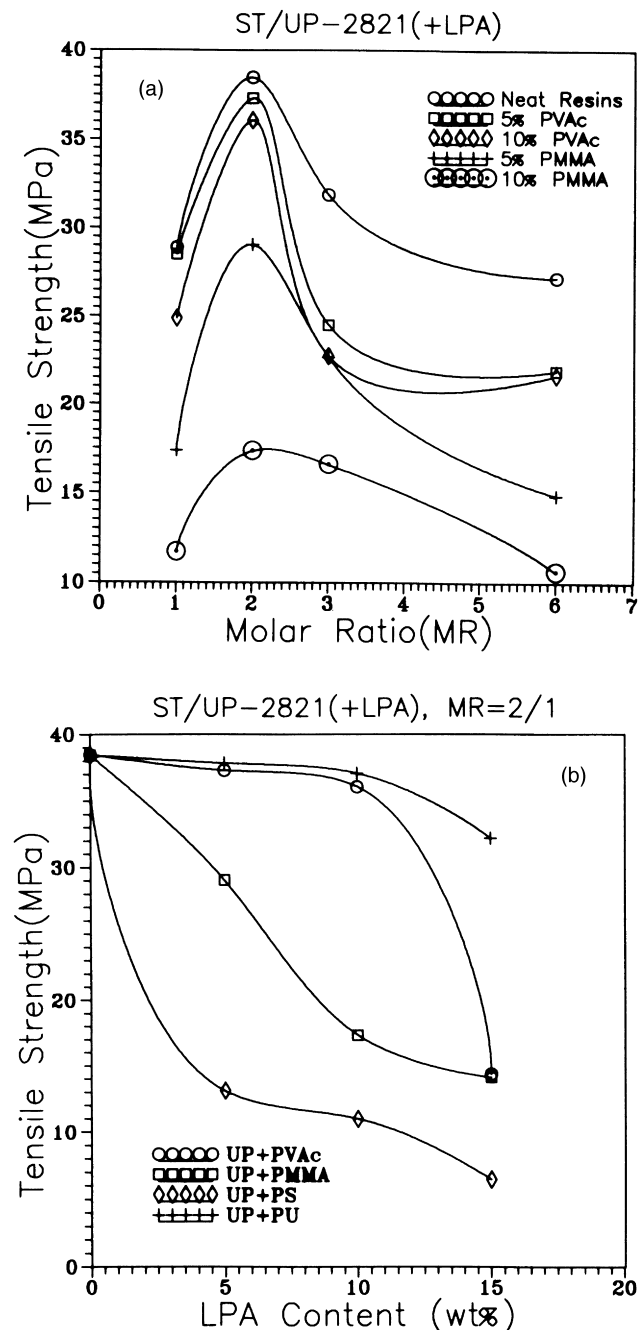


Figure 4 (a) The effects of styrene to polyester C=C bonds (MR) on tensile strength of cured UP resins. (b) The effects of LPA type and concentration on tensile strength of cured UP resins at MR 2/1

and 10% LPA concentration respectively. In contrast, for the PMMA and PS systems, it decreased with LPA concentration. The impact strength for the former two systems was higher than for the latter two systems, which would be due to the better interfacial adhesion resulting from the more compatible system, such as PU and PVAc systems. It would also be ascribed to the fact that the PVAc ($T_g \approx 27^\circ\text{C}$) and PU ($T_g \approx -45^\circ\text{C}$) added were either close to or in the rubbery state under the test condition at 25°C , while PMMA ($T_g \approx 105^\circ\text{C}$) and PS ($T_g \approx 100^\circ\text{C}$) were in the glassy state. Adding PMMA or PS as an LPA would result in the brittleness of the cured sample, and hence the decrease of impact strength as LPA content was increased. As for the PVAc and PU systems with a co-continuous microstructure (Figure 1b and d), the generally dispersed

microvoids^{13,14}, which would be generated during the cure at the interface between the LPA and the crosslinked UP phases as well as inside the LPA phase, were found⁵ to be more effective than the microvoids localized in the LPA dispersed phase for the PMMA and PS systems with a two-phase microstructure (Figure 1c and e). Since the microvoids could lead to a crack tip blunting effect²² releasing the stress concentration at the crack tip and delaying crack propagation, an improvement in impact strength was observed when compared with the neat resin system. As LPA (PVAc or PU) content increased, the volume fraction of microvoids was higher⁵, resulting in a favourable effect on impact strength. On the other hand, since the crack would eventually propagate through the voided plane during the impact testing of specimens, excessively higher volume fraction of microvoids could cause an adverse effect on impact strength. The opposing direction due to the former favourable effect and the latter adverse effect would then result in an increase followed by a decrease in impact strength with increasing LPA content. At a fixed LPA content, the volume fraction of microvoids was found⁵ to be higher for the cured resin system containing PVAc than that containing PU, the LPA concentration for the maximum impact strength was hence lower for the former system than for the latter one (5% versus 10%). At 15% of LPA content, the impact strength of the PU system was still higher than that of the neat resin system, while the trend was reversed for the PVAc systems.

