

Effect of Co-promoter and Secondary Monomer on Shrinkage Control of Unsaturated Polyester (UP)/Styrene (St)/Low-Profile Additive (LPA) Systems Cured at Low Temperatures

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ABSTRACT: The shrinkage of unsaturated polyester (UP)/styrene (St) resins cured at low temperatures can be reduced by the presence of low-profile additives (LPAs). It is believed that the reaction-induced phase separation and the polymerization shrinkage in both the LPA-rich and UP-rich phases result in the formation of microvoids, which partially compensates the resin shrinkage. The relative reaction rate in the two phases plays an important role in shrinkage control. In this study, secondary monomers [such as divinylbenzene (DVB) and trimethylpropane trimethacrylate (TMPTMA)] and a co-promoter, 2,4-pentandione (2,4-P), were added into the UP/St/LPA resin systems to investigate their effect on the shrinkage control of resins cured at low temperatures. Dilatometry results showed that the addition of both TMPTMA and 2,4-P resulted in an earlier volume expansion during curing and better shrinkage control. The phase separation, reaction kinetics, and viscosity changes in the LPA-rich and UP-rich phases during curing were also investigated. The results confirmed that the increased reaction rate in the LPA-rich phase led to an earlier formation of microvoids and, consequently, less volume shrinkage of the cured resin. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 738–749, 2001

Key words: unsaturated polyester resins; low-profile additive; low-temperature cure; secondary monomer; co-promoter

INTRODUCTION

Unsaturated polyester (UP) resins are the most widely used thermoset polymers in the composite industry. Severe polymerization shrinkage of this resin, however, induces many deficiencies in the molded products. Many thermoplastic materials can serve as low-shrinkage or “low-profile” additives (LPAs) to reduce the shrinkage of UP resins.

The effects of the LPA structure, molecular weight and concentration, thermal expansion coefficient, and glass transition temperature on the shrinkage control performance and surface quality of various resin systems cured at high temperatures have been extensively investigated.^{1–11} Several mechanisms have been proposed for the shrinkage control of LPA in high-temperature cures.^{1–3,8,9,11–14} Most of them involve the thermal expansion of the resin and LPA during heating, phase separation, and inversion between the LPA-rich and resin-rich phases during curing and the formation of microvoids either at the interface or inside the LPA-rich phase to compensate the resin shrinkage during curing and cooling.

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In recent years, demand for low-cost composite manufacturing processes such as low temperature, low-pressure compression molding of sheet-molding compound (SMC), resin-transfer molding (RTM), and vacuum-infusion liquid composite molding [e.g., the Seemann composites resin infusion-molding process (SCRIMP)] have grown considerably in industry. The molding temperature of these processes ranges from ambient temperature (e.g., SCRIMP), 60°C (e.g., RTM), to about 100°C (e.g., low-temperature SMC). This range of temperature is much lower than that of high-temperature processes such as SMC compression molding (150°C) or bulk molding compound (BMC) injection molding ($\geq 150^\circ\text{C}$).

Commercial LPAs, however, often do not work effectively in room-temperature processes like SCRIMP. Our recent studies on the UP/St/LPA systems cured at low temperatures^{15–18} indicated that the reaction-induced microvoid formation, instead of the thermal expansion/shrinkage dominated microvoid formation at high temperatures, is the main factor in shrinkage compensation. Microvoid formation is related to the buildup of reaction-induced stresses at the interface of the resin-rich and the LPA-rich phases. This, in turn, depends on the relative reaction rate and modulus of the two phases as well as the phase structure of the reacting mixture.

It was found¹⁸ that volume expansion, which can compensate volume shrinkage, during low-temperature curing occurs at very late stage of reaction and increasing the reaction rate in the LPA-rich phase results in an earlier volume expansion and better shrinkage control. A hypothesis was also proposed in this article to explain the late-stage volume expansion of UP/St/LPA systems cured at low temperature. It states that the slower reaction in the LPA-rich phase is the main reason why the microvoid formation occurs at the late stage of polymerization. The low reaction rate in the LPA-rich phase is a direct result of two factors: a low promoter concentration and a high St/UP ratio. The low promoter level in the LPA-rich phase is caused by the partition of the promoter into two phases, due to the complex formation between the cobalt ion and the carboxyl groups of UP and LPA molecules. A kinetic study of the samples with acid-modified LPA confirmed that the LPA containing more and stronger acid groups tends to attract more of the cobalt promoter to the LPA-rich phase, resulting in a higher reaction rate. Consequently, the samples with acid-modified LPAs show an earlier volume expansion

and better shrinkage control.¹⁸ The improvement, however, is modest.

It has been found¹⁹ that adding a highly reactive olefinically unsaturated chemical species, like divinylbenzene (DVB), to the UP/St/LPA systems is able to reduce shrinkage and increase physical properties such as tensile strength and resistance to crack of the cured resin in high temperature molding processes. However, the actual mechanism is unclear. One of the two tasks of this study was to investigate the effect of DVB and trimethylpropane trimethacrylate (TMPTMA), which has three acrylic functional groups and is often used as a crosslinking agent,^{20,21} as a secondary monomer, on the shrinkage control of UP/St/LPA systems cured at low temperatures.

It is well known that peroxide can be decomposed efficiently at low temperature with the aid of metal ions. The reactivity of metal ions in the redox decomposition of peroxide is appreciably influenced by the type of ligands that form a counterion.²² Acetylacetone or 2,4-pentanedione (2,4-P) was found to be synergistic with the reactive metals in redox polymerization.²³ This is because 2,4-P is an effective chelating agent, capable of interacting with metal ions to form a new complex. The formed chelate may decrease, enhance, or have no catalytic effect on the decomposition of peroxide, depending on its relative ability to take part in the redox reaction as compared to that without 2,4-P. The effect of 2,4-P on shrinkage control of the UP/St/LPA system was also investigated in this study.

The experimental methods used include differential scanning calorimetry (DSC), rheometry, dilatometry, and scanning electron microscopy (SEM). The reaction kinetics and viscosity change in both the LPA-rich and the UP-rich phases are compared to understand how the relative reaction rate and viscosity change in each phase influence shrinkage compensation. A dilatometer was used to study the volume change of UP/St/LPA systems cured at low temperature and SEM was used for the morphology observation. Composite samples were also prepared by room-temperature SCRIMP to measure the surface quality of the cured composites.

