

Volume shrinkage characteristics in the cure of low-shrink unsaturated polyester resins

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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), on volume shrinkage in the cure of unsaturated polyester (UP) resins at 110°C were investigated by the linear shrinkage method, density measurements, and dilatometry. Experimental results showed that, for the finally cured samples, the fractional volume shrinkage would generally decrease linearly with increasing LPA concentration. Also, the effectiveness of volume shrinkage control was the best for PVAc, followed by PMMA and PS, while the shrinkage control behavior of PU depends on its concentration. Based on an integrated approach of measurements for volume change–microvoid formation–morphology–static phase characteristics for styrene/UP/LPA systems at 25°C, the mechanism of shrinkage control in UP resins containing LPA during cure and factors which affect overall volume change after cure have been explored.

(Keywords: low-profile additives; volume shrinkage; unsaturated polyester resins)

INTRODUCTION

In the cure of unsaturated polyester (UP) resins, about 7% of volume shrinkage would result, leading to such problems as a surface distortion or fiber pattern appearance in moulded parts, inability to mould to close tolerances, warpage of moulded parts, internal cracks and voids, etc.¹. To overcome these problems, for the past 25 years, low-profile additives (LPA), which are usually specific thermoplastic polymers, have been widely used in SMC (sheet moulding compound) and BMC (bulk moulding compound) formulations, resulting in a low-shrinkage or even a zero-shrinkage moulding compound.

Among the extensive studies^{1–15} on the mechanism of volume shrinkage compensation caused by low-profile additives, it is now generally agreed that during reaction the LPA and crosslinked UP phases must phase separate first. Subsequent microvoid and/or microcrack formation at the interface between the LPA and crosslinked UP phases as well as inside the LPA phase due to the microstress cracking that is initiated at the interface between LPA and crosslinked UP phases could then lead to volume shrinkage compensation. However, the LPA mechanism of volume shrinkage control has not been fully understood, and interpretations of LPA action from different standpoints have been proposed^{1,6,11,13–15}.

Many researchers have measured volume shrinkage in the cure of UP resins containing LPA by a linear shrinkage method^{6,10,11,15,16}, density measurements¹¹, dilatometry^{1,9,10,12,14,19}, or a moulding simulator²⁰, where the former two methods could only provide volume change information for the finally cured samples,

while the latter two techniques would be capable of monitoring the volume change over the entire cure process. The effects of LPA concentration^{10,11,14,20}, LPA types^{6,9,10,16,17}, LPA molecular weights^{7,8,12}, UP resin structure^{6,10,17}, processing conditions^{10,12,14–17,20}, and thickening of UP resins^{10,14,15,21} on polymerization shrinkage have been investigated. However, experimental results concerning the effects of LPA concentration and LPA molecular weights are quite controversial, where the effectiveness of shrinkage control performance in the cure of UP resins has been reported to be independent of¹¹, decreasing with¹⁴, or increasing with^{10,20} PVAc concentration, while it has been found to be increased with PU molecular weights^{7,8} or decreased with PVAc molecular weights¹². Also, in-depth analysis for the shrinkage control action of LPA over the whole cure process has remained less than satisfactory.

The objective of this study is to investigate the effects of four LPAs, namely poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), thermoplastic polyurethane (PU), and polystyrene (PS), and their concentrations on volume shrinkage after the cure of UP resins at 110°C by linear shrinkage methods and density measurements. Also, a custom-built capillary-type dilatometer, which allowed for off-line measurements of monomer conversion and rheological change for the partially cured samples, has been employed to monitor the volume change during the entire cure. Based on integrated experimental results from volume change, microvoid formation, morphology, and static phase characteristics for ternary styrene/UP/LPA systems at 25°C, the mechanism of action of LPA in volume shrinkage control and factors which affect the overall volume change after the cure are discussed.

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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^{-1} . On average, the calculated number of C=C bonds in each polyester molecule was 8.13 (i.e., 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 $150\,000\text{ g mol}^{-1}$, respectively, by vapour pressure osmometry (v.p.o.). 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 2:1. The reaction was initiated by 1% by weight of *t*-butyl perbenzoate (TBPB) at 110°C . 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. The phase separation time was recorded and the mixture of each layer was separated and weighed. Composition of samples from upper and bottom layers could then be determined by FTi.r. (Digilab, FTS-40)^{9,22}. 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, where the PU system formed a homogeneous solution after a phase equilibrium.

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.

Differential scanning calorimetry (d.s.c.). The reaction kinetics were measured by a Dupont 9000 Differential Scanning Calorimeter with a 910 pressurized d.s.c. cell at atmospheric pressure. All the reactions were conducted in hermetically sealed aluminium sample pans with sample weights ranging from 6 to 10 mg. Isothermal reaction rate vs time profiles were measured at 110°C . The method of approach for obtaining the rate of overall reaction and total conversion at a given time during the entire reaction has been described in a previous paper²³.

Morphology. In the morphological study, the cured sample in the d.s.c. cell at 110°C was first broken into several pieces and extracted with dichloromethane for one day to remove all soluble materials. The gel fraction (undissolved sample) was placed on filter paper and dried at room temperature for one day. The dry sample was then gold-coated for morphological assessment. 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 1000–5000 \times .

The morphology of the sample during cure was also observed by means of an optical microscope (OM). One drop of sample (about 0.8 mg) was placed between two microscope cover glasses, which was then inserted into a hot stage (Mettler, FP82HT). The cured sample at 110°C was chilled in liquid nitrogen, and was subsequently observed at room temperature under an optical microscope using transmitted light at magnifications of 100–400 \times .

The quantity of microcracking in the morphology sample under OM was measured by means of an image analyzer^{10,24}. Since the samples were of uniform thickness, the fraction of the image area which was black (due to light scattering by the microcracks) would be proportional to the volume of the microcracks in the sample. Luminance values of less than 31 were taken to indicate microcracking by Mitani *et al.*¹⁰, where the scale of luminance ranged from 0 (pure black) to 255 (pure white). In this work, the image of the OM photomicrograph was first input to a computer using a scanner (Epson, GT-6500), and the lower one-third of the luminance scale obtained for each photomicrograph was employed to calculate the relative volume fraction of microcracks. It should be noted that¹⁰ the absolute quantity of microcracking cannot be measured by the image analyzer system since overlapping cracks cannot be distinguished and cracks normal to the incident light do not scatter light. Other methods for estimating the relative microcrack fraction include the BET surface area measurement technique demonstrated by Kinkelaar *et al.*¹⁵.

Volume change. For linear shrinkage measurement of cured UP resins containing LPA, the ASTM D2566-86 standard was followed, but with smaller specimen dimensions, where a stainless steel semicylindrical mould with flat ends having a length of 150 mm and an internal radius of 7.5 mm was used. First, 20 g of sample solution was degassed in a vacuum oven at 25°C for 1 h. The sample was then weighed, and the amount of styrene loss in the evacuation operation was compensated for by adding the same amount of pre-degassed styrene. The sample solution was poured into the mould slowly and sealed, which was then placed into a thermostated silicone oil bath at 110°C and cured for 1 h. The cured specimen was removed from the mould, cooled to room temperature in air, and the length difference between the mould and cured sample measured. The linear shrinkage data, $\Delta l/l_0$, can be converted to the volume shrinkage, $\Delta V/V_0$, by the following equation:

$$\Delta V/V_0 = (1 + \Delta l/l_0)^3 - 1 \quad (1)$$

where l is the length, V is the volume, $\Delta l = l - l_0$, $\Delta V = V - V_0$, and the subscript '0' represents the mould.