Tensile properties

Figure 4a shows the effects of molar ratio of styrene to polyester C=C bonds (MR) on the tensile strength of cured samples containing LPA (PVAc or PMMA) and no LPA. For all of the samples, as MR increased, the tensile strength exhibited an increase, followed by a decrease, and reached a maximum at MR 2/1, which shows the same trend as the impact strength. While increasing MR would reduce the concentration of polyester C=C bonds, and hence the crosslinkable density of the system prior to cure, yet it could enhance the conversion of polyester C=C bonds (see Table 2), and hence the degree of crosslinking after the cure. Since the tensile property of cured samples would be increased with increasing crosslinking density, which is a product of the crosslinkable density prior to cure and the degree of crosslinking after the cure, the effect of MR on the tensile strength shown in Figure 4a would reveal an optimal crosslinking density at MR of 2/1, either below or above which could reduce the crosslinking density.

Based on the iso-strain model in Figure 2c and d, the 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 co-continuous 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 4b shows the effect of LPA concentration (PVAc, PMMA, PS or PU) on the tensile strength of cured samples at a fixed MR of 2/1. For all of the four systems, the tensile strength decreased with increasing LPA concentration. This could be due to the increase of crosslinking density in the major continuous phase (to be explained in the section on glass transition temperatures later) being overwhelmed by the reduction of volume fraction in that phase. Although the microvoid formation in the cured samples has been employed to explain the lowering of tensile strength for

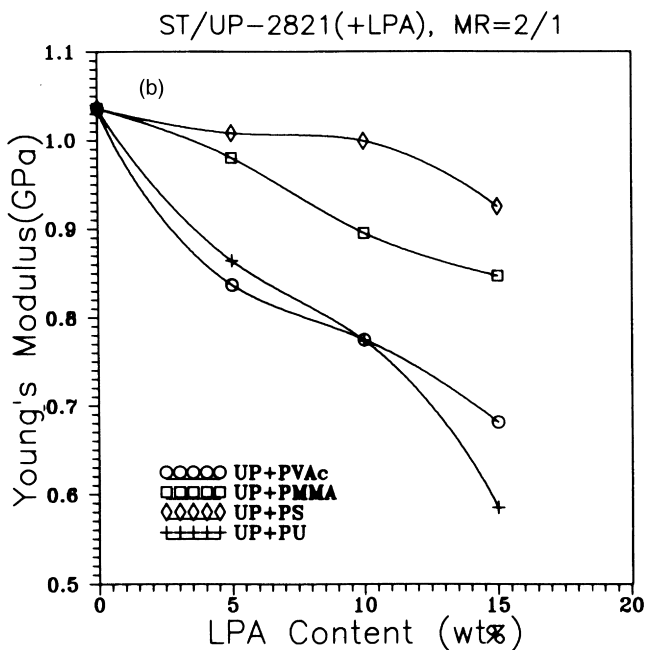
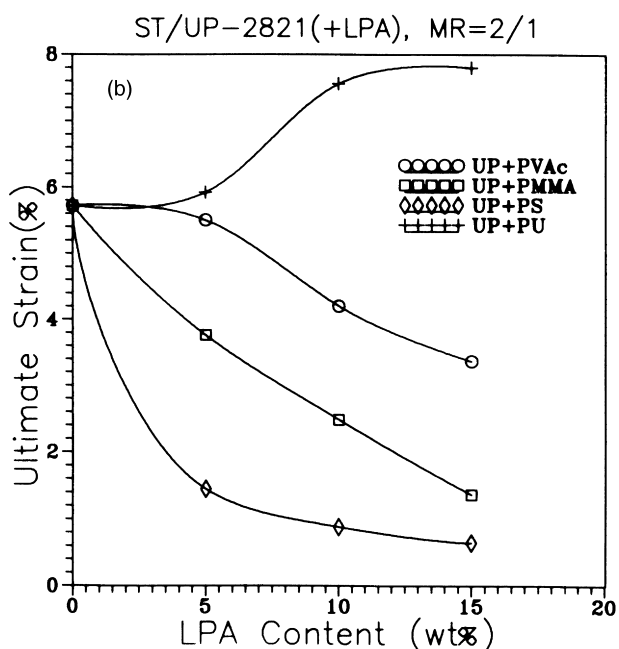
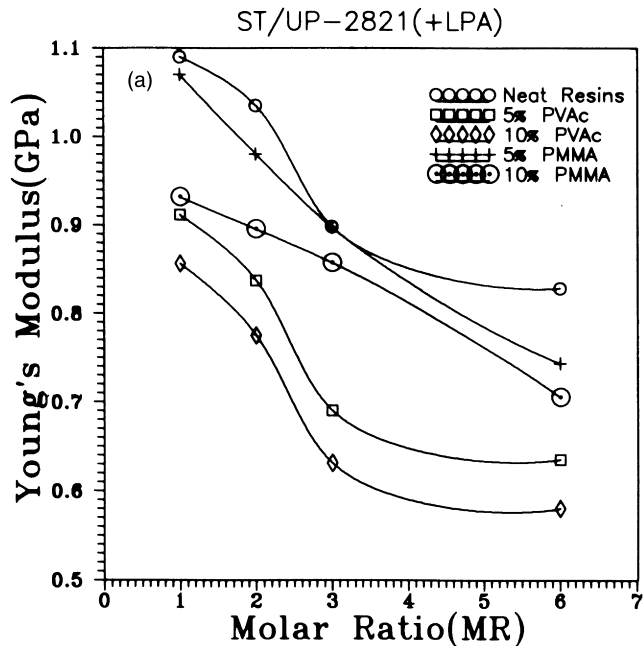
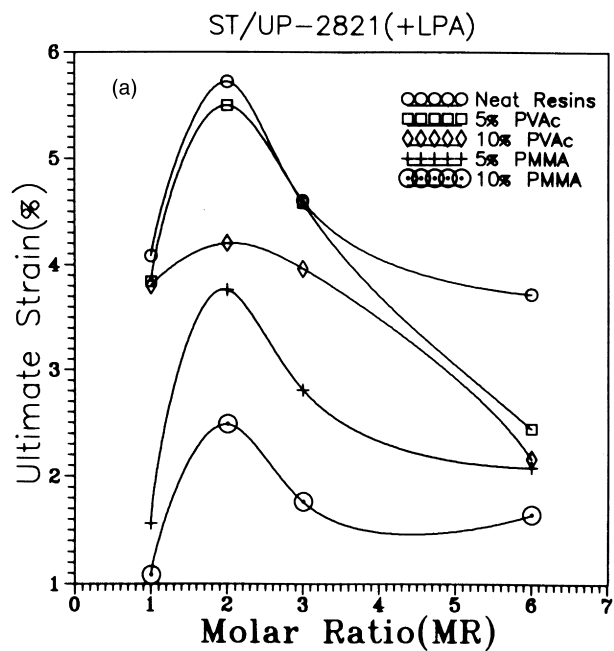


