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Control of shrinkage and residual styrene of unsaturated polyester resins cured at low temperatures: I. Effect of curing agents

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Abstract

In low temperature molding processes, control of resin shrinkage and residual monomer is an important concern. The presence of low profile additives (LPAs) can reduce the shrinkage of unsaturated polyester (UP)/styrene (St) resins under proper processing conditions but may increase the residual styrene content. A systematic study was carried out to investigate the effect of the initiator system and reaction temperature on sample morphology, final resin conversion, and resin shrinkage of UP resins with LPA. It was found that the final conversion of the resin system could be improved by using dual initiators. The effect is more obvious at low temperatures. Volume shrinkage measurements of the resin system initiated with dual initiators revealed that good LPA performance was achieved at low (e.g. 35 °C) and high (e.g. 100 °C) temperatures but not at intermediate ones. This can be explained by how temperature affects phase separation, reaction kinetics in the LPA-rich and UP-rich phases, micro-void formation, and thermal expansion.

Keywords: Unsaturated polyester resins; Residual styrene; Volume shrinkage

1. Introduction

Unsaturated polyesters are widely used in the composite industry. They can provide excellent mechanical and chemical properties, good chemical and weather resistance, and a low cost. Further advantages of unsaturated polyester resins over other thermosetting resins are that they are easy to handle, can be pigmented, and can be easily filled and fiber reinforced in a liquid form. The cross-linking reaction between unsaturated polyester resins and vinyl monomers, i.e. styrene, allows one polymer chain to connect with other polymer chains, and to produce a three dimensional network, which converts the resin system from a viscous liquid into a hard, thermoset solid.

In recent years, low temperature and low pressure molding processes like resin transfer molding (RTM) and vacuum assisted resin transfer molding (VARTM) are gaining increased attention because of their low cost and ease of operation. An accelerator or promoter such as cobalt octoate or naphthenate has to be added to the peroxide initiator in order to induce chemical decomposition at low temperatures. In addition, other curing agents, such as inhibitors, retarders, and co-promoters, are also needed to adjust the resin pot life, gel time, and cycle time [1]. In room temperature processes without any external heating source, polymer chains become more difficult to move after gelation and the reaction becomes diffusion controlled. This impedes unsaturated polyester resins from achieving high final conversion and low styrene residue when cured at low temperatures. Low profile additives (LPAs) are usually added into the unsaturated polyester resin system to compensate polymerization shrinkage during the molding process. Although LPAs can provide shrinkage control in unsaturated polyester resin systems, the reaction exotherm may decrease because LPA is a non-reactive component in the system. Consequently, it may further increase styrene residue.

The release of residual styrene from molded composite parts creates problems for the environment and is the source of odor in many applications. Residual styrene may also result in blisters and voids on the surface of molded products at elevated temperatures (e.g. in the painting line). Therefore, detection and control of styrene content in the fiber-reinforced unsaturated polyester resin are very important, especially in low temperature processes. Many researchers

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have studied the effects of resin system, curing agent and reaction conditions on residual styrene of polyesters [2–4] by using various analytical instruments to measure the residual styrene content and to determine physical properties (e.g. heat distortion temperature, flexural strength, compressive yield strength, and tensile strength) of cured resins. Available methods to determine residual styrene content have included chemical degradation [5,6], refractive indices [7], gas chromatography [8], infrared spectroscopy [9,10], and nuclear magnetic resonance (NMR) spectroscopy [11]; infrared spectroscopy has been the most commonly used among them. The researchers found that less styrene residue could be attained by adding more peroxide, choosing flexible resins, and increasing the reaction exotherm. Most studies emphasized on the influence of resin flexibility and initiator type on the residual styrene content of molding panels without addressing reaction mechanism. In this study, an in-depth kinetic analysis is carried out to better understand the reaction kinetics of unsaturated polyester resins with LPA under different curing agents cured at low temperatures. The volume shrinkage of the resin system is also investigated.

2. Experimental

2.1. Materials

An unsaturated polyester resin, Aropol Q6585, provided by Ashland Chemical was used in this study. It is a step-growth product of 1:1 maleic anhydride and propylene glycol with an average of 10.13 vinylene groups per molecule and an average molecular weight of 1580 g mole^{-1}, containing 35% by weight of styrene. The low profile additive used was Neulon-T plus, a modified carboxylated poly(vinyl acetate) from Union Carbide (now Dow Chemical). All of the samples to be tested were formulated to provide a monomer double bond to unsaturated polyester double bond ratio of 2.0.

Cobalt octoate (6% cobalt octoate in mineral spirits, Pfaltz & Bauer) was employed as the promoter to decompose the initiator at low temperatures. The inhibitor, 300 ppm benzoquinone (BQ, Aldrich), was used to control the curing process. The initiators used in this study included a single component initiator, methyl ethyl ketone peroxide (MEKP, Hi-point 90, Witco), and a dual initiator system, i.e. MEKP/*tert*-butyl peroxybenzoate (TBPB, Trigonox C, Akzo Noble). Trigonox C is a solution of 98% *tert*-butyl peroxybenzoate with 8.0% activate oxygen, while Hi-point 90 contains 38% peroxide with 9.0% activate oxygen. All materials were used as received without further purification in order to mimic industrial applications.

2.2. Instrumentation and procedures

2.2.1. Differential scanning calorimeter (DSC)

The overall reaction rate was measured by a differential scanning calorimeter (DSC2910, TA Instruments). The sample was sealed in a hermetic aluminum sample pan that can withstand 2 atm internal pressure after sealing. After mixing the reactants, about 10 mg sample was placed in a DSC pan. Isothermal runs were conducted at pre-specified temperatures (i.e. 35, 60, 75, 100 °C) for long enough time until no further reaction exotherm could be detected. The samples were then followed by scanning from 30 to 300 °C to determine the residual exotherm with a heating rate of 5 °C min^{-1}. The total heat of reaction during curing was calculated from the area under both isothermal and residual scanning DSC curves and the reaction rate or conversion was based on the total heat calculated by this method.

