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Control of volume shrinkage and residual styrene of unsaturated polyester resins cured at low temperatures. II. Effect of comonomer

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Abstract

The effect of a comonomer, methyl methacrylate (MMA), on volume shrinkage and residual styrene content of an unsaturated polyester (UP) resin with low profile additives (LPAs) cured at low temperature was investigated by an integrated reaction kinetics-morphology-property analysis. MMA affects the volume shrinkage and residual styrene content differently depending on MMA to styrene (St) C=C bond molar ratio. At low MMA/St ratio, residual styrene decreases and the volume shrinkage of the resin system remains unchanged. At high MMA/St ratio, residual styrene can be substantially reduced, but the resin system suffers poor volume shrinkage control. Reactivity of the comonomer MMA and its compatibility to other components in the resin system can explain the observed results. A series of Seemann composites resin infusion molding process (SCRIMP) were conducted to study the relationship among materials, processing, and properties of molded composites in low temperature curing processes.

Keywords: Unsaturated polyester resins; Volume shrinkage; Residual styrene

1. Introduction

In Part I of this series, we found that the residual styrene content can be decreased by using a dual initiator system. However, the residual styrene content is still quite high at low temperatures. Most studies on final conversion of UP resin systems have emphasized improving the resin flexibility and initiator type [1–3]. Few works have been carried out to improve the reaction at later stage by increasing the reactivity of monomer, such as introducing more reactive comonomers (e.g. methyl methacrylate and trimethylolpropane trimethacrylate) into the resin system [4,5].

The addition of thermoplastics as low profile additives (LPAs) to the unsaturated polyester resin can substantially reduce the shrinkage caused by polymerization. The performance of LPAs is strongly dependent on the phase separation and the formation of micro-voids during polymerization. Both factors are strongly related to the compatibility and partition of chemical components in the resin system and the relative reaction rate in separated phases [4–8]. Introducing a comonomer into the resin system may influence not only the reactivity but also the compatibility of the resin system. In this study, an integrated analysis is carried out to investigate how the residual styrene content and volume shrinkage of cured resins are affected by the addition of a comonomer.

2. Experimental

An unsaturated polyester resin, Aropol Q6585, provided by Ashland Chemical was used in this study. Q6585 is a step-growth product of 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 wt% of styrene. Methyl methacrylate (MMA, Aldrich) was introduced into the resin system as a comonomer. All of the samples being tested were formulated to provide a monomer double bond to unsaturated polyester double bond ratio of 2.0. The initiator used was a dual initiator system, i.e. methyl ethyl ketone peroxide (MEKP, Hi-point 90, Witco)/*tert*-butyl peroxybenzoate (TBPB, Trigonox C, Akzo Noble). The compositions of resins used in this study are given in Table 1. All

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Table 1
Formulations used in this study

MMA/St (molar ratio)	Q6585 (g)	LPAs (g)	St (g)	MMA (g)
0	6.363	0.946	2.691	0
0.1	6.375	0.946	2.196	0.483
0.4	6.403	0.946	1.126	1.524
0.6	6.415	0.946	0.634	2
0.8	6.425	0.946	0.249	2.38
1.0	6.433	0.946	0	2.681

Q6585 contains 35 wt% of styrene; LPA contains 63 wt% of styrene.

materials were used as received without further purification in order to mimic industrial applications. The characteristics of Q6585 and other materials as well as the preparation procedures have been described in Part I [9].

A differential scanning calorimeter (DSC) and a computer-assisted Fourier transform infrared (FTIR) spectroscope were used to determine the overall and individual reaction rate and conversion profiles during reaction. Sample morphology was observed by a scanning electron microscope (SEM). Density and volume change of the cured sample were measured by weighing the cured sample in both air and distilled water. Details of instrumentation and procedures have been given in Part I [9]. MMA was introduced into the resin system as a comonomer. Its conversion and consumption rate can be followed by the peak area change at 945 cm^{-1} in FTIR. The analysis method is similar to that for styrene conversion. The same calibration procedure as described in Part 1 was followed to confirm that a linear relationship exists between the MMA concentration and the peak area at 945 cm^{-1}.

The glass transition temperature, T_g, is one of the most important material parameters for glassy polymers. It is not easy to determine the T_g of low temperature cured samples by the conventional method since all of the samples are partially cured. Several researchers reported that the derivative of the heat flow curve during a DSC scan of the partially cured sample at 5 °C/min could be used to determine T_g. A peak temperature in the plot of heat flow derivative vs. temperature has been used to represent the T_g partially cured sample [10,11]. Others have chosen the temperature when the residual reaction starts to occur during the scanning run of the partially cured sample [12]. In this study, T_g of the post-cured UP/St/LPA resins was measured through dynamic mechanical analysis, which was performed using a rheometer (Rheometrics Solid Analyzer, RSAII). Samples with the dimensions of 30 mm × 13 mm × 2 mm were first cured in a 35 °C oven with different MMA contents for 720 min, and then heated in the RSA chamber through scanning at 5 °C/min from room temperature to 250 °C. A sinusoidal deformation is applied to the sample in the three-point bending mode at a frequency of 1 Hz. The support span is 20 mm and the strain imposed is 0.015%. Runs were carried out from room temperature to 250 °C at a heating rate of 2 °C/min. T_g values were the average of three measurements and were determined from the tan δ peaks [13] that are shown in Fig. 1.