Figure 5 (a) The effects of styrene to polyester C=C bonds (MR) on ultimate tensile strain of cured UP resins. (b) The effects of LPA type and concentration on ultimate tensile strain of cured UP resins at MR 2/1

Figure 6 (a) The effects of styrene to polyester C=C bonds (MR) on Young's modulus of cured UP resins. (b) The effects of LPA type and concentration on Young's modulus of cured UP resins at MR 2/1

samples containing LPA^{11,12}, it could not account for all the experimental results shown in *Figure 4b*, especially for samples containing different LPA. For instance, the relative volume fraction of microvoids would be generally higher for the system with a co-continuous cured sample morphology (i.e. PVAc system) than that with a two-phase microstructure consisting of a continuous phase and a dispersed phase (i.e. PMMA and PS systems)⁵, however, the tensile strength was the highest for the PU system, followed by PVAc, PMMA, and PS in decreasing order. Among the four LPA-containing systems, the compatibility of LPA with UP resin would be ranked as PU > PVAc > PMMA > PS. The worse the compatibility of the system, the more significant the phase separation during the cure, and the molar ratio in the major continuous phase of styrene-

crosslinked polyester for the cured sample would be much smaller than MR 2/1 and the volume fraction in that phase would be smaller as well as inferred from *Table 1*, thereby leading to a lower tensile strength. Also, the worse interfacial adhesion resulting from the less compatible system would be unfavourable in elevating the tensile strength.

The effects of molar ratio and LPA concentration on the ultimate tensile strain (see *Figure 5*) show the same trend as those on the tensile strength (*Figure 4*) except for the PU system (*Figure 5b*). Since PU is in the rubbery state at room temperature, increasing PU content would thus enhance the ultimate tensile strain. It should be noted that at a fixed MR of 2/1, the molar ratio of styrene consumed to polyester C=C bonds reacted would be much less deviated from

MR 2/1 for the major continuous phase (i.e. phase P₁ in Figure 2c and d) than the minor co-continuous or dispersed phase of crosslinked polyester (i.e. phase P₂ in Figure 2c and d) as inferred from Table 1 (MR 0.72–1.92 versus 7.9–15.1). Hence, Figure 5a reveals that the major continuous phase would be less brittle and possess a higher ultimate tensile strain, which could justify the use of $(1-\lambda)\sigma_{p_1}$ as an approximation for the ultimate strength based on the iso-strain model in Figure 2c and d.