2.2.2. Fourier transform infrared (FTIR) spectroscopy

Because it is difficult to get information by means of DSC measurements to differentiate overlapped multiple reactions, a computer-assisted Fourier Transform Infrared (FTIR) spectroscope (Nicolet, Magna 550II) with a resolution of 4 cm^{-1} in the transmission mode was used in this study for kinetic measurements of individual reaction of both St and UP C=C bonds. FTIR has the ability to accurately monitor the complex reactions based on spectra changes of different functional groups. After the reactants were mixed, one drop of mixture was placed between two sodium chloride plates, which were then mounted on a sample holder located in the FTIR chamber. A temperature controller was designed to maintain the reaction temperature. Four consecutive, 10-s scans were taken at each sampling time. The sampling interval was 1 s to 5 min during the reaction, depending on the reaction rate. Each measurement ended at a preset time. All IR spectra in this study are shown in absorbance mode.

Infrared absorption is based on the fact that each chemical group in a sample absorbs infrared radiation of some characteristic frequencies. The amount of light intensity of transmission relative to the amount of light intensity incident on the sample can be related directly to the concentration of the absorbing species by Beer's law

$$A_i = \beta_i l C_i \tag{1}$$

where A_i is the absorbance of species which can be determined from the peak height or peak area, β_i is the absorptivity which is characteristic of absorbing species i, l is the pathlength (sample thickness), and C_i is the concentration of absorbing species i.

Fig. 1 shows typical FTIR spectra of an unsaturated polyester resin during reaction. Consumption of styrene C=C bonds is indicated by changes of peak area at 912 and 992 cm^{-1} (CH_2=CH deformation), while consumption of unsaturated polyester C = C bonds is indicated by a peak area change at 982 cm^{-1} (trans CH=CH deformation) [7].

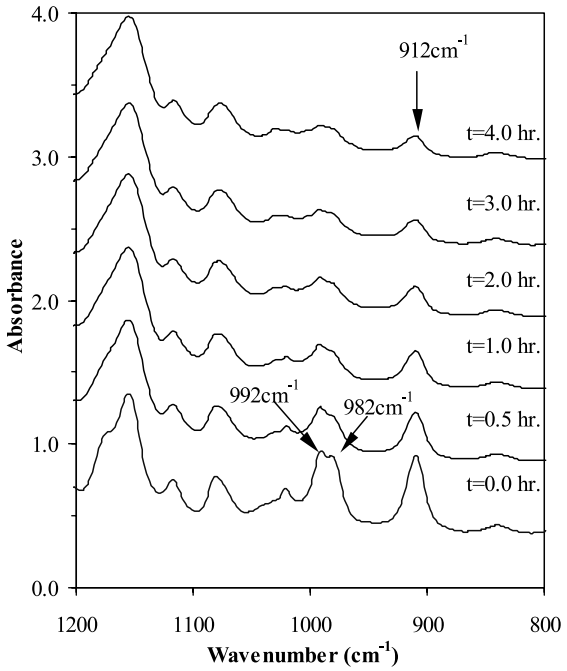


Fig. 1. FTIR spectra of an unsaturated polyester resin during curing (St/UP C=C bond ratio = 2/1, 0.5% CoOct, 1.5% MEKP, 60 °C, 300 ppm BQ).

To compensate for the changes of thickness and opacity in the sample during curing of the UP resin, the C–H peak at 2942 cm^{-1} was chosen as the internal standard to normalize the interested spectra area.

Before applying Beer's law to the quantitative analysis, the calibration curves for styrene C=C bonds and unsaturated polyester C=C bonds were established by preparing a series of styrene-dibromomethane solutions and unsaturated polyester-dibromomethane solutions of known concentration. During calibration, the solutions were placed between two sodium chloride plates with a 25 μm thick Teflon spacer to keep all the samples in the same thickness. The calibration curves based on the change of peak area for styrene-912 cm^{-1}, styrene-992 cm^{-1}, and UP- 982 cm^{-1} are shown in Fig. 2. A linear relationship between the peak area and monomer concentration was obtained for all three peaks. The absorptivity for each peak can be determined from the slope of the calibration line.

In the reaction system of unsaturated polyester and styrene, the styrene consumption during the reaction can be determined easily from the peak area change at 912 cm^{-1} based on Beer's law. The styrene conversion (α_{St}) can then be determined according to the following equation:

$$\alpha_{St} = 1 - \left(\frac{\bar{A}_t}{\bar{A}_0}\right)_{912} \tag{2}$$

where $\bar{A}_0$ and $\bar{A}_t$ are the normalized absorbance of the functional group before the reaction and at reaction time t, respectively. However, the consumption of polyester C=C bonds cannot be followed directly from peak 982 cm^{-1} because it overlaps with peak 992 cm^{-1} as shown in Fig. 1.

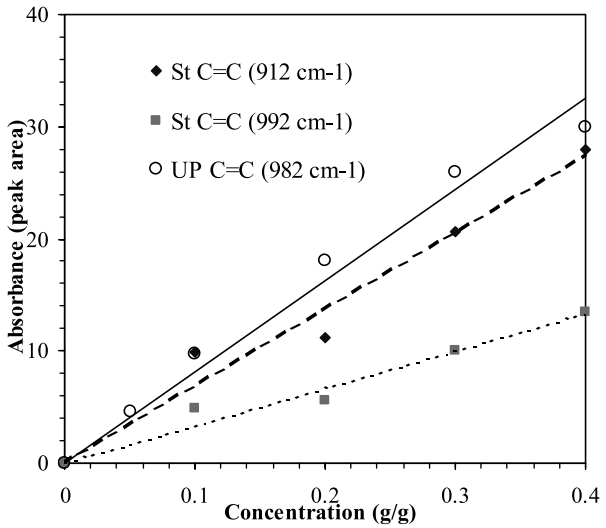


Fig. 2. FTIR calibration curves for peaks of styrene vinyl (912 and 992 cm^{-1}) and UP vinylene groups (982 cm^{-1}) at 35 °C.