For comparison, density measurements were also employed for obtaining volume shrinkage data. About

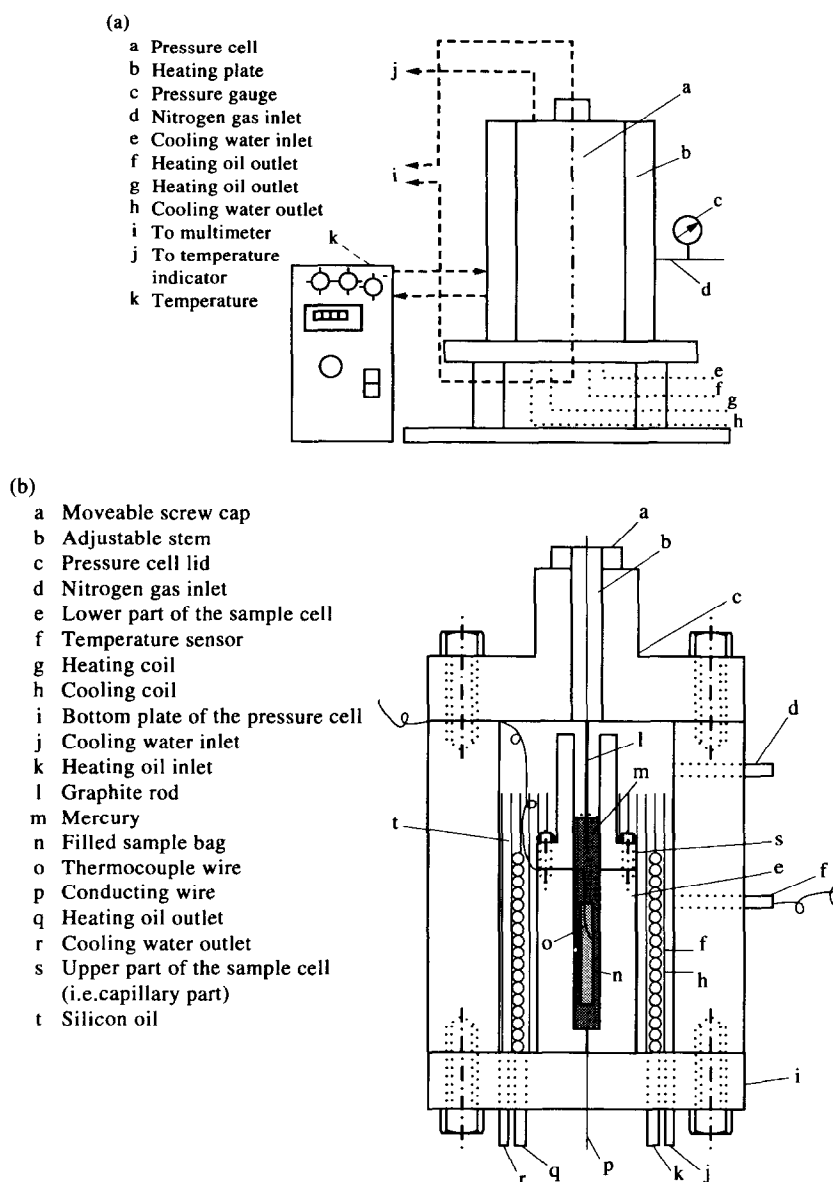


Figure 1 Schematic of the self-made capillary type of dilatometer for thermoset cure: (a) set-up, and (b) sample cell design

10 g of degassed sample solution was placed into a 10 ml density bottle, and its density at 25°C prior to reaction, ρ_1 , was measured. Another 10 g of degassed sample solution was sealed in a 50 × 6 mm thin aluminium disc mould, which was then placed into a thermostated silicon oil bath at 110°C and cured for 1 h. The density of the cured sample at 25°C, ρ_2 , was determined by an immersion method using distilled water. The volume shrinkage can then be calculated by $(1/\rho_2 - 1/\rho_1)/(1/\rho_1)$.

Dilatometry. In order to monitor volume change of UP resins throughout the cure process, a custom-built capillary dilatometer was employed, as shown schematically in Figure 1. The apparatus includes three parts, namely, systems for temperature control and measurement, pressurization, and volume change measurements (Figure 1a). The dilatometer is essentially composed of a stainless steel sample cell, which is placed in a pressure cell (and screwed on its bottom) partially filled with silicon oil and equipped with heating and cooling coils

(Figure 1b). The lower part is the container for the resin sample and confining fluid (mercury in this case), while the upper part acts as a capillary for measuring internal volume changes. During the dilatometric experiments, the sample cell may be readily detached from the pressure cell, quickly chilled in liquid nitrogen to stop further reaction, and off-line measurements of monomer conversion and rheological change can be conducted for partially cured samples. In this work, all dilatometric studies have been carried out at 0.1 MPa (1 atm).

Prior to the experiment, 1 g of sample solution, with 0.1 wt% benzoquinone added as an inhibitor to delay the reaction, was placed in a plastic bag made of high-density polyethylene (30 mm × 35 mm in size, 0.1 mm in thickness, melting point, $T_m = 128.7^\circ\text{C}$ as measured by d.s.c. at $2.5^\circ\text{C min}^{-1}$). After the sample had been degassed in a vacuum oven at 25°C for 1 h, an ultra-thin thermocouple wire (Omega TFCC-003, diameter $\phi = 0.0762$ mm) was inserted into the sample through the bag opening, which was then heat-sealed by a plastic bag sealer machine, in order for measurement of sample temperature during the

experiment. The filled sample bag, about 1 mm in overall thickness, was subsequently placed in a cavity (35 mm deep and with a 40 mm × 4 mm rectangular cross-section) located in the lower part of the sample cell. The upper part (i.e., capillary part, with diameter $\phi = 4$ mm) and the lower part of the sample cell were then bolted together and sealed with a gasket. Enough mercury was introduced into the sample cell to surround the sample and reach an appropriate position (see below) in the upper sample cell. After the sample cell had been degassed in a vacuum oven for 25 min, it was transferred back to the pressure cell, and a graphite rod (diameter $\phi = 2$ mm) was inserted through the center of pressure cell lid, via the capillary of the sample cell, and into the mercury. The immersion length should be such that the lengths of graphite rod in the capillary both above and below the mercury level (i.e., Δh_1 and Δh_2) are enough to accommodate volume expansion and contraction during the experiments, respectively. In our case, $\Delta h_1 = 4.7$ cm and $\Delta h_2 = 1.5$ cm were chosen.

During the experiment, variations in the resistance caused by changes in the mercury level as a function of time were measured by a digital multimeter (HP 3478A) and recorded by an on-line computer data acquisition system. Since the minimum scale of resistance for the digital multimeter used was 0.01 Ω , for a sample volume of 1 cm³, an annular area in the capillary during the measurement = 0.03 π cm², and a resistance of the graphite rod = 1 Ω cm⁻¹, the relative volume change measurement could be accurate to about 0.1% (i.e., (0.01 Ω / (1 Ω /cm) × 0.03 π cm²) / (1 cm³) × 100% = 0.094%).

RESULTS AND DISCUSSION

Effects of LPA types and concentrations on volume shrinkage after the cure

Figure 2 shows the effect of LPA (PVAc, PMMA, PS, and PU) concentration on fractional volume shrinkage measured by the linear shrinkage method. For all four LPAs, as LPA concentration increased, the fractional volume shrinkage decreased. Except for the PU system, linear relationships were also obtained for the other three systems. In general, at a fixed LPA content, the effectiveness of volume shrinkage control would be ranked as PU > PVAc > PMMA > PS. However, as the content of LPA exceeded 10 wt%, PU was less effective in volume shrinkage control than PVAc and PMMA.