EXPERIMENTAL

Materials

The UP resin used in this study was Q6585 from Ashland Chemical (Columbus, OH). Q6585 is a

Table I Formulations Used in This Study (Based on Weight)

Materials	No SM	6% DVB	6% TMPTMA	0% 2,4-P	0.03% 2,4-P	0.05% 2,4-P	6% TMPTMA, 0% 2,4-P	6% TMPTMA, 0.03% 2,4-P	6% TMPTMA, 0.05% 2,4-P
Q6585	63.65	63.65	63.65	63.65	63.65	63.65	63.65	63.65	63.65
Neulon-T ⁺	9.48	9.48	9.48	9.48	9.48	9.48	9.48	9.48	9.48
Styrene	26.91	26.91	26.91	26.91	26.91	26.91	26.91	26.91	26.91
DVB	—	6	—	—	—	—	—	—	—
TMPTMA 2,4-P	—	—	6	—	—	—	6	6	6
MEKP	—	—	—	—	0.03	0.05	—	0.03	0.05
MEKP	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cobalt octoate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
BQ	—	—	—	0.003	0.003	0.003	0.001	0.001	0.001

1:1 mixture of maleic anhydride and propylene glycol with an average of 10.13 vinylene groups per molecule and an average molecular weight of 1580 g/mol. It contains 35% by weight of styrene. The crosslinking monomer used was styrene (St) from Aldrich (Milwaukee, WI). The LPA used in this study was Neulon-T plus, a modified poly(vinyl acetate) (PVAc), from Union Carbide (South Charleston, WV). The two secondary monomers (SMs) from Aldrich used in this study were DVB (an 80% isomer mixture of *m*-DVB and *p*-DVB) and TMPTMA (with three vinylene groups per molecule). One co-promoter used in this study, also from Aldrich, was 2,4-P.

All the samples being tested were formulated to provide an St double bond to UP double bond ratio of 2.0. The initiator used was 1.0% methyl ethyl ketone peroxide (MEKP) with 0.1% cobalt octoate. All the samples were cured at 35°C. The compositions are listed in Table I.

Instruments and Procedures

Dilatometer

The volume shrinkage of the sample materials was measured by an in-house constructed dilatometer. The sample, weighing from 5 to 6 g, was sealed in a polyethylene pouch, then degassed under vacuum. A small hole was poked at the edge of the pouch, and air bubbles inside the pouch that had been formed under the vacuum were squeezed out. The pouch was heat-sealed again, then placed inside the sample chamber of the dilatometer. The measurements were taken under a pressure of 0.69 MPa (100 psi) at 35°C. More details regarding the construction and operation procedures of the dilatometer can be found elsewhere.^{15,24}

DSC

A differential scanning calorimeter (DSC2910, TA Instruments) was used to measure the reaction kinetics. The sample was sealed in a volatile aluminum sample pan which can withstand 2 atm internal pressure. Isothermal runs were followed by scanning the samples from 30 to 300°C to determine the residual heat with a heating rate of 5°C/min. The total heat of the reaction during curing was calculated from the areas under both isothermal and residual scanning DSC curves and the reaction rate or conversion was based on the total heat calculated by this method.

Rheometrics Mechanical Spectrometer (RMS)

The rheological changes during curing were measured by a Rheometrics Mechanical Spectrometer (Rheometric ScientificTM RMS-800). A set of parallel plates with an air oven as a heating chamber was employed. The diameter of the plates was 50 mm, and the gap between them was about 1 mm. Viscosity was measured under an isothermal condition (35°C) and at a shear rate of 1.0 s⁻¹. The gel point is defined as the point where the reduced viscosity $\eta_r = \eta/\eta_0$ (η is the instantaneous viscosity, and η_0 , the initial viscosity) reaches 10³.

SEM

For the morphological measurement, a Philip XL-30 scanning electron microscope was used. The sample cured in the dilatometer without etching by any solvent was gold-coated for morphological measurements. The fracture surfaces were observed under 10 kV power. The magnification in this study varied from 200× to 10,000×.

SCRIMP

Before molding, three layers of dry glass fiber mats (QM6408 from Brunswick Technologies, Inc.) were laid upon a glass plate. The fiber stack was covered by a polyester film to form a vacuum bag whose outer edges were sealed by a tacky tape. A resin inlet and a vacuum outlet on each end of the mold were also formed. During molding, a vacuum was applied through the outlet, forcing the bag to press tightly against the fiber stack. The liquid resin was introduced into the inlet through a supply line, then cured in the vacuum bag for 24 hours.

The surface quality of the molded samples was measured by a profilometer, Federal Surfanalyzer 4000. The chosen tracing length was 2.54 cm. An average roughness (R_a), which is the arithmetic average height of surface irregularities measured from the mean line within the sample length, was used as a quantitative standard to compare the surface quality.

RESULTS AND DISCUSSION

Reaction Kinetics and Volume Shrinkage

Effect of 2, 4-P

To investigate the influence of acetylacetone or 2,4-P on the reaction kinetics and volume change of the UP/St/LPA systems, the resin samples with different amounts of 2,4-P were cured at 35°C in the DSC. The same isothermal runs were carried out under the pressure of 0.69 MPa (100 psi) in the dilatometer. The ratio between the styrene double bond and the UP resin double bond was adjusted to 2.0 by adding extra styrene. All samples contained 3.5% LPA. The initiation system included 0.1% cobalt octoate and 1.0% MEKP. Benzoquinone (BQ), 300 ppm, was added into the system to allow enough sample preparation time, i.e., 30 minutes.

The results of the reaction kinetics are shown in Figure 1(a,b). When the content of 2,4-P increases, the reaction starts earlier with a shorter induction time and higher reaction rate. Therefore, 2,4-P is a co-promoter for UP resins cured by cobalt and MEKP.²⁵ The resin conversion shows the same trends, but the final conversion is independent of the 2,4-P content, that is, 58%.