A subtraction method was used to separate the overlapping peaks [7] and the unsaturated polyester conversion (α_{UP}) can be calculated according to the following equation:

$$\alpha_{UP} = 1 - \frac{1}{BI} \times \left[\left(1 - \left(\frac{\bar{A}_t}{\bar{A}_0}\right)_{982+992}\right)(1+BI) - (1-\alpha_{St})\right] \tag{3}$$

where $B = \beta_{982}/\beta_{992}$ and $I = (C_{UP}/C_{St})_0$ which is the initial concentration ratio of UP (C_{UP}) and styrene (C_{St}) C=C bond. The overall conversion of C=C bonds (α_T) can be expressed as

$$\alpha_T = \frac{\alpha_{St} + I\alpha_{UP}}{1+I} \tag{4}$$

In the resin system with LPA, styrene, UP and LPA are observed to have a weak absorption peak at 1020 cm^{-1} that overlaps somewhat with the absorption peak at 992 cm^{-1}, and this makes the calculation more complex. However, the absorptivity at 1020 cm^{-1} may be negligible because it is much weaker than at 992 and 982 cm^{-1}. In order to confirm this assumption, the absorbance of peak at 992 and 982 cm^{-1} in the resin system at different St/UP ratios was determined by FTIR. The absorbance of the St C=C bond at 992 cm^{-1} in the St/UP or St/UP/LPA mixture can be calculated on the basis of Beer's law:

$$A_{992} = (\beta_{992}/\beta_{912})A_{912} = KA_{912} \tag{5}$$

where the absorbance of St at 912 cm^{-1} can be easily obtained because no other absorbance peaks are found in this region. The constant K was obtained by plotting the absorbance at 912 cm^{-1} vs. that at 992 cm^{-1} at different styrene concentrations in dibromomethane. A linear relationship can be clearly seen in Fig. 3 where K has a value of 0.48. A_{982} in the resin mixtures can then be determined by subtracting $A_{992}$from the overall peak area of

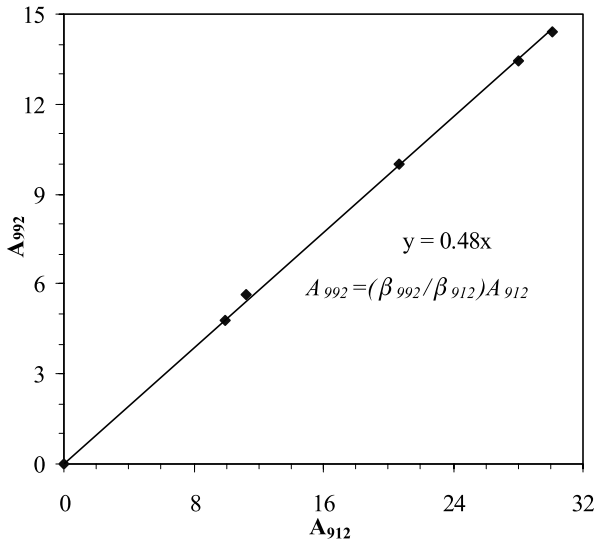


Fig. 3. Calibration of absorption peaks at 912 and 992 cm^{-1} of styrene vinyl groups in FTIR.

overlapped peaks. As shown in Fig. 4, the peak area ratio vs. the concentration ratio gives a linear relationship for the two peaks of interest, 982 and 992 cm^{-1}, and verifies the constant B according to Beer's law $A_{982}/A_{992} = B(C_{UP}/C_{St})$. Therefore, the absorbance at 1020 cm^{-1} due to the presence of LPA can be neglected and Eqs. (2)–(4) can also be used to calculate the individual and overall conversions of resin systems with LPA.

2.2.3. Volume shrinkage determination

The density and volume change of the cured sample were measured in this study. About five grams of a liquid resin with initiators were sealed in a plastic pouch with a surface dimension of 70 × 60 mm^2 and a thickness of almost 1 mm. The sealed sample pouch was degassed under vacuum and the air bubbles inside the pouch were squeezed out through a hole made at the edge of the pouch. The pouch was then heat sealed again and placed in an oven to cure isothermally. The density of the cured samples was determined by weighing the samples in air and in water, respectively, at 25 °C. The density of the cured sample (ρ_s) and the volume shrinkage were calculated according to the following equations:

$$\rho_{s_0} = 1/\sum_{i=1}^{n}(W_i/\rho_i) \quad (6)$$

$$\rho_s = \rho_{H_2O} \times W_s/(W_s - W_w) \quad (7)$$

$$\text{Volume Shrinkage}(\%) = (1 - \rho_{s_0}/\rho_s) \times 100 \quad (8)$$

where ρ_{s_0} is the theoretical density of the resin before cure as calculated by the summation of the weight content (W_i) and density (ρ_i) of each component i, and n is the total number of components in the resin system before cure. ρ_{H_2O} is the density of water at 25 °C. W_s and W_w are the sample weight when weighed in air and in water, respectively.

2.2.4. Scanning electron microscopy (SEM)

The sample morphology was observed by a scanning electron microscope (SEM, Philip XL-30). The fracture surfaces of the cured sample without solvent etching were gold-coated and observed under 10 kV power.

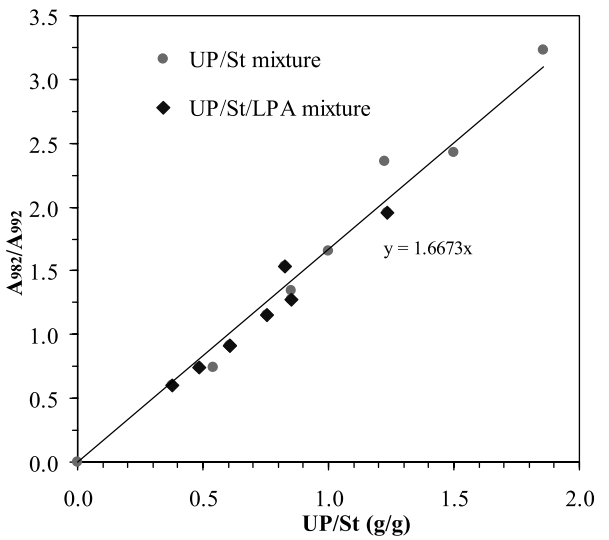


Fig. 4. Calibration curve of polyester vinylene and styrene vinyl groups in FTIR with and without LPA.