For the UP resins containing no LPA, PVAc, and PMMA, the volume shrinkage of the finally cured sample obtained by density measurements and dilatometry also showed very good agreement with those obtained by the linear shrinkage method (see Table 1). For neat UP resin at a mole ratio of 2:1, cured at 110°C, the fractional volume shrinkage would be about 7.2–7.4%. Adding 10 wt% LPA (PVAc or PMMA) reduced the fractional volume shrinkage to about 2.8–4.0%. The extrapolated LPA concentration to give zero volume shrinkage cured at 110°C was about 15–20 wt%.

Effect of microvoid formation on volume shrinkage control

Pattison *et al.*^{2,4} have proposed that as the cross-linking of LPA-containing UP resins proceeds, strain due to polymerization shrinkage, develops in the system, particularly at the interface of LPA phase and

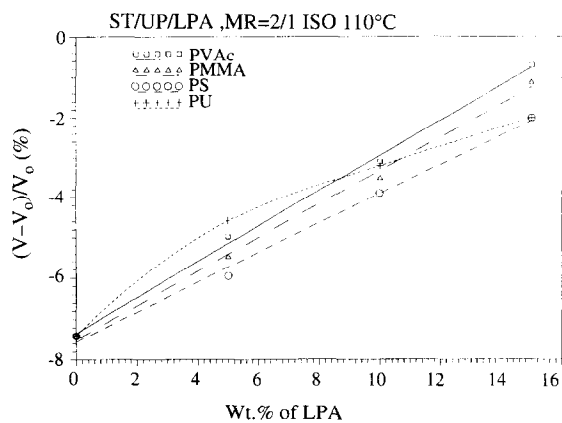


Figure 2 Effects of LPA type and concentration on the fractional volume change of UP resins after the cure at 110°C

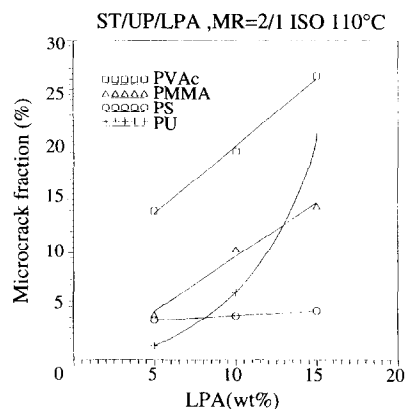


Figure 3 Relationships between volume fraction of microcrack and LPA type and concentration

Table 1 Volume shrinkage data for UP resins at a mole ratio of 2:1 with and without LPA (PVAc or PMMA) after isothermal cure at 110°C

wt% of LPA	ST/UP		ST/UP/PVAc		ST/UP/PMMA		
	0	5	10	15	5	10	15
ρ_1 (g cm ⁻³)	1.1059	1.1090	1.1098	1.1114	1.1148	1.1159	1.1170
ρ_2 (g cm ⁻³)	1.1938	1.1622	1.1470	1.1305	1.1826	1.1581	1.1388
$\Delta V/V_0$ (%) ^a	-7.36	-4.58	-3.24	-1.69	-5.73	-3.64	-1.91
$\Delta V/V_0$ (%) ^b	-7.41	-4.98	-3.11	-0.71	-5.47	-3.51	-1.11
$\Delta V/V_0$ (%) ^c	-7.21		-2.83	-0.86		-3.98	

^a By density methods

^b By linear shrinkage measurements (i.e., by equation (1))

^c By dilatometry

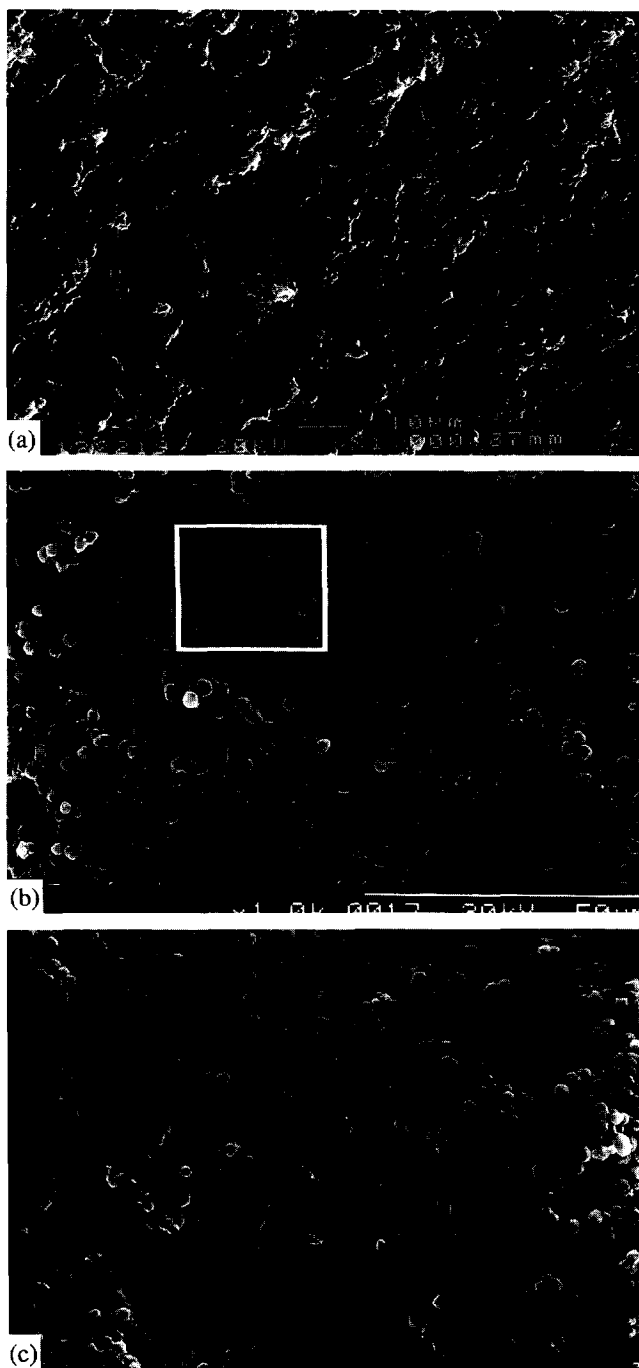


Figure 4 SEM micrographs of fractured surfaces for UP resins (mole ratio = 2:1) containing (a) 5% PVAc, (b) 10% PVAc, and (c) 15% PVAc, respectively, after the cure at 110°C and with final conversions of $\alpha = 74.7\%$, 70.4%, and 65.2%, respectively, as measured by d.s.c.; micrographs obtained at 1000 \times

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.

Figure 3 shows the relative microcrack volume fraction at varied concentrations of LPA. As the LPA concentration increased, the volume fraction of microcrack also increased. Again, except for the PU system, linear relationships were obtained. Also, at a fixed LPA content, the volume fraction of microcrack was the highest for the PVAc system, followed by PMMA and PS