Figure 2 presents the volume change profiles of samples with various amounts of 2,4-P (0, 0.03, and 0.05 wt %). For the system with 0.03% 2,4-P,

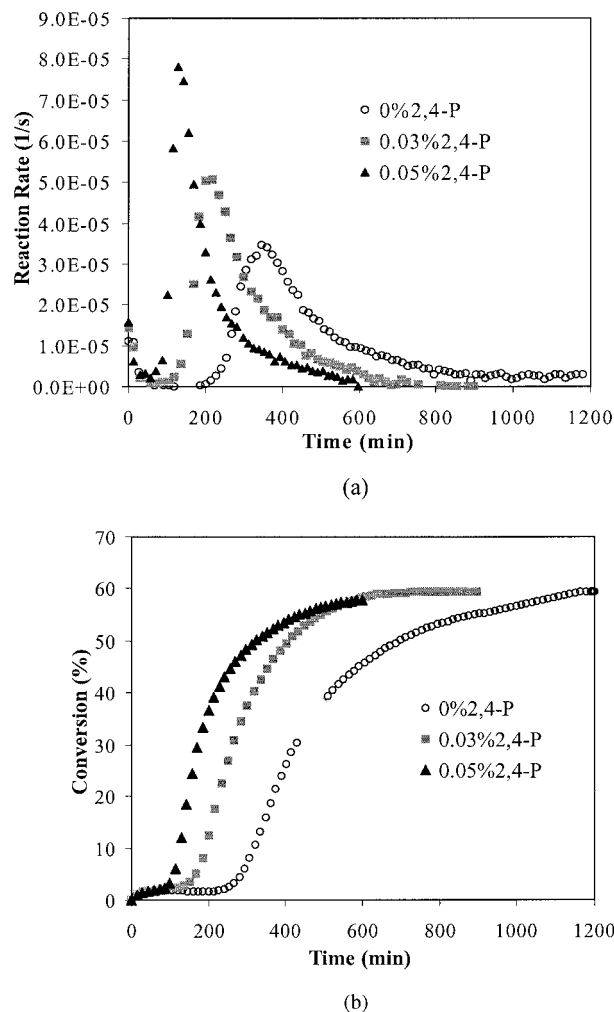


Figure 1 Reaction kinetics of UP/St/LPA system with different concentrations of 2,4-P cured at 35°C (300 ppm BQ, 0.1% cobalt octoate, and 1.0% MEKP): (a) reaction rate; (b) conversion.

the volume expansion occurred earlier compared to the system without 2,4-P. It also had a larger volume expansion at the latter stage of the reaction. Consequently, the final shrinkage of the sample containing 0.03% 2,4-P is lower (2.9–3.0% versus 4.2%). For the sample with 0.05% 2,4-P, its volume expansion occurred at about the same time as the sample with 0.03% 2,4-P and the final shrinkage was the same for both samples. Since 2,4-P is a promoter, the presence of more 2,4-P sped up the reaction rate, causing larger volume shrinkage in the early stage of the reaction and larger volume expansion at the latter stage of the reaction. According to Figure 1(b), the conversions of the samples with 0.03% 2,4-P and 0.05% 2,4-P at the time when volume expansion occurred are 43.6% and 50.9% respectively.

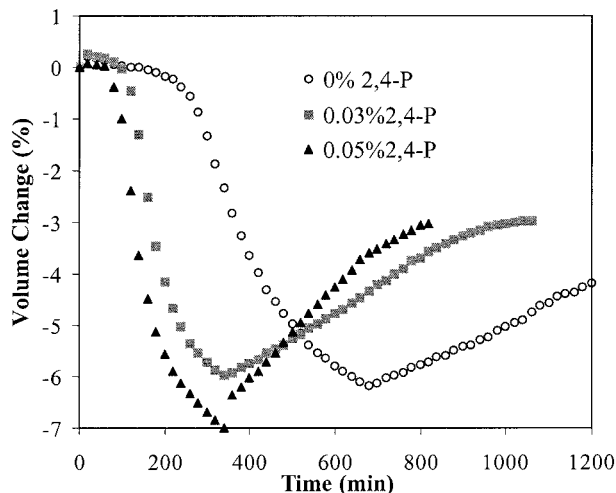
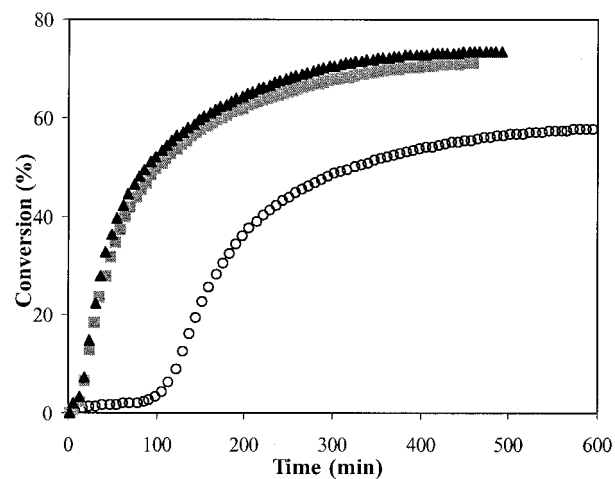


Figure 2 Volume change profile of UP/St/LPA system with different concentrations of 2,4-P content cured at 35°C (300 ppm BQ, 0.1% cobalt octoate, and 1.0% MEKP).

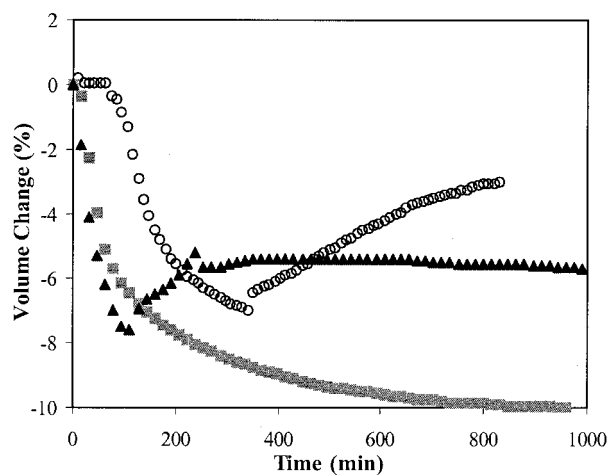
From the dilatometry results, it is clear that the addition of 2,4-P leads to an earlier volume expansion, which improves the shrinkage compensation. DSC results showed that the reaction rate increased by adding 2,4-P. To study the effect of reaction rate on shrinkage control of the UP/LPA/St system, a series of experiments were carried out by changing the content of the initiator/promoter or 2,4-P. The kinetics and dilatometer results are summarized in Figure 3.