3. Results and discussion

3.1. Reaction kinetics and final conversions of unsaturated polyester resins

3.1.1. Effect of initiators

The type of initiator can influence the residual UP unsaturation and styrene monomer in the curing of unsaturated polyester resins [10,11]. An earlier study found that a low residual styrene content could be obtained with high levels of peroxide in polyester resins cured at room temperature [12]. However, a high initiator content may shorten the gel time. A sufficiently long gel time is very important for mold filling and fiber wetting. Recently, more effort has been given to the design of efficient curing agent systems to achieve desired performance at low temperature cure, i.e. high final conversion, long pot life, and short cycle time [13,14].

Most high temperature molding processes involving UP resins use a combination of two or three peroxides. They work in a stepwise fashion. The low temperature peroxides start to decompose first, while the higher temperature peroxides are slow to decompose in the beginning, but become highly activated to propel the reaction towards the end due to reaction exotherm. This concept can be used in low temperature molding processes as well by choosing different initiator combinations.

In this study, MEKP/TBPB was chosen as a dual initiator

combination since both MEKP and TBPB can be accelerated with metal-based promoters. MEKP alone can be used as an initiator when the temperature is higher than 60 °C. At ambient temperature, it decomposes into free radicals very slowly and cannot cure unsaturated polyester resin without promoters. In the presence of cobalt octoate or naphthenate, it can be decomposed rapidly for fast polymerization and to achieve short curing cycle. On the other hand, TBPB is a typical high temperature initiator with a half-life of 1 h at 122 °C (Trigonox C). The effect of cobalt on the decomposition of TBPB at low temperature is not as significant as on MEKP.

Fig. 5 shows the scanning DSC results of the unsaturated polyester resin with 3.5% LPA cured at a heating rate of 2 °C min^{-1} by different initiator combinations. Under this scanning rate, the reaction in the system initiated by 0.4% TBPB occurs only when the temperature reaches 110 °C, which is intrigued by the thermal decomposition of peroxybenzoate. In the presence of promoter (CoOct), the redox initiation takes place so that the reaction may occur at a lower temperature, i.e. 90 °C, as compared to the case without any promoters. When the resin system is initiated by 1.3% MEKP, the reaction could occur when the temperature is 75 °C at the absence of CoOct, and at 30 °C with 0.5% CoOct.

TBPB alone (even with 0.5% CoOct) cannot be considered a low temperature initiator because the reaction temperature needs to reach almost 90 °C to ensure the occurrence of reaction. However, TBPB is more active compared to MEKP at high temperatures. For systems initiated by TBPB, when the temperature reaches the decomposition temperature of TBPB the reaction takes place and completes rapidly with a very narrow reaction peak. Although MEKP decomposes at a lower temperature, the reaction is gradual and has a broad peak. Therefore, TBPB is a good initiator to finish the reaction if the reaction exotherm can reach its decomposition temperature.

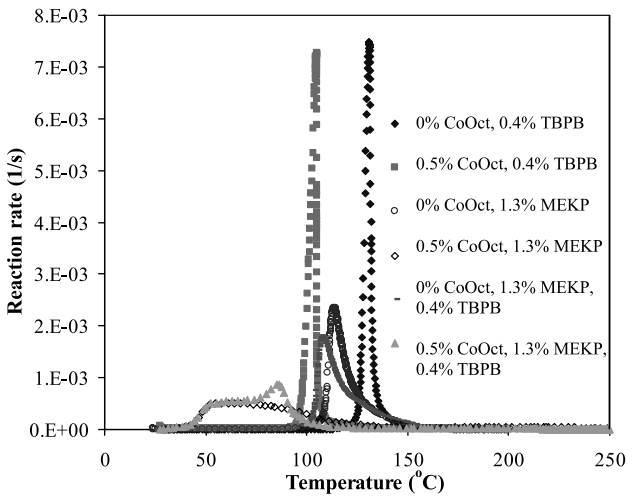


Fig. 5. DSC scanning profiles of UP/St/LPA system initiated by MEKP and TBPB (3.5% LPA, no BQ).

The resin systems were also initiated by a dual initiator of MEKP/TBPB. A combination of MEKP and TBPB was found to have a synergistic effect on the reaction of unsaturated polyester resin systems. As shown in Fig. 5, the reaction of a system initiated by MEKP/TBPB without CoOct occurs at a lower temperature than the system initiated by either MEKP or TBPB. This is probably because the decomposition of TBPB can be induced by free radicals already existing in the system, such as radicals derived from MEKP [15,16]. In the presence of 0.5% CoOct, the reaction initiated by MEKP/TBPB has almost the same profile as that by MEKP alone at a temperature lower than 75 °C. However, a reaction peak is observed at 88 °C by using MEKP/TBPB, which is lower than the decomposition temperature of TBPB with 0.5% CoOct. These results clearly demonstrate that the effective temperature of TBPB in the presence of CoOct at this curing condition can be as low as 75 °C when TBPB is combined with MEKP. Therefore, if the reaction exotherm increases the system temperature to 75 °C, the presence of TBPB may push the reaction to a higher conversion.

In order to study the efficacy of dual initiator on the final conversion of resin systems, unsaturated polyester resins with LPA cured by different initiator combinations under the same temperature profile were carried out in FTIR. The temperature profile was chosen according to the reaction exotherm profile of a UP/St/LPA system cured at room temperature. The system temperature was raised from 25 to 110 °C at a rate of nearly 6 °C min^{-1}, and then decayed to 25 °C. As shown in Fig. 6, the resin reaches nearly complete conversion when initiated by the dual initiator MEKP/TBPB, while the conversion is lower when initiated by MEKP alone even at a higher MEKP content. It is also observed that the reaction initiated by the dual initiator completes earlier than the reaction by MEKP only. The reaction rate profile shows an additional reaction peak in the resin system initiated by the dual initiator after 12 min (when the temperature reaches around 90 °C) and the reaction completes very quickly. This agrees well with the DSC results shown in Fig. 5. The final individual conversions of St and UP in Table 1 show that St and UP residue can be as low as 0.06 and 0.25 wt%, respectively, when initiated by the dual initiator, which is much lower compared to 2.44 and 2.69 wt%, respectively, when initiated by 2.0% MEKP at the same condition. An extra amount of MEKP does not provide the same efficacy as the dual initiator for resin conversion.