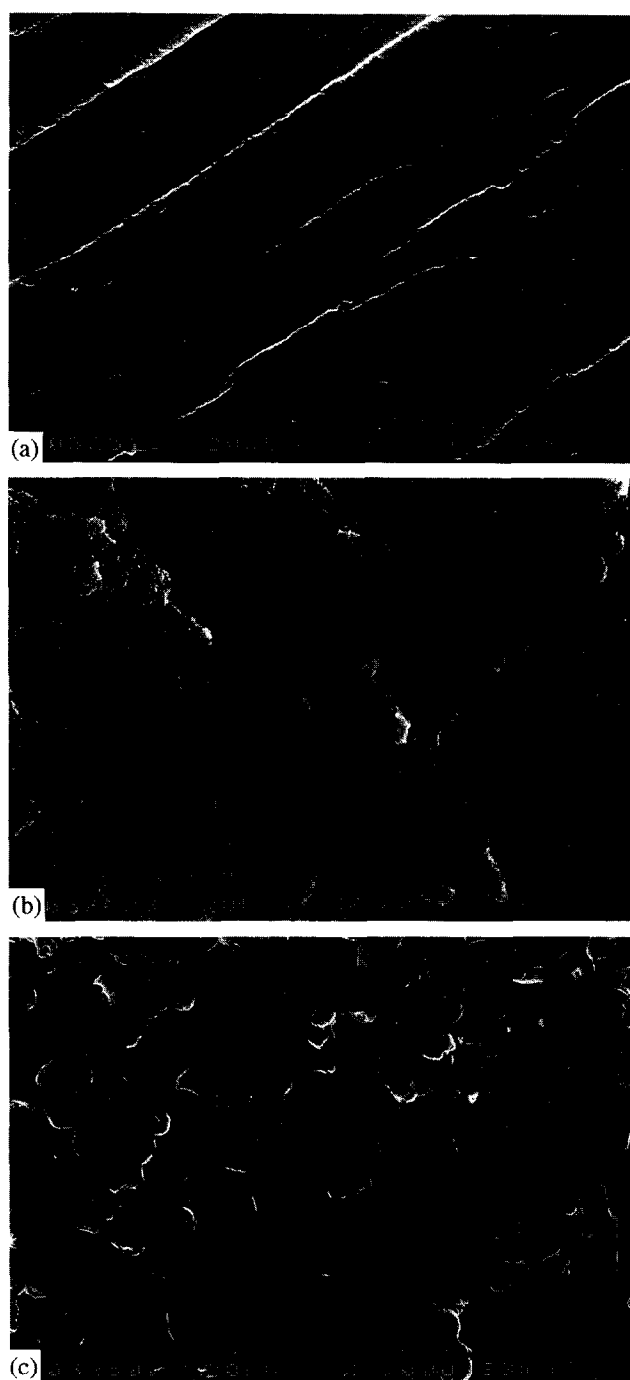


Figure 5 SEM micrographs of fractured surfaces for UP resins (mole ratio = 2:1) containing (a) 5% PU, (b) 10% PU, and (c) 15% PU, respectively, after the cure at 110°C and with final conversions of $\alpha = 76.0\%$, 74.9%, and 73.4%, respectively, as measured by d.s.c.; micrographs obtained at 1000 \times

systems. Experimental results in Figures 2 and 3 generally support the volume shrinkage mechanism of strain relief through stress cracking, and that greater microcrack formation would give less volume shrinkage.

Effect of sample morphology on volume shrinkage control

Adding PVAc or PU to 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 after the cure (see Figures 4 and 5). The LPA phase surrounding the microgel particles was washed off in the extraction procedure. For PU

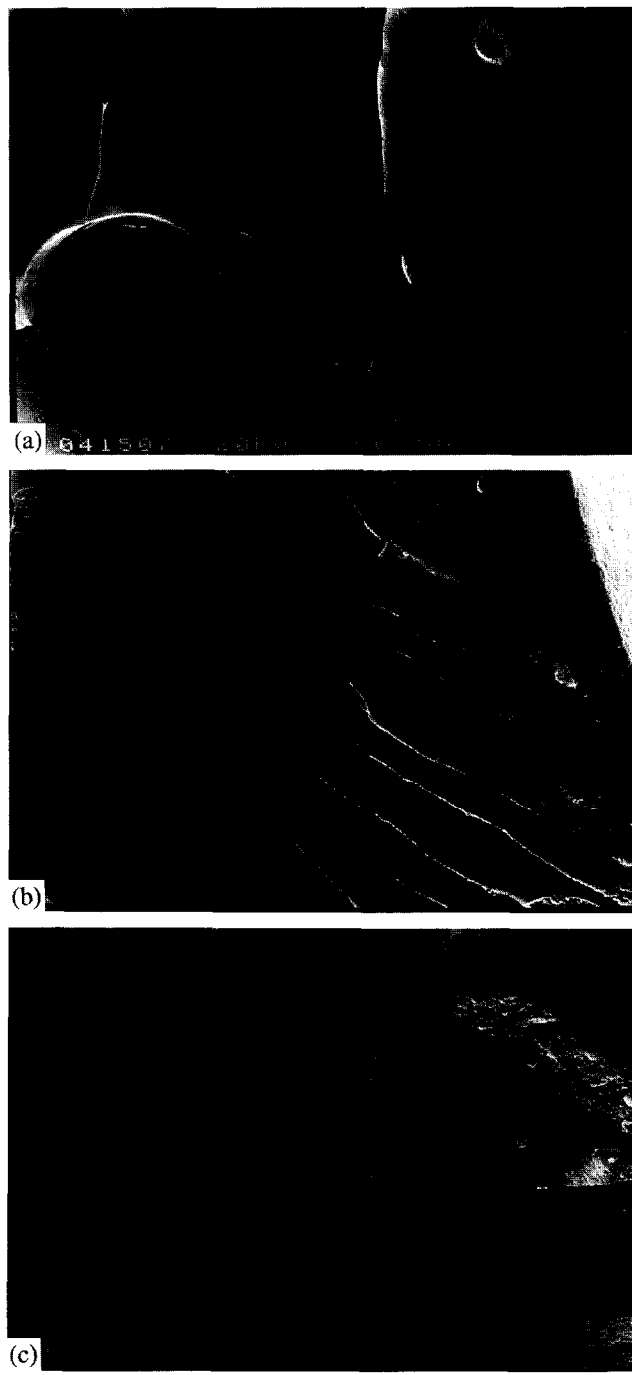
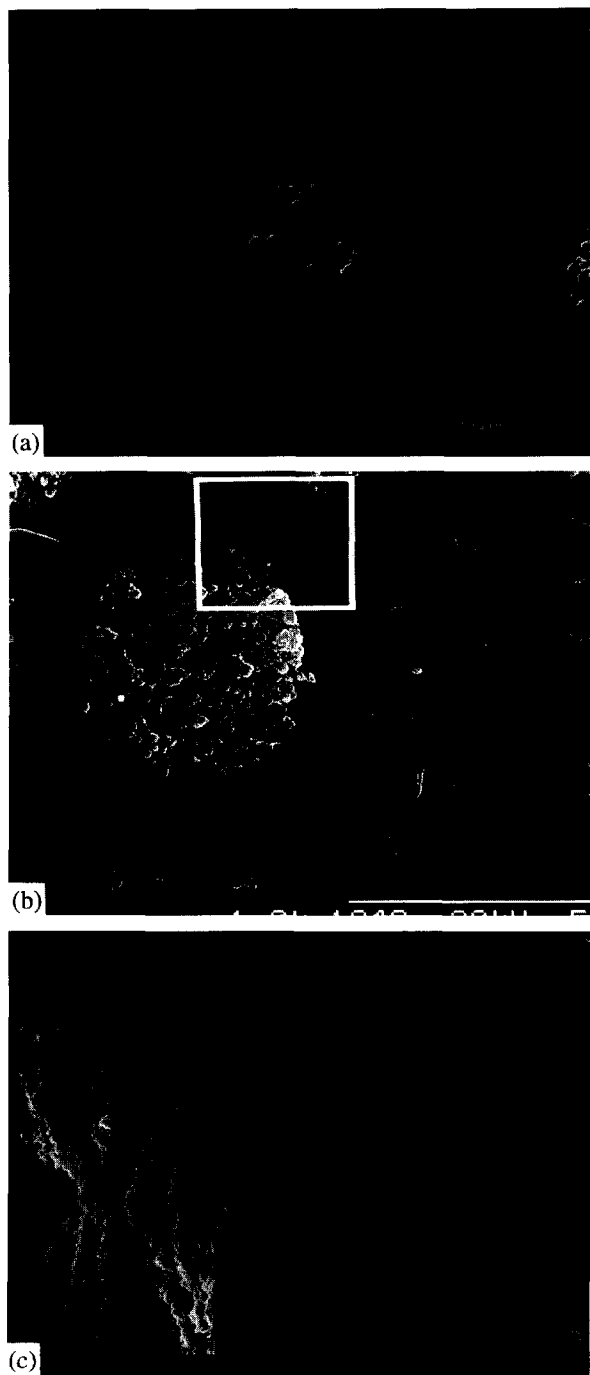