Figure 6a shows the effects of molar ratio or styrene to polyester C=C bonds (MR) on the Young's modulus of cured samples containing LPA (PVAc or PMMA) and no LPA. The Young's modulus decreased with increasing molar ratio for all of the samples, which exhibited a different trend from that of tensile strength with a maximum at MR 2/1 shown in Figure 4a. Since 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 the degree of tightness of the network rather than the degree of crosslinking of the sample.

In general, the higher the styrene content in the initial sample solution, the lower the crosslinkable density of the system prior to cure. The cured sample would then possess a higher average crosslink length of styrene and a more loose network, which, in turn, could result in a lower Young's modulus.

Based on the iso-strain model in Figure 2c and d, the Young's modulus of the sample would be dominated by $(1-\lambda)E_{p_1}$ since the moduli of phases R, P₂, and P₃ multiplied by their corresponding volume fractions would generally be much smaller than that of phase P₁ multiplied by its volume fraction (i.e. $(1-\lambda)E_{p_1}$), where E_{p_1} is the Young's modulus of the major continuous phase. It should be noted that although from Figure 6a, the modulus of resin is ≈ 1.09 GPa, which is lower than those of rigid LPAs, such as PS and PMMA ($E_R \approx 2.2\text{--}3.3$ GPa²³, and hence $E_{p_1} \approx 0.33\text{--}0.5E_R$), yet the much lower volume fraction of the LPA phase ($\xi < 0.05\text{--}0.15$ in Figure 2c and d since the LPA in the sample was 5–15% by weight) than that of the major continuous phase ($1-\lambda > 0.8$ as observed from Figure 1b–e) could justify our assumption that Young's modulus would be dominated by $(1-\lambda)E_{p_1}$.

Figure 6b shows that the Young's modulus decreased with increasing LPA concentration for all of the four LPA-containing systems at a fixed MR of 2/1. Although the trend is the same as that of tensile strength shown in Figure 4b, the reasons behind them would be different. Increasing LPA content could reduce $1-\lambda$, and it could also decrease E_{p_1} due to the increase of molar ratio of styrene consumed to polyester C=C bonds reacted in the major continuous phase [the molar ratio (MR) in the continuous phase before cure shown in Table 1 could not always reflect that of the cured sample due to the interaction of phase separation and chemical reaction in the curing process, which will be explained in the section on class transition temperatures later], leading to a lower Young's modulus. On the other hand, at a fixed LPA concentration, the Young's modulus was higher for the PS and PMMA systems than for the PU and PVAc systems. This could be mainly attributed to a lower average crosslink length of styrene and a more compact network in the major continuous phase of crosslinked polyester (P₁ phase in Figure 2c and d) for the former two systems, where the concomitant smaller volume fraction of the major continuous phase would be well made up for by the much more compact network therein.