3.1.2. Effect of temperature

Reaction exotherm plays an important role in the curing of polyester resins. The peak temperature depends, among other factors, on the curing system and the thickness of samples. In low or ambient temperature cure, the peak temperature may reach 200 °C for very thick pure resin samples, or only 40 °C for thin samples with a large amount of fillers and fibers in typical composite molding processes.

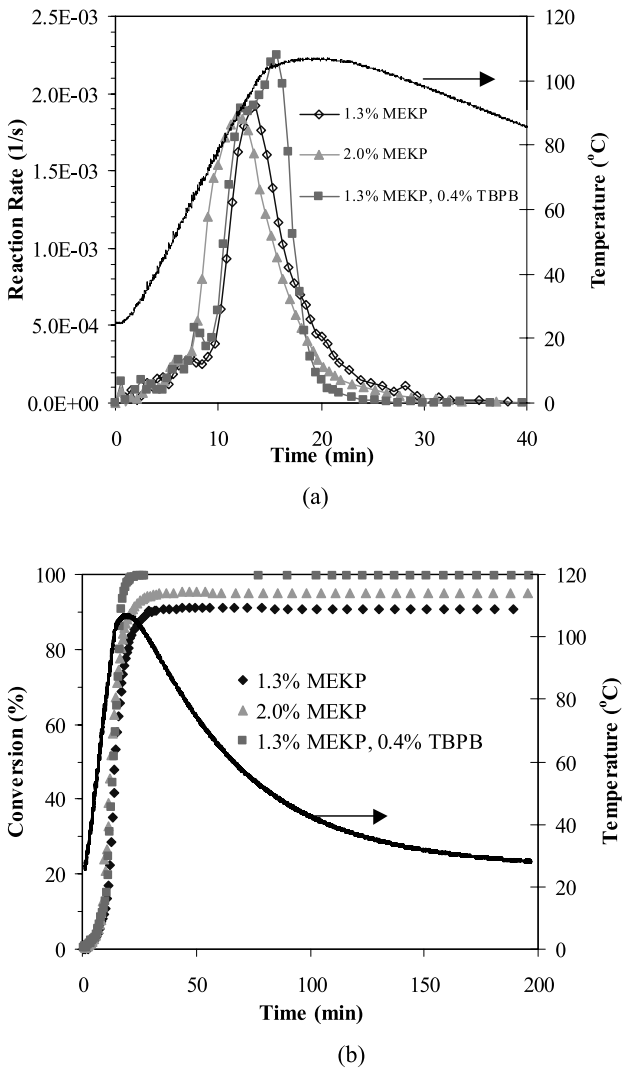


Fig. 6. FTIR (a) reaction rate and (b) conversion profiles of UP/St/LPA systems initiated by MEKP and TBPB (3.5% LPA, 0.5% CoOct, 300 ppm BQ)

In order to study the effect of temperature on the reaction kinetics and final conversion of UP/St/LPA systems cured by different initiator combinations at different temperatures, a series of isothermal experiments were carried out at 35, 60, 75, 100 °C in both DSC and FTIR. In Fig. 7, the resin conversion profile at 100 °C measured by FTIR shows the same trend as the DSC profiles, but is slightly different from DSC results especially at the later stage of the reaction. The difference exists because of instrument variation and the sensitivity limitation of DSC at high conversion. Within experimental error, the results from both methods agree with each other fairly well. Fig. 8 shows that the reaction rate and final resin conversion of UP/St/LPA increase with the reaction temperature as expected. This occurs because the chains of the polymer network become more mobile and the resin can further react at higher temperatures,

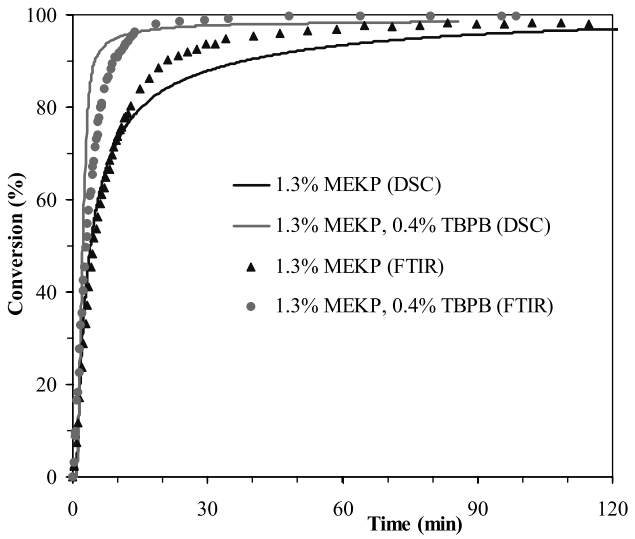


Fig. 7. DSC and FTIR resin conversion profiles of unsaturated polyester with different initiators cured at 100 °C isothermally (3.5% LPA, 0.5% CoOct, 300 ppm BQ).

resulting in higher final conversion and lower styrene residue. When the resin systems are initiated by MEKP only, the final conversion at each temperature is not as high as the conversion in the dual initiator system. This effect is more obvious at lower temperatures.

The reaction of polyester resin is a copolymerization between styrene and unsaturated polyester C=C bonds. The structure formation depends on the relative reaction rates of styrene vinyl to unsaturated polyester vinylene groups. Fig. 9 shows the relative reaction rates of styrene vs. unsaturated polyester C=C bonds measured by FTIR at different temperatures with different initiator combinations. The dashed lines shown in the figure represent two extreme cases: the upper one is under the azeotropic condition and the lower one is for alternating copolymerization. As can be seen from this figure, the actual reaction profiles lie between these two extremes and are concave upward. In the beginning, the curves are nearly linear (with a slope around 0.75). In the later stage, the reaction of the unsaturated polyester vinylene group slows down after 70% conversion, while the styrene reactivity remains relatively high depending on the reaction temperature and initiator used. The results imply that, at low conversion, both styrene and unsaturated polyester molecules are active, and the copolymerization follows a constant consumption rate of both monomers. At higher conversion, due to the low mobility of unsaturated polyester vinylene groups in the highly crosslinked network, most of the reaction occurs between styrene vinyl groups. The addition of TBPB further increases the reaction of St at the later stage since it can provide free radicals then.