Figure 6 SEM micrographs of fractured surfaces for UP resins (mole ratio = 2:1) containing (a) 5% PMMA, (b) 10% PMMA, and (c) 15% PMMA, respectively, after the cure at 110°C and with final conversions of $\alpha = 75.6\%$, 73.4%, and 70.3%, respectively, as measured by d.s.c.; micrographs obtained at 1000 \times

Figure 7 SEM micrographs of fractured surfaces for UP resins (mole ratio = 2:1) containing (a) 5% PS, (b) 10% PS, and (c) 15% PS, respectively, after the cure at 110°C and with final conversions of $\alpha = 74.7\%$, 72.8%, and 70.2%, respectively, as measured by d.s.c.; micrographs obtained at 1000 \times

systems, the microdomain of the crosslinked UP phase appeared much smaller than that of PVAc systems at 5% and 10% LPA content ($< 0.1 \mu\text{m}$ vs $1 \mu\text{m}$), while it was larger than that of the PVAc system at 15% LPA content ($5 \mu\text{m}$ vs $1\text{--}2 \mu\text{m}$). 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 arise (see *Figures 6* and *7*). In the LPA dispersed phase, the number of microgel particles was much larger for the PMMA-containing sample than the PS-containing sample.

Since microvoids and microcracks essentially exist in the phase region with a co-continuous globule microstructure, where the interface generated between the LPA phase and the crosslinked UP phase makes strain relief through stress cracking possible 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 PU and PVAc systems than for the PMMA and PS systems. Hence, PU and PVAc could generally provide better volume shrinkage control than PMMA and PS.

Microgel formation is the main feature in the cure of UP resins²⁵⁻²⁷, where styrene-unsaturated polyester copolymerization is involved. Huang and Su²³ have pointed out that adding LPA to the neat UP resin reaction system could enable microgel particles to be clearly identified throughout the reaction. This is because a layer of LPA could cover the surface of microgel particles when the microgel particle phase separates from the matrix of unreacted resins containing LPA. The LPA could then be used as a segregating agent, which could cause much less merging of microgel particles and thus retain the identity of the individual microgel particle.

As LPA content increased, the interfacial area between LPA phase and the crosslinked UP phase would be enhanced due to better segregating effects of LPA on microgel particles (see *Figures 4-7*). As a result, the volume fraction of microvoids and microcracks in the cured sample could be elevated, and the sample would display lower fractional volume shrinkage after cure.

Volume change during curing by dilatometry

For the five reacting systems of styrene and UP resins containing no LPA, 10% PVAc, 15% PVAc, and 10% PMMA, respectively, the three-stage volume changes due to thermal expansion of uncured resins in the heating step, ΔV_1 (25–110°C), polymerization shrinkage during cure, ΔV_2 (essentially at 110°C, but a peak temperature of about 120°C was reached during the cure for the four UP reacting systems) and thermal contraction of cured resins in the cooling step, ΔV_3 (110–25°C), were measured. *Figure 8a* shows the fractional volume change of the system for UP resins containing 10% PVAc (based on the sample volume, $V_{r,0}$, at 25°C) during the entire reactive scan of the experiment. After the reactive scan, the experiment was conducted once again on the cured system using the same temperature program to obtain the baseline. The baseline shown in *Figure 8a* had been shifted upward so that the starting points for both curves of the reactive scan and the baseline coincided with each other.

The volume change due to the reactive scan in *Figure 8a* was attributed to the resin sample, plastic sample bag, mercury, and dilatometer, while that due to the unshifted baseline was caused by the cured resin sample, plastic bag, mercury, and dilatometer. The upward shift of volume change for the baseline would be equal to the difference in volume between the uncured resin and the cured resin at 25°C. By subtracting the shifted baseline from the reactive scan profile, the volume changes resulting from sample bag, mercury, and dilatometer were cancelled out, and the following uncorrected fractional volume change of resin ($\Delta V_r/V_{r,0}$)_{exp.} was obtained:

$$\begin{aligned} (\Delta V_r/V_{r,0})_{\text{exp.}} &= (\Delta V_r/V_{r,0})_{\text{exact}} - [\Delta V_r^{\text{cured}} \\ &\quad + (V_{r,0} - V_{r,0}^{\text{cured}})]/V_{r,0} \\ &= (\Delta V_r/V_{r,0})_{\text{exact}} - \int_{25^\circ\text{C}}^T \beta_r^{\text{cured}} \\ &\quad dT/V_{r,0} \end{aligned} \quad (2)$$

where $\Delta V_r = V_r - V_{r,0}$, $\Delta V_r^{\text{cured}} = V_r^{\text{cured}} - V_{r,0}$, V_r and V_r^{cured} are the volumes of uncured and cured resin, respectively, at a sample temperature T during the

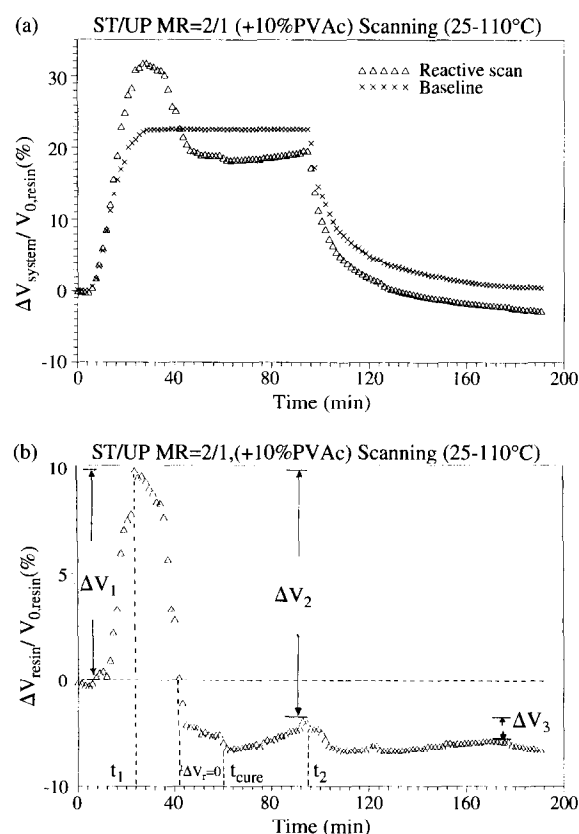


Figure 8 Fractional volume change profiles for UP resins containing 10% PVAc under the three stages of heating (25–110°C), curing (essentially at 110°C), and cooling (110–25°C) as specifically designated in *Table 2*. (a) Original reactive scan and baseline runs for the system, and (b) net fractional volume change of the resin

experiments, $V_{r,0}$ and $V_{r,0}^{\text{cured}}$ are the volumes of uncured and cured resin at 25°C, respectively, $(\Delta V_r/V_{r,0})_{\text{exact}}$ is the exact fractional volume change of resin, and β_r^{cured} is the volume coefficient of thermal expansion for the cured resin. Equation (2) reveals that the experimentally obtained $(\Delta V_r/V_{r,0})_{\text{exp.}}$ at a sample temperature T would be lower than the exact value by a fractional volume change of cured resin from 25°C to T (based on the volume of uncured resin at 25°C). *Figure 8b* shows the $(\Delta V_r/V_{r,0})_{\text{exp.}}$ profile vs time by the procedure described above, where at the initial time and final time, $T = 25^\circ\text{C}$ and $(\Delta V_r/V_{r,0})_{\text{exp.}} = (\Delta V_r/V_{r,0})_{\text{exact}}$.