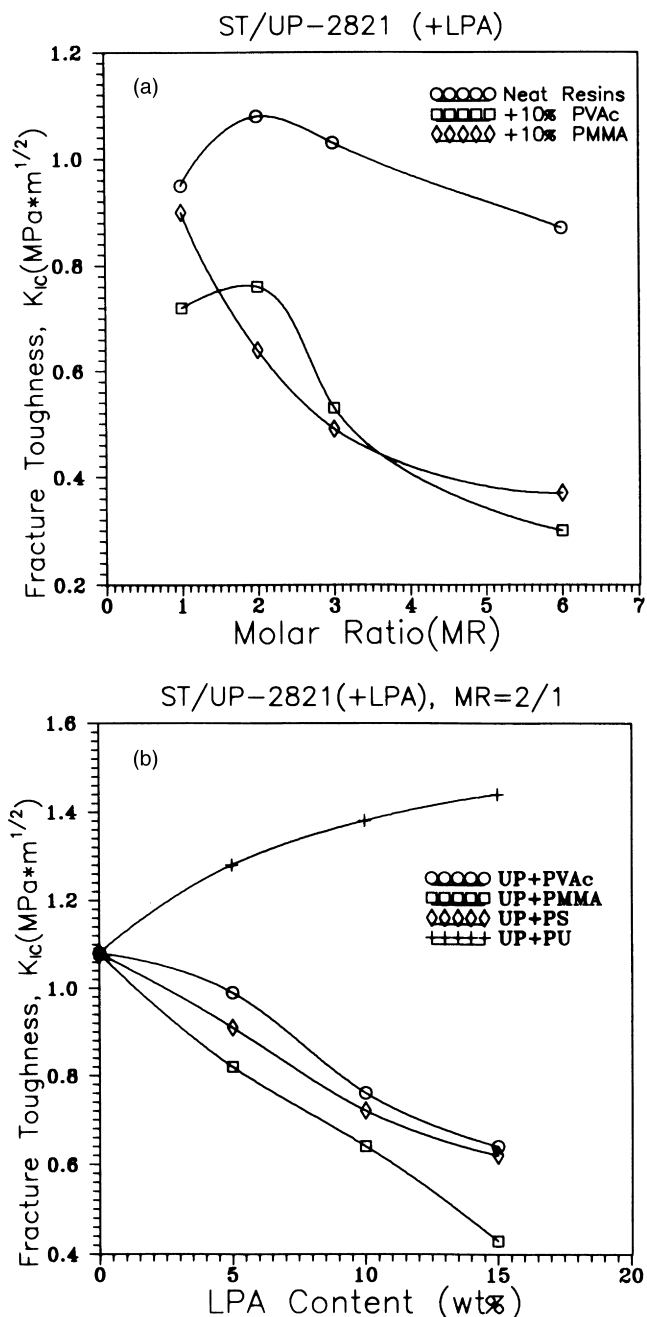


Figure 7 (a) The effects of styrene to polyester C=C bonds (MR) on fracture toughness, K_{IC} , of cured UP resins. (b) The effects of LPA type and concentration on fracture toughness, K_{IC} , of cured UP resins at MR 2/1

The higher tensile modulus for the PS and PMMA than those of PVAc and PU could also cause higher Young's modulus for the styrene-crosslinked polyester systems containing former LPAs (contribution by the term ξE_R).

Fracture properties

Figure 7a shows the effects of molar ratio of styrene to polyester C=C bonds (MR) on the fracture toughness of cured samples containing 10% LPA (PVAc or PMMA) and no LPA. For neat UP resin and PVAc-containing samples, as MR increased, the fracture toughness exhibited an increase, followed by a decrease, and reached a maximum at MR 2/1, which shows the same trend as that of impact strength as shown in Figure 3a. In contrast, for the PMMA-containing sample, the fracture toughness

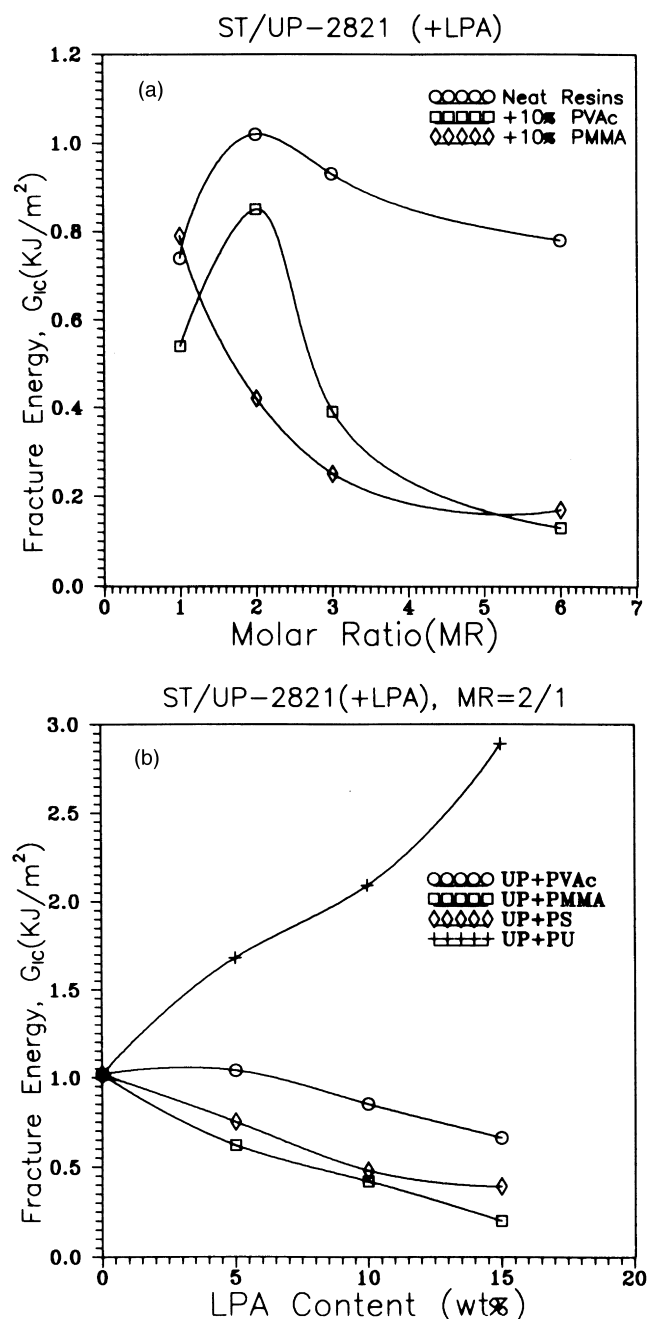


Figure 8 (a) The effects of styrene to polyester C=C bonds (MR) on fracture energy, G_{IC} , of cured UP resins. (b) The effects of LPA type and concentration on fracture energy, G_{IC} , cured UP resins at MR 2/1