As shown in Figure 3, the reaction rate can be increased by either increasing the content of initiator/promoter but without adding any 2,4-P or keeping the 2,4-P content at 0.05 wt % but increasing the amount of initiator/promoter. Both methods increased the reaction rate significantly, but for the samples with a higher initiator/promoter content, the addition of 2,4-P only slightly accelerated the total reaction rate. The volume change behavior of these samples, however, was quite different: For the two samples with 0.05% 2,4-P, increasing the content of cobalt octoate and MEKP in the system resulted in a higher reaction rate and earlier volume expansion, but the final volume shrinkage did not decrease as the curing agent content increased. No volume expansion was observed for the sample with a higher reaction rate but without 2,4-P. It is obvious that higher total reaction rate alone cannot improve the shrinkage control, and it is 2,4-P that improves the volume shrinkage of UP/St/LPA systems.

An important feature in the cure of UP/St/LPA is the formation of a two-phase structure (LPA-rich and UP-rich phases). The polymerization shrinkage is compensated by the microvoid formation at the interface of the LPA-rich and UP-rich phases or in the LPA-rich phase. To further understand how the change in the total reaction rate or the addition of 2,4-P affects shrinkage control, the reaction rate and rheology changes of the LPA-rich and UP-rich phases of UP/St/LPA



(a)



(b)

Figure 3 Volume change profile and reaction conversion of UP/St/LPA system with different 2,4-P or initiator/promoter contents cured at 35°C (300 ppm BQ): (a) conversion; (b) volume change (○: 0.05% 2,4-P, 0.1% CoB, 1.0% MEKP; □: 0% 2,4-P, 0.5% CoB, 1.5% MEKP; ▲: 0.05% 2,4-P, 0.5% CoB, 1.5% MEKP).

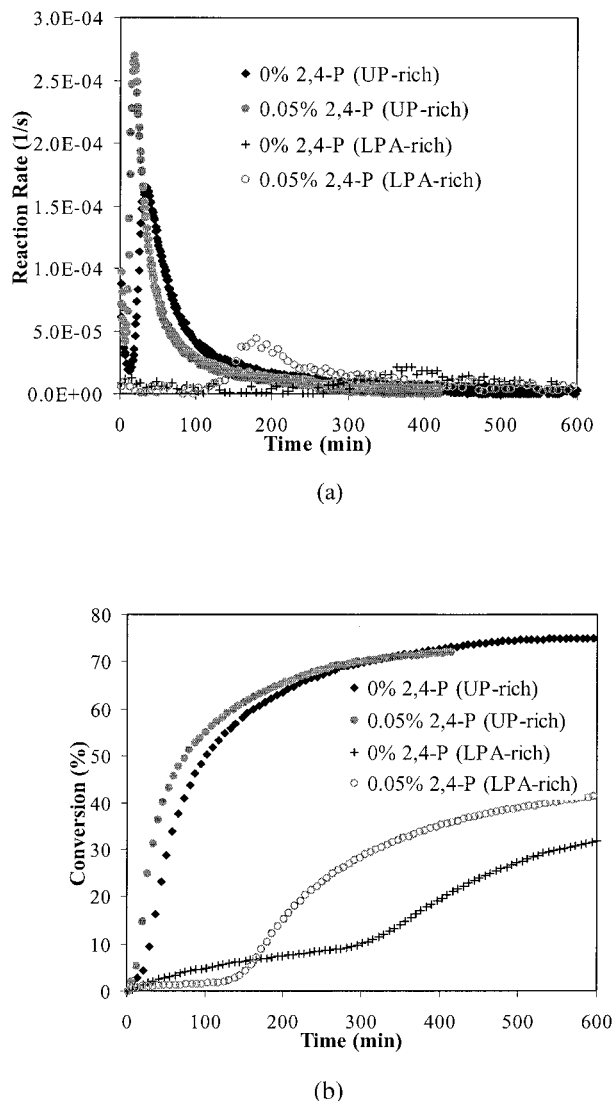


Figure 4 Effect of 2,4-P on reaction kinetics of LPA-rich and UP-rich phases of UP/St/LPA system cured at 35°C (300 ppm BQ, 0.5% cobalt octoate, and 1.5% MEKP): (a) reaction rate; (b) conversion.

systems with different amounts of 2,4-P during curing were investigated.

A reaction-induced phase separation in the actual resin polymerization is a dynamic and evolving process. It is impossible to track this unceasingly changing phase behavior. Here, a temperature forced phase separation method was used as a qualitative assessment of how the partition of chemical species during phase separation affects the resin reaction and the shrinkage control in the UP/St/LPA systems. Since this method takes more than 10 h, the initiator and the promoter have to be separated during phase separation.

Two resin mixtures were prepared for each formulation: One with a double amount of cobalt octoate but without MEKP and the other with a double amount of MEKP but without cobalt octoate. The mixtures were then forced into phase separation by decreasing the temperature to -2°C to form two layers. The upper layer is an LPA-rich phase, while the lower layer is a UP-rich phase. For the resin mixture with cobalt octoate, it appeared that most of the cobalt promoter went into the UP-rich phase, since the lower phase (UP-rich) was pink (color of cobalt ion) and the upper phase (LPA-rich) was colorless or very light pink.