As designated in *Figure 8*, t_1 is the end time of thermal expansion corresponding to the maximum point of the original reactive scan profile. It is also the approximate onset time for polymerization shrinkage. $t_{\Delta V_r=0}$ is the onset time of negative volume change (i.e., $\Delta V_r < 0$) approximately corresponding to the intersection of reactive scan and baseline. (The exact $t_{\Delta V_r=0}$ should be obtained at $(\Delta V_r/V_{r,0})_{\text{exact}} = 0$ and the corresponding $(\Delta V_r/V_{r,0})_{\text{exp.}}$ value in equation (2). t_{cure} is the end time of cure conversion, which could not be determined directly by the profile of volume change vs time. It was then estimated with the aid of the d.s.c. rate profile for the UP resins carried out isothermally at 110°C. Suppose the induction time (or inhibition time) and the end time of cure for the resin sample obtained from d.s.c. measurements are t_z^{D} and $t_{\text{cure}}^{\text{D}}$, t_{cure} may be estimated as $t_{\text{cure}}^{\text{D}} - t_z^{\text{D}} + t_1$. t_2 is the end of available time for polymerization shrinkage or the onset time of cooling contraction.

Table 2 Characteristic times and volume change information for five reacting systems during the heating, cure at 110°C, and cooling stages in the dilatometer

Reaction system (wt% of LPA)	Styrene 0	ST/UP (mole ratio = 2:1)		ST/UP/PVAc (mole ratio = 2:1)		ST/UP/PMMA (mole ratio = 2:1)
		0	10	15	10	
t_1 (min)	55	21	24	28	28	
$t_{\Delta V_i=0}$ (min)	66	32	42	102	41	
t_{cure} (min)		58	60	64	64	
t_2 (min)	305	95	95	95	100	
ΔV_1 (%)	16.7 (19.13) ^a	10.22 (11.16)	9.76 (10.70)	6.69 (7.63)	5.6 (6.54)	
ΔV_2 (%)	-30.93	-17.36	-12.16	-6.47	-9.6	
ΔV_3 (%)	0.55 (-1.88) ^b	-0.07 (-1.01)	-0.43 (-1.37)	-1.08 (-2.02)	0.02 (-0.92)	
ΔV_{total} (%) ^c	-14.11 ^d	-7.21	2.83	0.86	-3.98	
α_{cure} (%) ^e	97	77.3	70.4	65.2	73.4	
$\Delta V_2/\alpha_{\text{cure}}$	0.2887	0.2537	0.1666	0.1052	0.1373	
$\Delta V_{\text{total}}/\alpha_{\text{cure}}$	0.1454	0.0933	0.0402	0.0132	0.0542	

^a The values in parentheses are the corrected values by using equation (2). For the five reacting systems of styrene and UP resins containing no LPA, 10% PVAc, 15% PVAc, and 10% PMMA, respectively, $\beta_r^{\text{cured}} = 2.85 \times 10^{-4}$, 1.11×10^{-4} , 1.58×10^{-4} , 1.81×10^{-4} , and $1.21 \times 10^{-4} \text{ °C}^{-1}$, respectively^{28,29} (assuming linear additivity for β value). Adding 2.43% (styrene system), 0.94% (neat UP system), 1.36% (UP system with 10% PVAc), 1.56% (UP system with 15% PVAc) or 1.01% (UP system with 10% PMMA) to the exp. value could give the corrected value

^b Subtracting the same value as in *c* from the exp. value could give the corrected value

^c $\Delta V_{\text{total}} = \Delta V_1 + \Delta V_2 + \Delta V_3$

^d The calculated value was -14.21% based on the literature data³⁰ of $\rho_{\text{st}} = 0.909$ and $\rho_{\text{ps}} = 1.065 \text{ g cm}^{-3}$ and the final styrene conversion of 97%. A linear relationship between fractional volume contraction and monomer conversion was also assumed

^e α_{cure} is the final monomer conversion cured at 110°C as measured by d.s.c., and $\Delta V_2/\alpha_{\text{cure}}$ and $\Delta V_{\text{total}}/\alpha_{\text{cure}}$ are the average variations in fractional volume change due to 1% monomer conversion measured at 110°C and 25°C, respectively

Table 3 The viscosity and reaction conversions for the partially cured samples for UP resins (mole ratio = 2:1) containing 10% PVAc cured at 110°C in the dilatometer. The measurements were carried out at room temperature

Point	1	2	3	4	5	Gel point ^a
t (min)	0	24	29	39	44	32
Viscosity, η (Ns m ⁻²)	5.03	19.5	134	solid	solid	∞
η_0/η	1	0.2579	0.0375			0
D.s.c. conversion ^b : α_s	0	0.024	0.088	0.37	0.619	0.116

^a The last column lists the gel time and gel conversion measured by d.s.c., which were obtained by plotting the viscosity ratio, η_0/η , vs time, and d.s.c. conversion, respectively, followed by extrapolating the corresponding curve to zero viscosity ratio

^b α_s is the conversion of total C=C bonds measured directly by d.s.c. for the partially cured sample, the method of which has been discussed elsewhere³¹

For the five systems studied, the characteristic times and variations in fractional volume changes due to thermal expansion of uncured resin, polymerization shrinkage and cooling contraction of cured resin, i.e., ΔV_1 (from 0 to t_1), ΔV_2 (from t_1 to t_2), and ΔV_3 (from t_2 to the end), respectively, are displayed in Table 2. It is seen that among the three stages of fractional volume change, the largest variation generally lies in polymerization shrinkage (i.e., ΔV_2). For the PVAc-containing samples, as PVAc concentration increases, ΔV_1 and ΔV_2 decrease (i.e., less thermal expansion and less cure shrinkage), while ΔV_3 increases (i.e., more cooling contraction). Since the resulting change in ΔV_2 is greater than that of ΔV_1 and ΔV_3 , an effective LPA for volume shrinkage control should be one which essentially leads

to a significant reduction in ΔV_2 , rather than favourable changes in ΔV_1 and ΔV_3 .

Interrelationships between volume change, monomer conversion, and rheological change

For UP resins containing 10% PVAc, the partially cured samples during the volume change measurement by dilatometry at 110°C were also analysed for viscosity and monomer conversion at several preset times. (The time taken from the detachment of sample cell from the pressure cell to quenching the sample cell in the liquid nitrogen was less than 10 s.) The approach used was the same as that reported in a previous paper³¹, and the data are listed in Table 3. Gelation was found to occur at a monomer conversion of 11.6%.

Figure 9 shows the integrated fractional volume change, viscosity change, and monomer conversion vs time in the cure UP resins containing 10% PVAc at 110°C. At the maximum point of volume change profile ($t = 24$ min), a monomer conversion of 2.4% was attained, which indicated that before completion of the heating stage to 110°C, reaction had already started. At $t = 42$ min, where the ongoing volume change was zero (i.e., $t_{\Delta V_i=0}$, the time when the ongoing polymerization shrinkage totally counterbalanced the thermal expansion), the reaction had progressed to a great extent, and reached a monomer conversion of 52.9%, which far exceeded the gel conversion at 11.6%. It should be noted that it was around 50% monomer conversion (where the d.s.c. rate profile descended shortly after the maximum point and the cured sample became rigid enough) that microvoids and microcracks developed markedly in the system³².