Table 1 summarizes the final residual St and UP content of UP/St/LPA systems cured at different temperatures and using different initiator combinations measured by FTIR. As the temperature increases from 35 to 100 °C, the residual St

Table 1
Final individual and overall conversions and residual contents in UP/St/LPA systems at different cure temperatures and using different initiators (3.5% LPA, 0.5% CoOct, 300 ppm BQ)

	Temperature (°C)	α_{Total} (%)	α_{St} (%)	α_{UP} (%)	Residual (wt%)	
					St	UP
1.3% MEKP, 0.4% TBPB	35	78.7	77.8	80.6	12.3	8.0
	60	96.1	98.4	91.5	0.9	3.5
	75	98.0	99.5	94.9	0.3	2.1
	100	99.6	100.0	98.4	0.0	0.7
1.3% MEKP, 0% TBPB	35	72.0	68.2	79.7	17.6	8.4
	60	86.9	86.9	87.0	7.2	5.4
	75	87.4	87.2	87.5	7.1	5.2
	100	98.8	99.2	98.1	0.5	0.8
1.3% MEKP	Non-isothermal	90.7	90.2	91.9	5.44	3.35
2.0% MEKP	Non-isothermal	94.9	95.6	93.5	2.44	2.69
1.3% MEKP, 0.4% TBPB	Non-isothermal	99.7	99.9	99.4	0.06	0.25

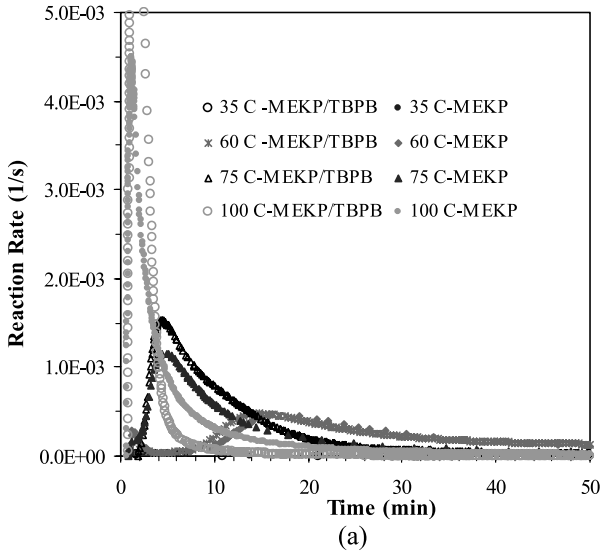
content decreases from more than 10% to nearly 0% when initiated by the dual initiator systems. It was also observed that the final conversion of systems initiated by MEKP only was lower compared to that initiated by the dual initiator system. It is clear that St monomers can further react in the presence of TBPB when the UP vinylene double bonds become immobile.

3.2. Volume shrinkage of unsaturated polyester resins

Unsaturated polyester resins have very large volume shrinkage during polymerization. There are several problems associated with the high shrinkage of UP resins, including sink mark formation, surface waviness, warpage, poor dimension accuracy, internal crack, etc. These problems can be solved by adding LPAs. The shrinkage control mechanism of LPAs has been investigated extensively. Although not fully understood, it is generally accepted that the shrinkage compensation is due to the stress-related micro-void formation in the LPA phase and interfacial regions between the LPA and UP resin [17–20]. A phase separation between the LPA and UP resin during curing is necessary for stress cracking because it provides an LPA-rich phase and an interface between the UP-rich and LPA-rich phases. The phase separation is related not only to the chemical structure, molecular weight, and dipole moment of LPAs [17,21,22], but also to the structure and composition of UP resin and monomer [23]. The micro-void and micro-crack formation for volume shrinkage compensation is influenced by the relative reaction rate in the LPA-rich and the UP-rich phases, which also depends on the resin and LPA structure and the reaction temperature and curing agent [24,25]. The results in the previous sections show that both the curing agent and reaction temperature have strong influence on the reaction kinetics and final conversion of UP/St/LPA resins systems. In this section, the effect of reaction temperature on volume shrinkage control of UP/St/LPA resins initiated by dual initiator is studied.

Fig. 10 summarizes the volume shrinkage of UP/St/LPA initiated by the dual initiator MEKP/TBPB at different temperatures. Samples were cured in an oven at preset temperatures. In order to achieve a nearly isothermal condition, 5 g of sample were cured in a plastic pouch with a large surface area and the sample thickness was about 1 mm. This figure shows that LPA performance in samples with the same formulation varies as curing temperature changes. The volume shrinkage of the sample becomes larger as the temperature increases from 35 to 75 °C, but is smaller when the curing temperature reaches 100 °C. Li and Lee [23] explained the shrinkage control behavior of UP/St/LPA systems cured at different temperatures by two competing factors: shrinkage caused by polymerization and expansion induced by micro-void formation. A difference in curing temperature may also cause a remarkable change on sample morphology. It can affect the size and the amount of micro-voids formed in the materials, which in turn has an effect on the volume shrinkage of the systems [26]. As shown in Fig. 11, the sample morphology reveals a two- phase co-continuous structure at 35 °C. One is a particulate phase (LPA-rich) in which spherical particles with diameters ranging from 1 to 5 μm are loosely packed. The other phase is a flake-like region (UP-rich) with domain sizes ranging from 10 to 20 μm. When the curing temperature reaches 60 °C, a similar two-phase structure is again observed but it is no longer co-continuous. The particulate region is smaller and becomes the dispersed phase with a domain size less than 20 μm, while the flake-like region forms the continuous phase. By further increasing the curing temperature to 75 and 100 °C, the structures of the samples become similar to that cured at 60 °C except that the size of the particulate region is even smaller. The various morphological structures result in different interface areas, strongly affecting the shrinkage control.