The two phases were separated, and their reaction rate and viscosity change were measured at 35°C by mixing an equal amount of resin from the same phase of the two mixtures. The results in Figure 4 show that the reaction rate of each phase increased due to the addition of 2,4-P; however, the reaction rate increase in the LPA-rich phase is much larger than that in the UP-rich phase. The viscosity change and gel time of the LPA-rich phase and the UP-rich phase were also measured. The results are summarized in Table II. The gel time of the UP-rich phase of systems with and without 2,4-P was 10.8 and 20.3 min, respectively. Due to the very slow reaction rate in the LPA-rich phase, using a conventional rheometer to measure the gel time is difficult because of styrene evaporation. The method used here is to place the LPA-rich phase with initiator in a small glass bottle and record the time when the resin cannot flow in a 35°C water bath. It was found that the gel time of the LPA-rich phase with and without 2,4-P was much longer than that of the UP-rich phase, that is, 170 and 324 min, respectively. It was also found that the gel conversion of the UP-rich phase was lower than 5%. Although the gel time of the systems with or without 2,4-P is different, the gel conversion of the same phase

Table II Gel Time and Gel Conversion of UP/St/LPA System Cured at 35°C (0.5% Cobalt, 1.5% MEKP, 300 ppm BQ)

Measurement	UP-rich Phase		LPA-rich Phase	
	0% 2,4-P	0.05% 2,4-P	0% 2,4-P	0.05% 2,4-P
Gel time (min)	20.3	10.8	324	170
Gel conversion (%)	3.9	3.8	8.3	8.3

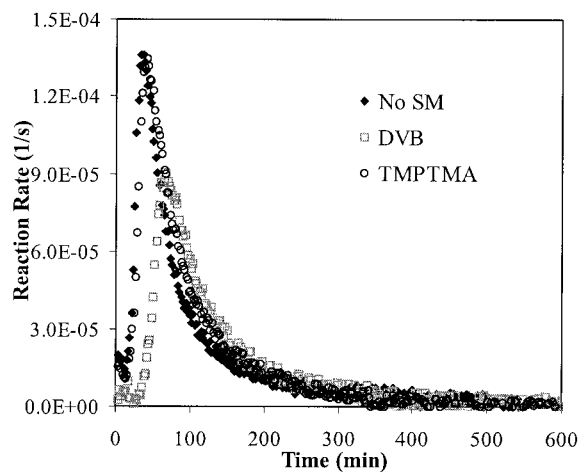
(i.e., the LPA-rich or UP-rich phase of both systems, with and without 2,4-P) is the same. The gel conversion of the UP-rich phase is lower than that in the LPA-rich phase (3.8% compared to 8.5%). This suggests that the styrene C=C double bond and UP C=C double bond ratio in the LPA-rich phase is higher. Other researchers²⁶ found a similar result by measuring the composition in each phase using FTIR and a different phase separation method.

Another important observation in this experiment is that the conversion of the UP-rich phase at the gel point of the LPA-rich phase gel is different for the systems with or without 2,4-P. For the sample with 0.05% 2,4-P, this conversion was 61.1%, which is lower than its final conversion (72.1%). But for the sample without 2,4-P, the conversion reached 70.6%, which is almost the final conversion of the UP-rich phase. The LPA-rich phase has to reach a sufficiently high modulus in order to form microvoids, because a liquid LPA phase can release stress resulting from polymerization shrinkage. After gelation of the LPA-rich phase, the stress-induced local cracking caused by shrinkage in both phases is the main driving force for microvoid formation. In the UP/St/LPA system with 2,4-P, the UP-rich phase kept reacting after gelation of the LPA-rich phase. This polymerization shrinkage provided a greater chance to generate microcracking in the system to compensate the volume shrinkage. On the other hand, in the system without any 2,4-P, the UP-rich phase reached its final conversion when the LPA-rich phase gelled. The driving force for microvoid formation, therefore, is quite weak.

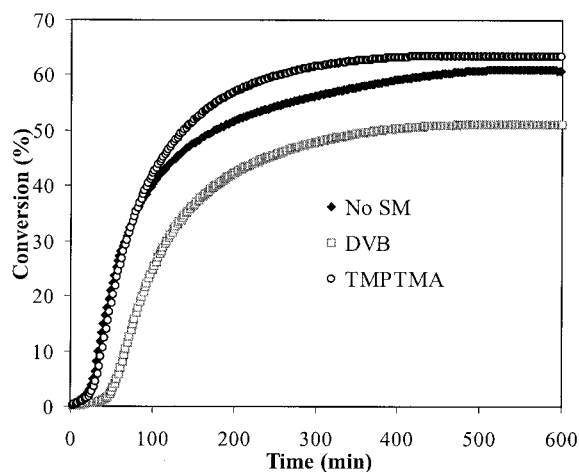
The above results reveal that the addition of 2,4-P can accelerate the reaction in the LPA-rich phase more than it can in the UP-rich phase. This difference results in an earlier volume expansion and lower final volume shrinkage. A higher overall reaction rate does not necessarily achieve a better shrinkage control.

Effect of SM

To study the effect of an SM on the reaction kinetics of the UP/St/LPA system, an isothermal cure was carried out at 35°C. The ratio between the styrene double bond and the UP resin double bond was adjusted to 2.0 by adding extra styrene. The initiation system included 0.1% cobalt octoate and 1.0% MEKP. The samples contained 3.5% LPA and 6% SM based on the total resin weight. Two SMs were used, that is, DVB and TMPTMA.



(a)



(b)

Figure 5 Reaction kinetics of UP/St/LPA system with 6% SM cured at 35°C (0.1% cobalt octoate and 1.0% MEKP): (a) reaction rate; (b) conversion.

Figure 5 presents the effect of SMs on the reaction kinetics of the UP/St/LPA system. The overall reaction rate and final conversion of the sample with DVB are lower than those of the sample without any SM. The reaction of the sample with TMPTMA does not show much difference compared to the sample without SM, and the final conversion is slightly higher than that of the sample without any SM.

A series of dilatometry tests were conducted with SMs at 35°C to investigate the shrinkage control behavior of UP/St/LPA with SMs. The formulas were the same as those used in the reaction kinetics study. Figure 6 shows the volume change

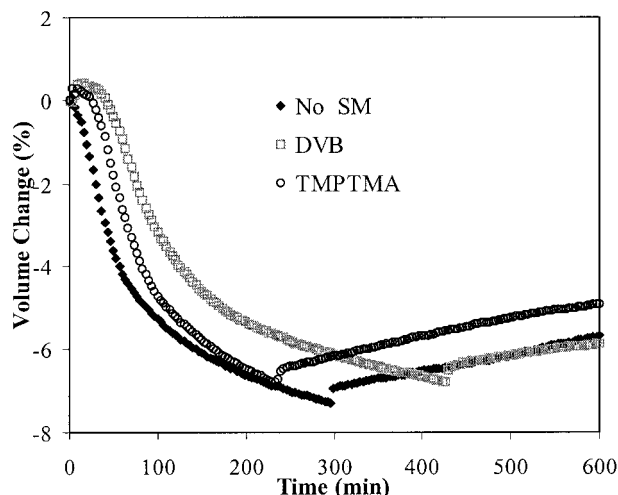


Figure 6 Volume change profile of UP/St/LPA system with 6% SM cured at 35°C (0.1% cobalt octoate and 1.0% MEKP).