Figure 10 shows that in the second stage of volume

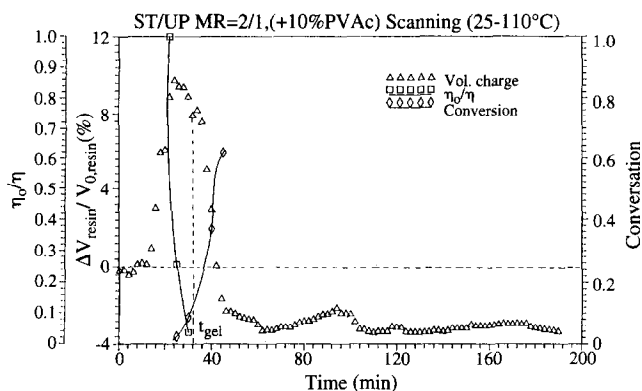


Figure 9 Interrelationships between volume change, viscosity change and monomer conversion for UP resins containing 10% PVAc during the cure at 110°C as conducted in the dilatometer

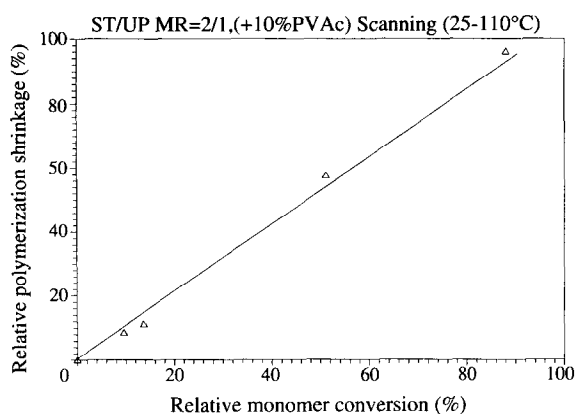


Figure 10 Relationship between the relative polymerization shrinkage measured at 110°C and the relative monomer conversion progressed for UP resins with 10% PVAc in the second stage of volume change as shown in Figure 8

change, the relative polymerization shrinkage as a function of time (i.e., $(\Delta V_f/V_{r,0} - \Delta V_1)/\Delta V_2$ in Figure 8b) was approximately proportional to the relative monomer conversion progression (i.e., $(\alpha - \alpha_1)/(\alpha_f - \alpha_1)$, where $\alpha_1 = 2.4\%$, and $\alpha_f = 70.4\%$ (final conversion as measured by d.s.c.)). At the gel point, the relative monomer conversion was 13.6%, and the relative polymerization shrinkage reached 13.0%.

Intrinsic polymerization shrinkage vs microvoid formation

As shown in Table 2, the average variation in fractional volume change due to 1% monomer conversion either measured at 110°C (i.e., $\Delta V_2/\alpha_{\text{cure}}$) or measured at 25°C (i.e., $\Delta V_{\text{total}}/\alpha_{\text{cure}}$) is higher for the styrene homopolymerization system than for the styrene-UP copolymerization system at a mole ratio of 2:1 (0.2887 %/% vs 0.2537 %/% at 110°C and 0.1454 %/% vs 0.0933 %/% at 25°C). The final conversion also shows the same trend. Therefore, in the cure of UP at 110°C, a higher styrene content enhanced the intrinsic polymerization shrinkage (i.e., ΔV_2 corrected for any possible volume compensation by microcracks), especially when the molar ratio of styrene to polyester C=C bonds > 2, where the final conversion at 110°C greatly increased with styrene content²³.

As shown in Figures 2 and 3, for the PU system at 5%

LPA content, a lower volume fraction of microvoid could still lead to a lower fractional volume shrinkage after the cure as compared with the PVAc, PMMA and PS systems. This implies that the overall volume change after the cure could not be solely determined by the volume compensation for shrinkage due to a microvoid formation. The intrinsic polymerization shrinkage of the resin system is also important for determining the overall volume change.

For the PU system at 5% LPA content, the degree of phase separation during the cure was considerably less than that of the other systems, as evidenced by the much smaller size for the microdomain of the crosslinked UP phase (see Figure 5a). This could result from the better miscibility between PU and the uncured UP resins as well as the chemical reaction between the NCO end group of PU and OH and/or COOH end groups in UP molecules during the cure. The lower degree of phase separation for the PU system is advantageous for reducing the intrinsic polymerization shrinkage during the cure, since phase regions of very high styrene content resulting from extensive local phase separations seldom arise. This in turn could make up for the smaller volume fraction of microvoids generated during the cure. Moreover, the measured volume fraction of microvoids was smaller than it should have been for the system. This is because during the propagation of stress cracking through the weak LPA phase, the presence of rubbery PU ($T_g = -45^\circ\text{C}$ in this case) greatly induces the LPA phase to undergo plastic deformation, increasing the total work required to create the microcrack or microvoid. Thus, the microvoid generated during the cure would be both tiny in size⁸ ($< 0.1\ \mu\text{m}$) and small in number, which would not appreciably interfere in visible light transmission through the sample.

As shown in Figure 2, PU is a less effective LPA than PVAc and PMMA at 15% LPA content. This is associated with the large domain of microgel particles generated at a high concentration of PU addition (Figure 5) due to the extensive polycondensation between the end groups of PU and UP molecules. First of all, the UP molecules, through the linking of PU, would become much more entangled, and the mobility of polyester C=C bonds would thus be reduced considerably. Therefore, during the formation of large microgel particles and the subsequent intramicrogel crosslinking reactions, self-bonding of styrene in the copolymerization of styrene and polyester C=C bonds would thus be greatly facilitated, and would result in a longer crosslink length of styrene³³ between two adjacent polyester C=C bonds. The significant self-bonding of styrene could lead to excessive polymerization shrinkage. As the PU content is increased from 5% to 15%, the enhanced polymerization shrinkage effect would greatly counterbalance the increasing volume compensation effect due to more microvoid formation (Figure 3), leading to a less effective volume shrinkage control than that of PVAc and PMMA systems.

Interrelationships between static phase characteristics and volume shrinkage control

For the phase characteristics of the static ternary systems of styrene/UP/LPA prior to reaction at 25°C, the global phase separation time shown in Table 4 reveals that PS < PMMA < PVAc < PU. (The PU system

Table 4 Static phase characteristics of three styrene-UP-LPA systems prior to reaction at 25°C

System	ST/UP/PVAc			ST/UP/PMMA			ST/UP/PS		
	2:1			2:1			2:1		
Molar ratio (ST/UP C=C)									
LPA conc. (wt%)	5	10	15	5	10	15	5	10	15
Phase separation time (min)	∞	180	270	90	115	130	40	50	60
Upper layer (dispersed phase)									
Relative wt(%)		19.8	21.4	2.7	22.2	30.5	15.1	28.6	43.0
ST (wt%)		50.2	47.0	65.7	59.3	49.5	59.7	57.2	57.4
UP (wt%)		14.7	10.9	11.6	13.5	16.8	13.4	11.3	10.4
LPA (wt%)		35.1	42.1	22.7	27.2	33.7	26.9	31.5	32.2
Mole ratio (ST/UP C=C)		9.1	11.6	15.1	11.8	7.9	11.9	13.6	11.9
Bottom layer (continuous phase)									
Relative wt(%)		80.2	78.6	97.3	77.8	69.3	84.9	71.4	57.0
ST (wt%)		35.7	33.7	40.0	32.7	30.8	37.3	31.1	20.8
UP (wt%)		60.5	58.7	55.5	62.2	62.4	61.6	67.5	77.2
LPA (wt%)		3.8	7.6	4.5	5.1	6.8	1.1	1.4	2.0
Mole ratio (ST/UP C=C)		1.57	1.53	1.92	1.40	1.31	1.61	1.23	0.72