decreased with increasing MR. Figure 7b shows the effect of LPA concentration (PVAc, PMMA, PS or PU) on the fracture toughness of cured samples at a fixed MR of 2/1. For the PVAc, PMMA, and PS systems, the fracture toughness decreased with increasing LPA concentration, while it increased with increasing LPA concentration for the PU system, which shows a somewhat different trend from that of impact strength for PU and PVAc systems shown in Figure 3b.

It should be noted that the three-point bending fracture test was carried out under a much slower speed than the impact test. Both test results would not necessarily show the same trend due to possibly varied fracture mechanisms regarding crack initiation and crack propagation. Experimental data on fracture toughness implies that for

the PVAc system, as LPA concentration increased, the increasing volume fraction of microvoid generated during the cure could not lead to an appreciable crack tip blunting effect to delay crack propagation in such a relatively slow speed fracture test, while for the PU system, this effect would be getting remarkable to improve the fracture toughness considerably. This could be due to the size of microvoid generated being smaller for the PU system than for the PVAc system ($< 0.1 \mu\text{m}$ versus $1 \mu\text{m}$)⁵.

The effects of molar ratio of styrene to polyester C=C bonds and LPA concentration on the fracture energy of cured samples are displayed in Figure 8a and b, which show essentially the same trend as those on the fracture toughness. However, for the PVAc system, as LPA concentration increased, the fracture energy exhibited a slight increase, followed by a decrease, and reached a maximum at 5 wt% of LPA concentration, which shows a somewhat similar trend to that of impact strength in Figure 3b. The slight increase in G_{IC} at 5% LPA concentration implies that the increase in crack propagation energy could be somewhat greater than the concomitant decrease in crack initiation energy due to the ever increasing volume fraction of microvoids as LPA concentration was increased.

Glass transition temperatures

Figure 9a shows the effects of molar ratio of styrene to polyester C=C bonds (MR) on the glass transition temperature of the major continuous crosslinked polyester phase, T_{g1} , for cured samples containing LPA (PVAc or PMMA) and no LPA by TMA. For all of the samples, as MR increased, T_{g1} exhibited an increase, followed by a decrease, and reached a maximum at MR 2/1, which shows a similar trend to those reported by Cook and Delatycki²⁴ and Lucas *et al.*²⁵ for the neat UP resin systems and by Bucknall *et al.*¹⁰ for the PVAc-containing UP resin systems. Since T_{g1} would be closely connected with the crosslinking density in the major continuous phase of styrene-crosslinked polyester, its trend of variation with MR is the same as that of tensile strength shown in Figure 4a. As MR deviated from MR 2/1, T_{g1} of the PMMA system was higher than that of neat UP and PVAc systems, which would be due to the variation of MR, LPA concentration, and reaction conversion in the major continuous phase of styrene-crosslinked polyester in favour of T_{g1} .

Figure 9b shows the effect of LPA concentration (PVAc, PMMA, PS or PU) on the T_{g1} of cured samples at a fixed MR of 2/1. For all of the four systems, the T_{g1} decreased with increasing LPA concentration. Also, except for the PU system, T_{g1} was the highest for the PVAc system, followed by the PMMA system, and the lowest for the PS system. Both findings exhibit the same trend as the tensile strength shown in Figure 4b. As for the PU system, due to the low T_{g1} of -45°C for PU additive, the adverse plasticization effect of PU on the major continuous phase of styrene-crosslinked polyester in raising T_g would counterbalance the favourable molar ratio effect (i.e. less deviation from MR 2/1) in that phase, leading to a lower T_{g1} than that of the PVAc and PMMA systems.

The glass transition temperatures have also been measured by DMA in facilitation of obtaining T_g for both the major continuous phase of styrene-crosslinked polyester, T_{g1} , and the co-continuous or LPA-dispersed phase, T_{g2} , since the latter could be more easily identified by DMA than by TMA¹⁵. Figure 10 shows DMA results for cured UP resins containing no LPA and 10% LPA at MR 2/1. Based