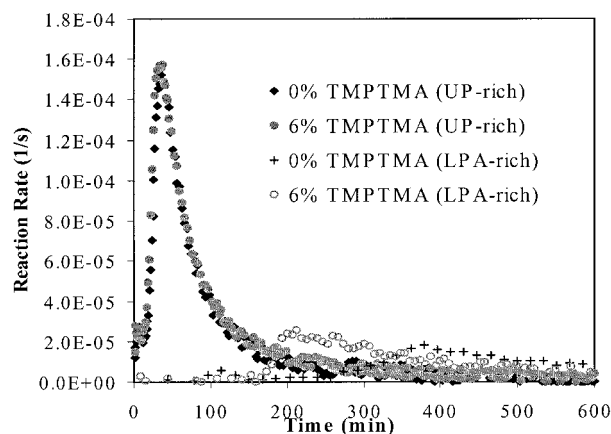
profile versus the time during curing. The volume expansion of the system without SMs occurred at 296.3 min, when the volume shrinkage reached 7.28%. For the system with TMPTMA, volume expansion occurred at 236.3 min and volume shrinkage at this point was 6.73%. It can be seen that the sample with TMPTMA exhibits an earlier volume expansion and better shrinkage control. The volume expansion of the sample with DVB occurred later than the other two samples and the addition of DVB did not show any improvement in shrinkage control.

To further study this phenomenon, a formulated UP resin, LPA, TMPTMA, and cobalt octoate were mixed simultaneously so that a transparent (single-phase) mixture was obtained. The formulation is the same as that used in the kinetic and dilatometry study except the content of promoter or initiator was doubled. The method used for the phase-separation study is the same as that used before. The two phases were separated, and their reaction rate and viscosity change were measured at 35°C by mixing an equal amount of resin from the same phase of the two mixtures.

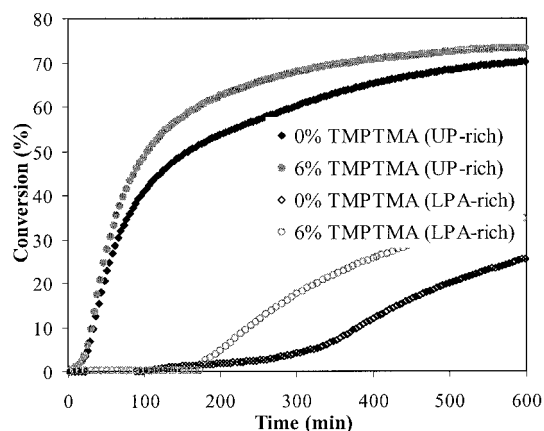
The results are shown in Figure 7. It is obvious that the reaction in the UP-rich phase is much faster than that in the LPA-rich phase, both with and without TMPTMA. The addition of TMPTMA can increase the reaction rate in both UP-rich and LPA-rich phases, but the effect of TMPTMA on the reaction rate in the LPA-rich phase is more profound. Although the reaction in the LPA-rich

phase is still much lower than in the UP-rich phase, the increasing reaction rate in the LPA-rich phase due to the addition of TMPTMA results in microvoid formation occurring at an earlier stage. It leads to earlier volume expansion and, consequently, better shrinkage control.

The viscosity change of each phase was also measured during curing and is summarized in Table III. The gel time of the UP-rich phases in systems with and without TMPTMA is 21.8 and 25.7 min, respectively. However, the gel time of the LPA-rich phase is much longer than in the UP-rich phase, that is, 188 and 231 min, respectively. It was also found that the gel conversion of each phase is lower than 5%. Compared with Figure 6, it can be seen that the volume expansion



(a)



(b)

Figure 7 Effect of TMPTMA on reaction kinetics of LPA-rich and UP-rich phases of UP/St/LPA system cured at 35°C (0.1% cobalt octoate and 1.0% MEKP): (a) reaction rate; (b) conversion.

Table III Gel Time and Gel Conversion of UP/St/LPA System Cured at 35°C (0.1% Cobalt, 1.0% MEKP)

Measurement	UP-rich Phase		LPA-rich Phase	
	0% TMPTMA	6% TMPTMA	0% TMPTMA	6% TMPTMA
Gel time (min)	25.7	21.8	231	188
Gel conversion (%)	4.61	3.72	2.3	3.34

resulting from microvoid formation occurs after gelation of the LPA-rich phase.

Effect of Combining TMPTMA and 2,4-P

The above results reveal that addition of either TMPTMA or the co-promoter 2,4-P can decrease the final shrinkage of the UP/St/LPA system. TMPTMA and 2,4-P can increase the reaction rate in both LPA-rich and UP-rich phases, but the effect on the LPA-rich phase is more profound, which results in an earlier volume expansion and, in turn, better shrinkage control.

To investigate the effect of the combination of 2,4-P and TMPTMA on the volume shrinkage control of UP/St/LPA systems, a series of experiments were carried out on samples with various amounts of 2,4-P (0, 0.03, and 0.05%) in UP/St/LPA with 6% TMPTMA. Again, the ratio between the styrene double bond and the UP resin double bond was adjusted to 2.0 by adding extra styrene. All samples contained 3.5% LPA. The initiation system included 0.1% cobalt octoate and 1.0% MEKP. BQ, 100 ppm, was added into the system to allow a 30-min sample preparation time.

Figure 8 presents the volume change profiles of several samples cured at 35°C and 0.69 MPa (100 psi). As the concentration of 2,4-P increased in the presence of 6% TMPTMA, an earlier volume expansion was observed and the final volume shrinkage decreased. The trend is the same as that in the system without TMPTMA as shown in Figure 2. In Figure 2, the system with 0.05% 2,4-P but without TMPTMA has a 3.0% final shrinkage, while adding 0.6% TMPTMA into the system resulted in a final shrinkage of 2.8% (Fig. 8). Thus, the final volumetric shrinkage does not show any improvement with the combination of TMPTMA and 2,4-P. The reaction kinetics of UP/LPA/St systems with 6% TMPTMA and various contents of 2,4-P shown in Figure 9 indicates that reaction occurs earlier for samples with more 2,4-P.