remained compatible after mechanical mixing.) Since the UP molecule with ester linkages along the chain was reasonably polar, the relative times of global phase separation for styrene/UP/LPA systems suggested that the decreasing order of polarity for the four LPAs is PU (relatively polar) > PVAc > PMMA > PS (relatively nonpolar), which is in agreement with both their chemical structures and dipole moment data of LPAs reported by Atkins⁶ (uncured UP = 2.0–2.5, PVAc = 1.6, PMMA = 1.3, and PS = 0.3). In general, the more incompatible the ternary system prior to reaction at 25°C, the more significant the resulting volume shrinkage after the cure at 110°C (i.e., PS > PMMA > PVAc > PU). This is because the cured sample containing a relatively nonpolar LPA tends to exhibit a two-phase microstructure such as that in Figures 6 and 7, and the segregating effect of such an LPA on the microgel particles generated during the cure is also less profound, resulting in a lower volume fraction of microvoids for volume shrinkage compensation. Besides, for a less compatible ternary system, the intrinsic polymerization shrinkage of the cured sample is generally greater since both the relative weight of the dispersed phase region and the molar ratio of styrene to polyester C=C bonds therein during the cure would be higher, which could be judged by the ternary static phase characteristics of styrene/UP/LPA systems at 25°C prior to cure.

For instance, as shown in Table 4 for the PMMA and PS systems, the latter system possesses shorter global phase separation time, and higher equilibrium relative weight and molar ratio in the dispersed phase. Hence, it could be inferred that during the cure of UP resins at 110°C, both the molar ratio of styrene to polyester C=C bonds and the relative weight is also greater for the PS dispersed phase than the PMMA dispersed phase, leading to a higher intrinsic polymerization shrinkage for the PS-containing sample.

As also shown in Table 4, increasing LPA concentration enhances both the degree of phase separation at 25°C prior to cure, as revealed by the increasing relative

weight in the dispersed phase, and the equilibrium LPA concentration in the dispersed phase. In the cure of UP resins containing PMMA and PS, respectively, it could be inferred that both the occupied volume of the dispersed phase after the cure and the segregating effect of LPA in microgel particles generated therein would also increase with increasing LPA concentration (Figures 6 and 7), resulting in favourable effects on microvoid formation and volume shrinkage control. On the other hand, increasing LPA concentration also prolongs the phase separation time at 25°C prior to cure. For the much less incompatible styrene/UP/PS system, one would expect that the rate of phase separation during the cure at 110°C could be reduced by increasing the PS concentration. Consequently, the amount of both small styrene molecules diffusing into the PS-dispersed phase and large UP molecules diffusing out of the PS-dispersed phase would become smaller before the cessation of a mass transfer process caused by chemical reaction early in the reaction. Considering that the equilibrium molar ratio of styrene to polyester C=C bonds in the dispersed phase at 25°C is generally independent of PS concentration (Table 4), it is inferred that the resulting molar ratio in the dispersed phase after a reaction-induced phase separation during the cure at 110°C would be decreased with increasing PS concentration, leading to an appreciable reduction in the intrinsic polymerization shrinkage. That would be the reason why for the PS-containing samples, the fractional volume shrinkage after the cure could decrease significantly with increasing PS concentration (Figure 2), while the corresponding relative volume fraction of microcracks would only show a slight increase (Figure 3). Indeed, our reasoning has been supported by SEM micrographs (Figure 7), where the number of microgel particles in the PS-dispersed phase decreases with decreasing LPA concentration, and at 5% LPA content there are essentially no microgel particles therein due to an excessively high styrene content (or a considerably low concentration of UP) early in the reaction.

The fractional volume change after the cure of UP

resins containing LPA has been found to decrease with increasing PU molecular weights^{7,8}, while it increases with increasing PVAc molecular weights¹². Based on our explanation, for the highly compatible styrene/UP/PU systems, increasing molecular weight of PU would be accompanied by a reduction in the concentration of NCO end groups of PU, and in turn could diminish the extent of the polycondensation reaction between PU and UP end groups during the cure. The enhancement of intrinsic polymerization shrinkage as explained earlier could thus be mitigated, leading to a decrease in the fractional volume change. As to the fairly compatible styrene/UP/PVAc systems, increasing the molecular weight of PVAc could shorten the phase separation time during the cure, which is similar to the effect of decreasing LPA concentration for the highly incompatible styrene/UP/PS systems mentioned earlier. Hence, a higher molar ratio of styrene to polyester C=C bonds in some local phase regions would result, leading to an increase in the intrinsic polymerization shrinkage and in turn a higher fractional volume change.

Atkins⁶ found that for styrene/UP/PMMA systems (weight ratio = 48/42/10), the sample morphology in a MA (maleic anhydride)-PG (propylene glycol) polyester (equivalent molecular weight per C=C bond = 156) exhibited a two-phase microstructure similar to that in *Figure 6*, while that in an IPA (isophthalic acid)-MA-PG polyester (equivalent molecular weight per C=C bond = 224) showed a co-continuous microstructure similar to that in *Figure 5*. (The overall globule microstructure found by Atkins was due to the fact that the globules generated in either the continuous or the dispersed phase appeared indistinguishable³².) However, the shrinkage control was superior with the MA-PG polyester system. Based on our explanation, since the initial molar ratio of styrene to polyester C=C bonds was 1.71 for the MA-PG polyester system, and 2.46 for the IPA-MA-PG system, the superior shrinkage control for the MA-PG polyester system was due to the reduction in intrinsic polymerization shrinkage (with a lower molar ratio) predominating over the decrease in volume shrinkage compensation by microvoid formation (with a two-phase microstructure).

CONCLUSIONS

In the cure of low-shrink UP resins at 110°C, increasing LPA concentration reduces the fractional volume shrinkage after the cure. The effectiveness of volume shrinkage control generally increases with increasing polarity in LPA, i.e., PS < PMMA < PVAc < PU, since the UP molecule is reasonably polar. The overall volume change after the cure would be determined not only by the volume compensation for shrinkage due to microvoid formation but also by the intrinsic polymerization shrinkage.

The volume fraction of microvoids depends on the sample morphology and the segregating effect of LPA on microgel particles generated during the cure, which could be enhanced either by increasing the LPA concentration or by employing a relatively polar LPA, such as PVAc. It is at around 50% of monomer conversion that the microvoids and microcracks develop markedly in the system, where the d.s.c. rate profile descends shortly after the maximum point and the cured sample becomes rigid

enough. On the other hand, the intrinsic polymerization shrinkage depends on the resulting molar ratio of styrene to polyester C=C bonds essentially at the dispersed phase region after a reaction-induced phase separation during the cure, which could be judged by the ternary static phase characteristics for styrene/UP/LPA systems at 25°C prior to the cure. In general, a higher molar ratio in the dispersed phase during the cure due to a less compatible styrene/UP/LPA system, either by employing a relatively nonpolar LPA, such as PS, or by decreasing LPA concentration, would cause a higher intrinsic polymerization shrinkage.

For relatively polar LPAs such as PVAc and PMMA, the fractional volume change after the cure is controlled by microvoid formation. In contrast, for relatively nonpolar LPAs, such as PS, it is dominated by intrinsic polymerization shrinkage. For polar LPAs capable of reacting with UP molecules during the cure, such as PU, both factors are competitive. However, variables which could affect the phase characteristics of the styrene/UP/LPA system, such as the initial molar ratio of styrene to polyester C=C bonds, UP resin structure, LPA concentration, LPA molecular weight, and the like, may alter the relative importance of the two controlling factors on volume change.

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