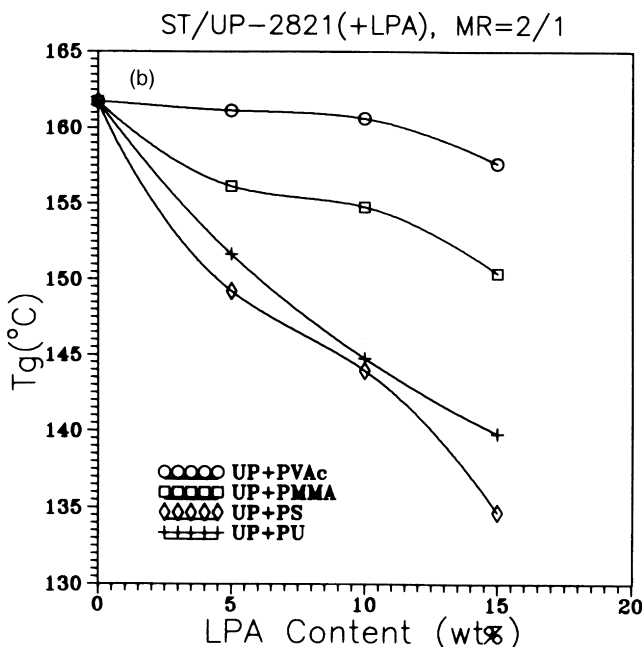
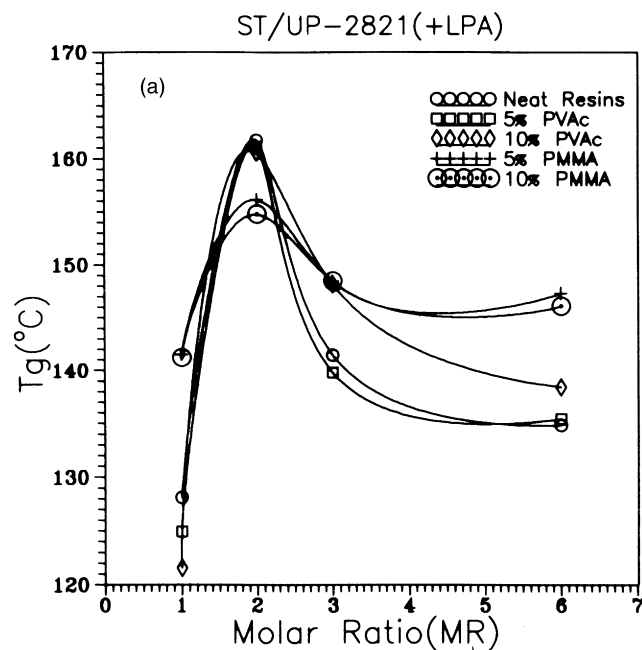


Figure 9 (a) The effects of styrene to polyester C=C bonds (MR) on glass transition temperatures of the major continuous phase of crosslinked polyester for cured UP resins. (b) The effects of LPA type and concentration on glass transition temperatures of the major continuous phase of crosslinked polyester for cured UP resins at MR 2/1

on the $\tan \delta$ curve of DMA, the maximum point at higher temperatures would be T_{g1} , while the shoulder (sometimes a local maximum peak, such as 10% PS system at MR 2/1) at lower temperatures would be identified as T_{g2} . T_g displayed in Table 3 reveals that the effects of MR and LPA concentrations on T_{g1} show the same trend as those measured by TMA shown in Figure 9. Also, due to the interaction of LPA and dispersed styrene-crosslinked polyester matrix, namely phases R and P_2 in Figure 2c and d, T_{g2} for the PVAc, PMMA, PS and PU-containing cured UP systems would be higher than the T_g of their neat LPA counterparts (i.e. 70–80°C, 110–125°C, 130–140°C, and –37°C versus 27°C, 105°C, 100°C, and –45°C). For

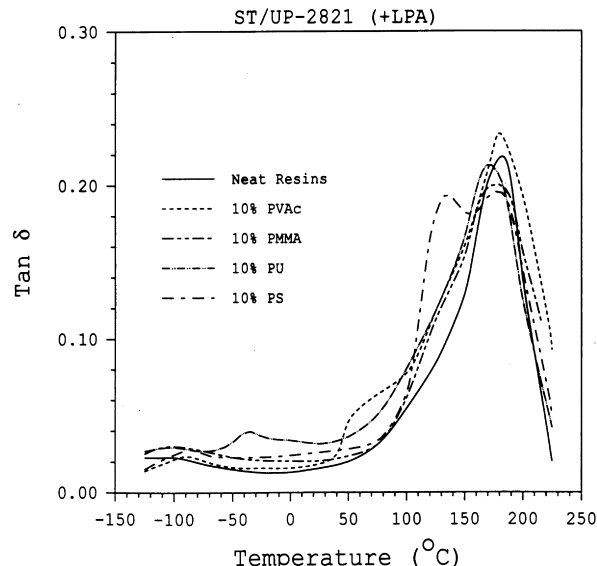


Figure 10 $\tan \delta$ versus temperature for cured UP resins containing no LPA and 10% LPA (PVAc, PMMA, PU, or PS) at MR 2/1 by dynamic mechanical measurements

PMMA and PS systems, the degree of phase separation was more pronounced for the latter system, which could be confirmed by the appearance of a peak instead of a shoulder at T_{g2} . On the other hand, for PVAc and PU systems, the compatibility was better for the latter system, which could be evidenced by the appearance of a smaller shoulder at T_{g2} .