To understand the relationship between the resin conversion and the volume change, the volumetric change of samples is plotted versus the resin conversion as shown in Figure 10. It was found that the samples, which give better shrinkage control (0.03 and 0.05% 2,4-P), show a volume expansion at a lower conversion.

Morphology

To understand the effect of 2,4-P and TMPTMA on the shrinkage control of UP/St/LPA, the morphology of cured samples was observed by SEM. Micrographs of samples cured in dilatometry at 35°C are shown in Figure 11. The morphology of samples with TMPTMA is different from that of the samples without TMPTMA. Adding 2,4-P does not make any significant difference on the sample morphology. However, the presence of 0.05% 2,4-P reduced the volume shrinkage of the sample from 4~6% to 3%.

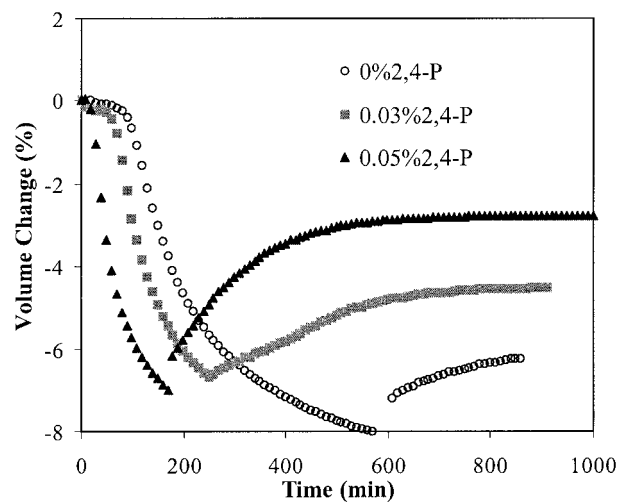


Figure 8 Volume change profile of samples with different 2,4-P content in UP/St/LPA system with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate, and 1.0% MEKP).

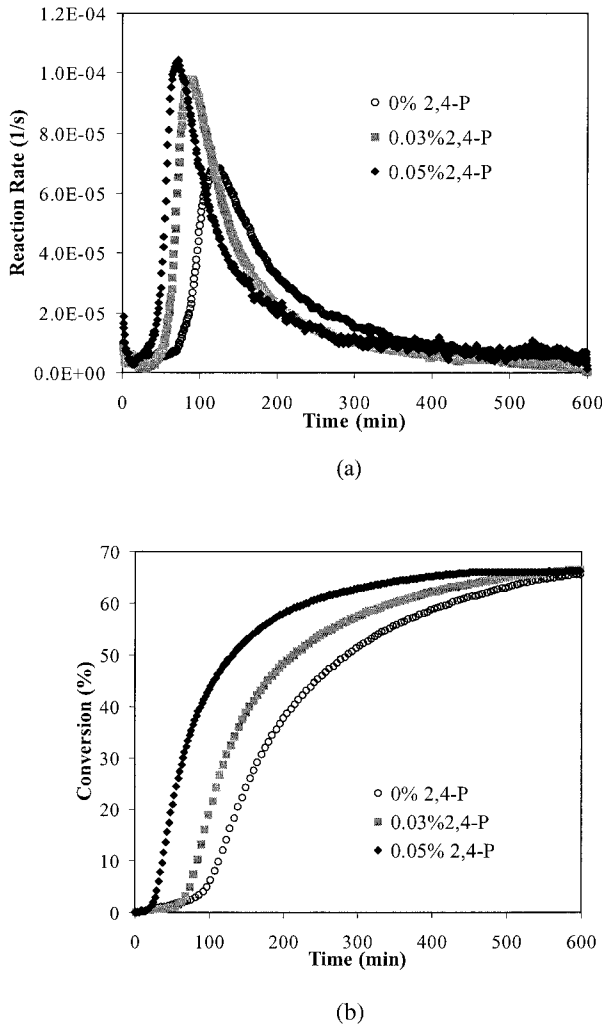


Figure 9 Reaction kinetics of samples with different 2,4-P content in UP/St/LPA system with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate, and 1.0% MEKP): (a) reaction rate; (b) conversion.

Surface Quality

A series of room-temperature SCRIMP experiments were carried out to test the effect of adding the SM and the co-promoter on shrinkage control. The samples were cured at room temperature and a 72 cm vacuum. The surface quality of the molded samples was measured by a profilometer, a Federal Surfanalyzer 4000. Every SCRIMP panel was measured at five different locations and the evaluation length chosen for calculation was 4 mm. An average roughness (R_a), which is the arithmetic average height of surface irregularities measured from the mean line within the sample length, was used as a quantitative standard to compare the surface quality. The results

are summarized in Figure 12. As seen from this figure, the surface quality of molded panels with 6% TMPTMA or 0.05% 2,4-P is better than that of those without any SM and co-promoter. It is also indicated in Figure 12 that the molded panel with 0.05% 2,4-P has a slightly better surface quality than that of the panel with 6% TMPTMA. This trend is the same as that of the dilatometry result. The standard deviation of surface roughness shows that samples with better surface smoothness also have a more uniform distribution. The results of the surface quality of the SCRIMP panels further confirm that both TMPTMA and 2,4-P can decrease the volume shrinkage of UP/St/LPA systems and yield an improved surface quality of molded products.