The curing temperature may also influence the relative reaction rate in the LPA-rich and UP-rich phases, which is



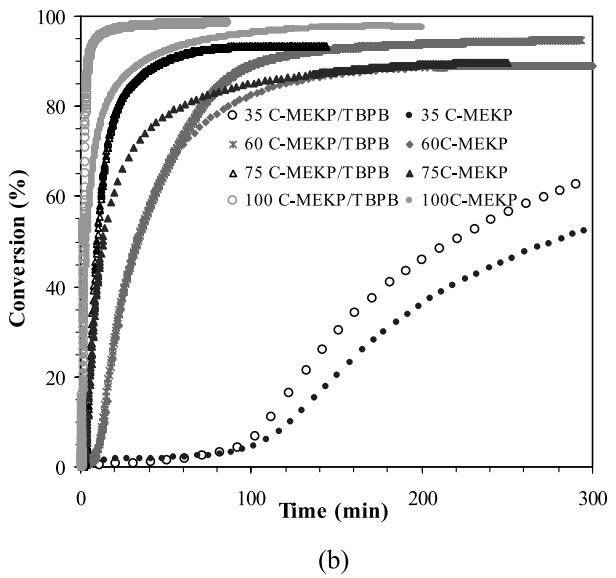


Fig. 8. DSC (a) reaction rate and (b) resin conversion profiles of UP/St/LPA at various temperatures and initiator combinations (3.5% LPA, 0.5% CoOct, 300 ppm BQ).

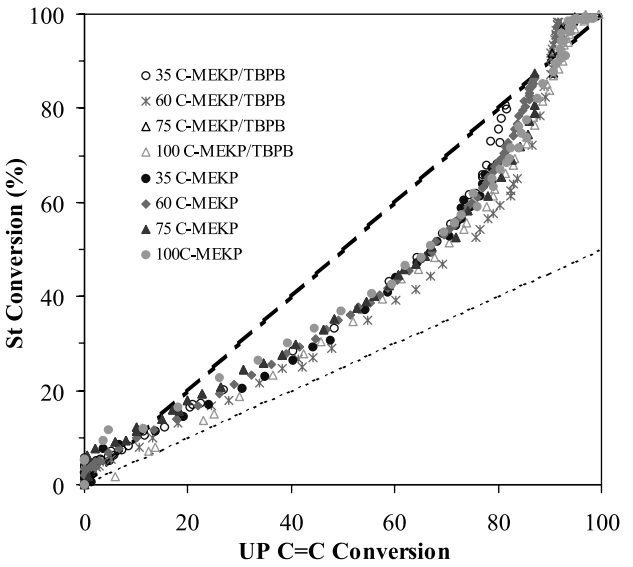


Fig. 9. Relative conversion of styrene vs. unsaturated polyester C=C bonds at various temperatures and initiator combinations (3.5% LPA, 0.5% CoOct, 300 ppm BQ).

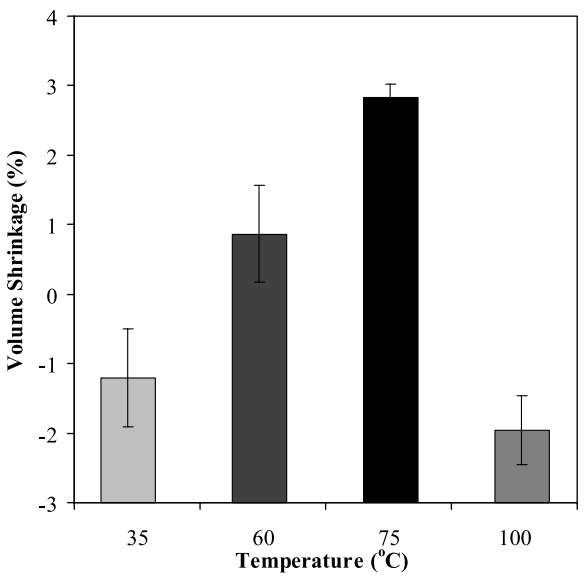


Fig. 10. Volume shrinkage of UP/St/LPA systems cured at different temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

an important factor for micro-void formation. Therefore, it is important to investigate the effect of temperature on reaction in each phase. Since reaction-induced phase separation in resin polymerization is a dynamic and evolving process, it is impossible to track this continuously changing phase behavior. In this study, a temperature-forced phase separation method was used as a qualitative assessment on how the partition of chemical species during phase separation affects resin reaction and shrinkage control in the UP/St/LPA systems. The formulated UP, St, LPA, and BQ were mixed with either CoOct or MEKP/TBPB simultaneously so that a transparent (single-phase) mixture was obtained. The formulation was the same as that used in the kinetic and volume shrinkage study, except that the content of promoter or initiators was doubled. The detailed procedures of temperature induced phase separation can be found in a previous paper [25]. After two phases were separated, their reaction conversion and gel time were measured at different temperatures by mixing an equal amount of resin from the same phase of the two mixtures. The results are shown in Fig. 12. It is obvious that the reaction in the UP-rich phase is much faster than in the LPA-rich phase at all temperatures. The dashed lines in the figure indicate the time when the LPA-rich phase gels. At this time, the UP-rich phase has a slightly lower conversion when cured at a higher temperature. Since the final conversion of the resin system cured at the higher