T_{g2} would be increased with increasing LPA concentration [Table 3(b)], indicating a higher crosslinking density in the minor co-continuous or LPA-dispersed phase. It is inferred that the molar ratio of styrene consumed to polyester C=C bonds reacted (MR) would be less deviated from (greater than) MR 2/1 in the minor co-continuous or dispersed phase of styrene-crosslinked polyester at a higher LPA concentration [opposite to that predicted in Table 1(a) and (c)]. This is due to the phase separation progressing to a lesser extent prior to gelation during the cure under a higher LPA concentration, where the higher viscosity of ST/UP/LPA system with a higher LPA concentration would lead to a slower rate of global phase separation. Concomitantly, the molar ratio in the major continuous phase of styrene-crosslinked polyester would also be less deviated from (smaller than) MR 2/1 at a higher LPA concentration (opposite to that predicted in Table 1). Hence, the crosslinking density in the major continuous phase of styrene-crosslinked polyester would be increased with increasing LPA concentration. The lowering of T_{g1} with increasing LPA concentration (Figure 9b) could then result from the increasing plasticization effect of LPA on the major continuous phase of styrene-crosslinked polyester outweighing the enhanced crosslinking density effect in that phase.

CONCLUSIONS

The effects of four LPAs including PVAc, PMMA, PU, and PS, and initial molar ratio of styrene to polyester C=C bonds (MR) on the mechanical properties and glass transition temperatures for styrene-crosslinked low-profile polyester matrices have been investigated by an integrated approach of static phase characteristics–cured sample morphology–reaction conversion–property measurements.

Table 3 Glass transition temperatures of cured UP resins based on $\tan \delta$ by DMA: (a) effects of molar ratios of styrene to polyester C=C bonds (MR) and (b) effects of LPA types and concentrations at MR 2/1

(a)	Molar ratio (MR)		1/1		2/1		3/1		6/1	
			T_{g1}^a	T_{g2}^b	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}
	Neat UP		161.4	—	180.0	—	153.8	—	143.9	—
	10% PVAc		160.2	—	178.4	75.0	160.7	77.6	124.1	—
	10% PMMA		164.6	—	178.2	—	175.3	—	149.1	—

(b)	Neat LPA		Neat UP resins		5% LPA		10% LPA		15% LPA	
	LPA	T_g	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}
	PVAc	27	180.0	—	179.3	72.4	178.4	75.0	177.9	77.6
	PMMA	105	180.0	—	179.9	113.2	178.2	118.1	176.7	125.0
	PS	100	180.0	—	178.4	132.1	175.8	135.1	174.3	139.5
	PU	-45	180.0	—	178.9	—	174.3	-37.0	164.5	—

^a T_{g1} is the glass transition temperature for the major continuous phase of styrene-crosslinked polyester.

^b T_{g2} is the glass transition temperature for the co-continuous or LPA-dispersed phase of styrene-crosslinked polyester.

The mechanical properties would generally depend not only on cured sample morphology but also on the volume fraction and the molar ratio of styrene consumed to polyester C=C bonds reacted (MR) in the major continuous phase of styrene-crosslinked polyester. These controlling factors could generally be judged by the static phase characteristics of styrene/UP/LPA ternary systems at 25°C prior to cure. The cured sample morphology could affect the interfacial adhesion and the volume fraction of microvoids generated during the cure, while the MR in the major continuous phase would determine the average crosslink length of styrene, tightness of network, degree of crosslinking, and crosslinking density in that phase, which, together with the volume fraction of major continuous phase, would generally dominate the mechanical properties of the entire sample based on the Takayanagi mechanical models and control T_g in that phase.

In general, there would be an optimal initial molar ratio of styrene to polyester C=C bonds at MR 2/1, either below or above which would cause inferior mechanical properties for the entire sample [except Young's modulus, and fracture properties (for PMMA system)] and lower T_g in the major continuous phase due to a decrease of crosslinking density. Also, at a fixed initial MR of 2/1, both the mechanical properties and T_g in the major continuous phase would be lower with increasing LPA concentration for the cured samples (except impact properties, tensile strains, and fracture properties for PU and PVAc systems). The former could be mainly due to a reduction of volume fraction and a decline in network tightness in the major continuous phase, while the latter due to an enhanced plasticization effect of LPA on the major continuous phase.

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