CONCLUSIONS

In a previous study from our group,¹⁸ we proposed that a low reaction rate in the LPA-rich phase due to the low promoter concentration and high styrene/UP ratio is the main reason for the observed late volume expansion in the UP/St/LPA systems cured at low temperatures. In this study, we found that the addition of SM or co-promoter can improve the shrinkage control of the UP/St/LPA systems. For the samples with the co-promoter 2,4-P, the reaction rate of both LPA-rich and UP-rich phases increases as compared to the sample without 2,4-P, and the increase in the LPA-rich

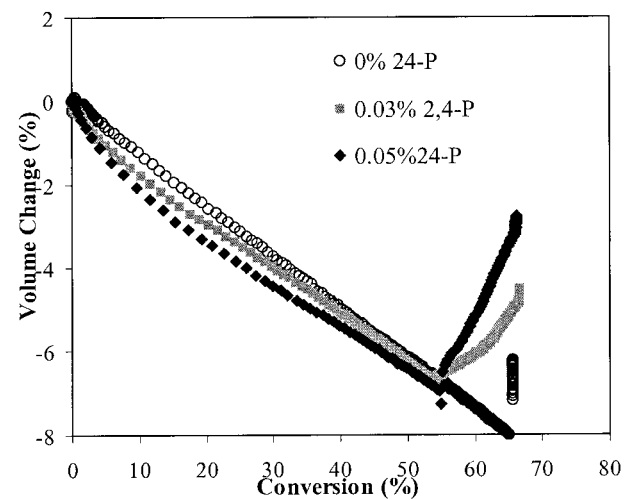
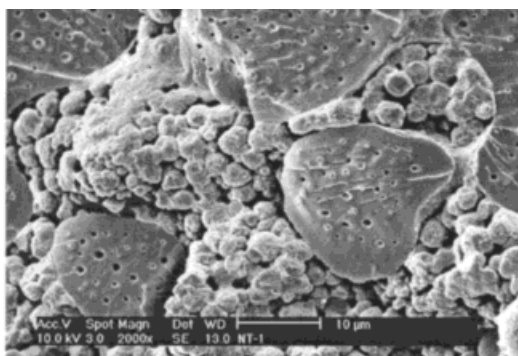
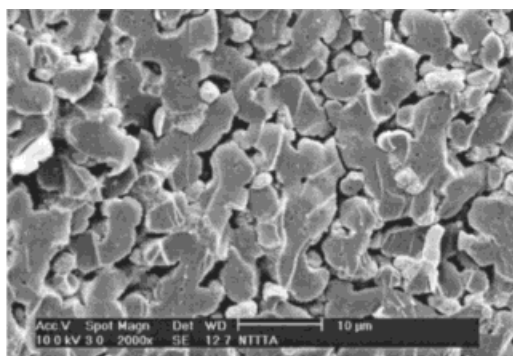


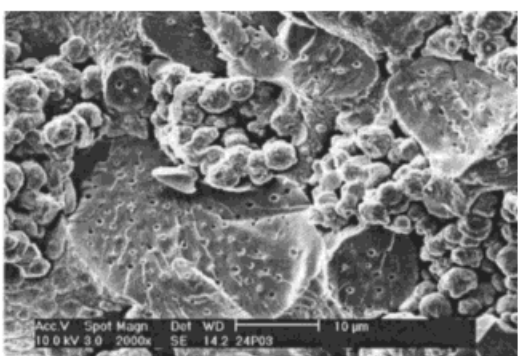
Figure 10 Volume change versus conversion of samples with different 2,4-P content in UP/St/LPA system with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate, and 1.0% MEKP).



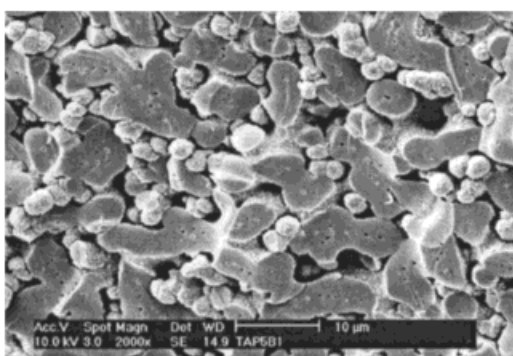
No 2,4-P or TMPTMA (final shrinkage: 4.9%)



6%TMPTMA (final shrinkage: 4.0%)



0.03% 2,4-P (final shrinkage: 3.0%)



6% TMPTMA+0.05%2,4-P(final shrinkage: 2.8%)

Figure 11 SEM micrographs of cured UP/LPA/St with different amounts of 2,4-P and 6% TMPTMA cured at 35°C ($\times 2000$).

phase is more pronounced. It was also found that the gelation of the LPA-rich phase occurs earlier by adding 2,4-P into the resin system. This turns out to be critical for the earlier onset of microvoid formation and volume expansion, which, in turn, gives better shrinkage control. For the sample containing the SM, TMPTMA, the reaction rate of the LPA-rich phase is faster than that of the sample without TMPTMA. The sample showed an earlier volume expansion and a better shrinkage control than those of the sample without TMPTMA. It further confirms the hypothesis mentioned above.

The kinetics and volume change study of UP/St/LPA systems with both 2,4-P and TMPTMA also showed that a better shrinkage control can be obtained when the volume expansion occurs at a lower conversion. The final volume shrinkage, however, shows no further improvement.

The morphology of the samples with TMPTMA is quite different from that without TMPTMA. It is obvious that TMPTMA affects both crosslinking and phase-separation processes in the UP/St/LPA systems. The samples with 2,4-P show no morphology changes. Both approaches, either adding TMPTMA or 2,4-P, can reduce the shrinkage of the resin system. The relationship between the sample morphology and shrinkage control is still not well understood and needs to be further investigated.

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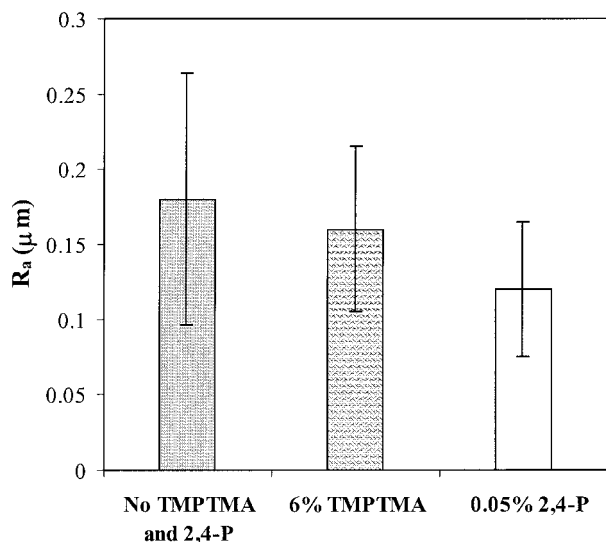


Figure 12 Surface quality of SCRIMP samples (by using 28 in. of vacuum at room temperature).

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