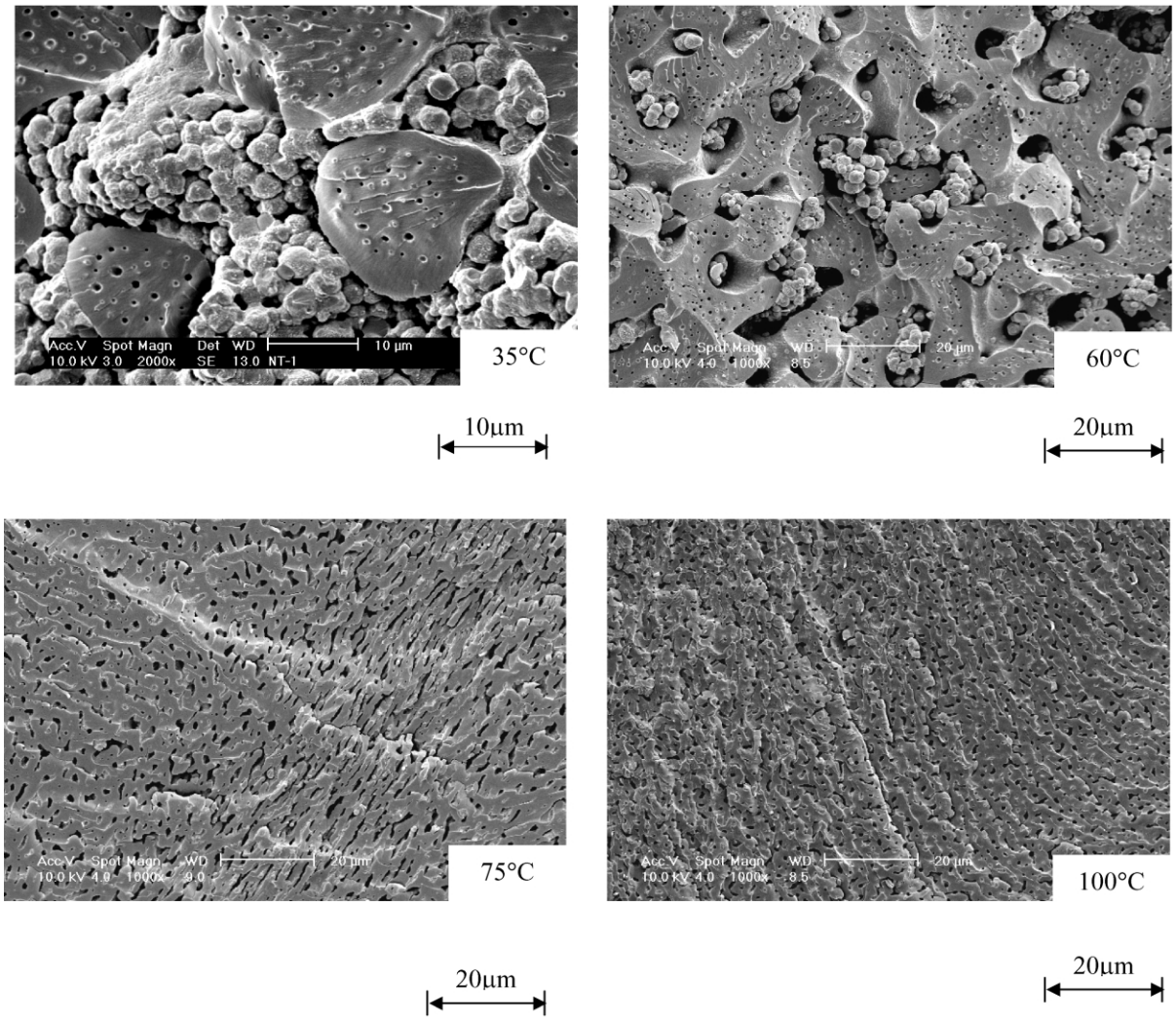


Fig. 11. Morphology of St/UP/LPA samples cured at different temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

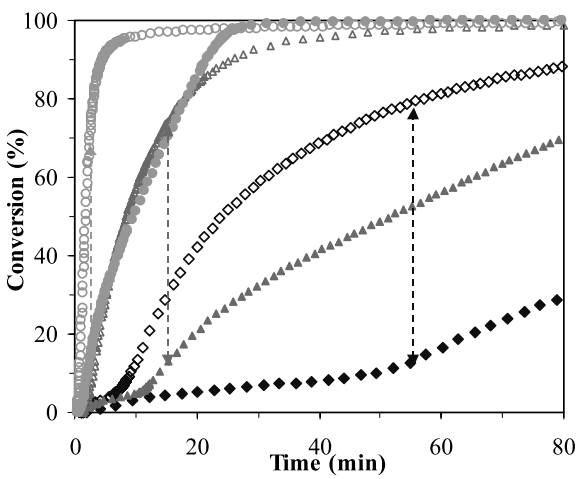


Fig. 12. DSC conversion profiles of LPA-rich and UP-rich phases of UP/St/LPA system cured at various temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ); (◆) 60 °C (LPA-rich); (◇) 60 °C (UP-rich); (▲) 75 °C (LPA-rich); (△) 75 °C (UP-rich); (●) 100 °C (LPA-rich); (○) 100 °C (UP-rich).

temperature is higher, a larger extent of polymerization has occurred in the UP-rich phase after gelation of the LPA-rich phase. The large polymerization shrinkage in the UP-rich phase may have induced substantial micro-void formation that compensates the overall resin shrinkage [25].

As the reaction temperature increases, the LPA may change from the glassy state to the rubbery state. This may provide a large thermal expansion to compensate polymerization shrinkage of the UP resins in the non-isothermal curing cases, and weaken the LPA-rich phase to facilitate micro-void formation in the isothermal curing cases. The T_g of the LPA used in this study was measured by DSC to be 43–45 °C. In the cured system, the T_g of the LPA-rich phase should be higher than 43–45 °C, but lower than 100 °C (T_g of polystyrene). Therefore, the thermal effect on LPA performance cannot be neglected in the temperature range used in this study.

From the above discussion, many factors such as phase separation, relative reaction rates in the LPA-rich and UP-rich phases, and the T_g of the LPA will affect the final volume shrinkage of the cured resin. The resin systems with

the same formulation but cured at different temperatures show different volume shrinkage because of the competition from all these factors. At 35 °C, the LPA is in the glassy state. The system shows fairly good shrinkage control since it has a clear phase separation and a large interface area for micro-void formation. When the system is cured at 100 °C, the thermal effect dominates and the resin system can again provide good shrinkage control. When the resin system is cured at the intermediate temperatures, the phase separation is not very clear and the thermal effect is not very strong; consequently, the shrinkage control turns out to be poor.

4. Conclusions

The residual styrene and volume shrinkage of an unsaturated polyester resin with a low profile additive cured with low temperature curing agents at different reaction temperatures and initiator combinations were investigated. In the study of reaction kinetics, both DSC and FTIR were employed to obtain the overall and individual reaction rates and conversion profiles. It was found that the final conversion and residual styrene could be greatly improved by introducing a dual initiator system. The relative reaction profiles of styrene vs. UP C=C bonds tend to merge into a single master curve, which suggests that the structure formation is similar at different reaction temperatures and using different types of initiators. The study on shrinkage control shows that LPA performs worse in the intermediate temperature range (e.g. 60 and 75 °C). The effect of temperature on morphology, the relative reaction rate in the LPA-rich and UP-rich phases and micro-void formation all influence the final shrinkage.

Acknowledgements

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