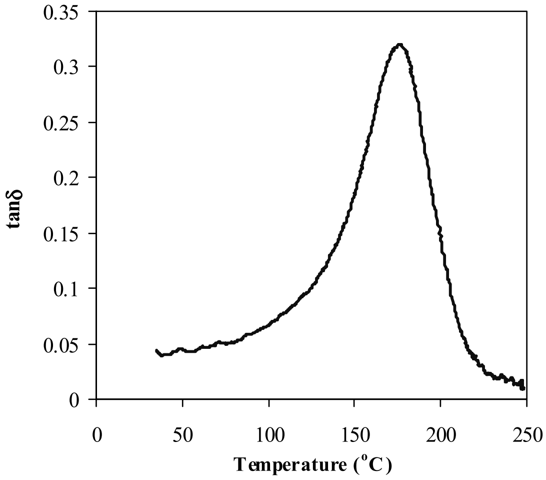


Fig. 1. Determination of T_g of post-cured sample from RSA scanning (St/UP = 2, 3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

The surface quality of the molded samples was measured by a profilometer, Federal's Surfanalyzer 4000. During a test, a hinged probe rides along the surface of the part, and the stylus tip moves up and down in relation to the probe body. The chosen tracing length was 2.54 cm. Each sample was tested randomly at six different locations, and the average value was calculated from the six tests.

The average roughness (R_a) is used to quantify the surface quality. R_a is the arithmetic average deviation of the roughness profile from the roughness centerline. It is computed as the following equation:

$$R_a = \frac{1}{N}\sum_{i=1}^{N} y_i$$

where N is the number of points in the roughness profile and y_i is the individual point in the roughness profile. A smaller value of R_a represents a better surface quality.

To characterize the flexural properties of the composite, a three-point bending test according to ASTM D790-96a was used. For flexural measurements, five rectangular bars of 130 mm in length and 13 mm in width were cut from each sample. The speed of cross-head motion was 2.8 mm/min. The load was recorded as a function of displacement for five specimens of each material. Values of modulus and strength at failure were obtained from the resulting load–displacement curves and the average values were reported.

3. Results and discussion

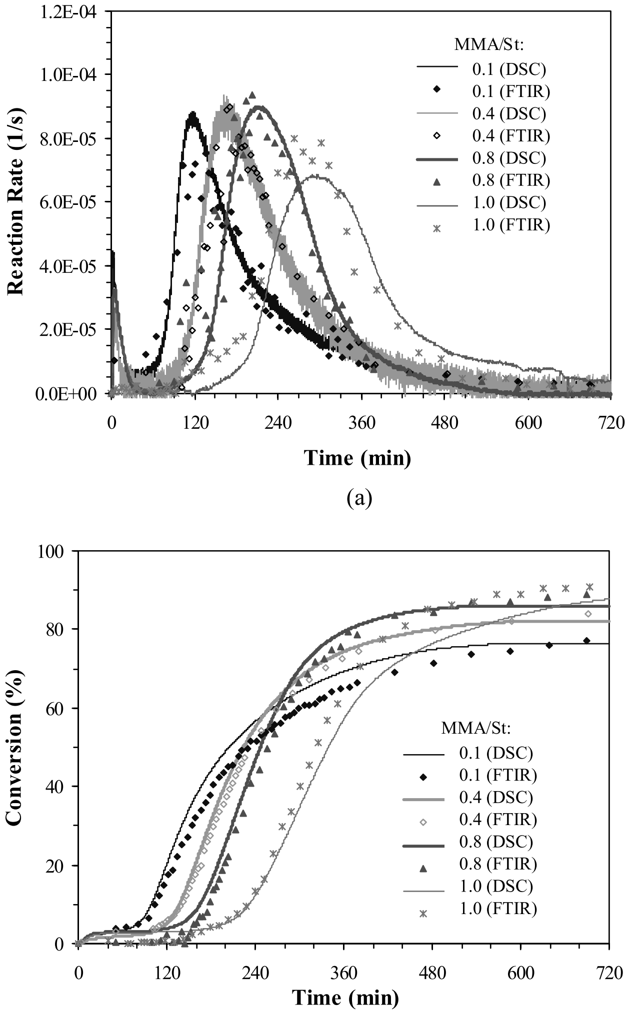
3.1. Reaction kinetics and final conversion

During the free radical copolymerization of unsaturated polyester (UP) and styrene (St), cross-linking causes the formation of a three-dimensional network, which results in gelation and microgel formation [14]. The reaction becomes diffusion controlled near and after gelation since the mobility of free radicals and reactants is impeded by the network structure. Unsaturated polyester is much less mobile than styrene monomer because of the size and the functionality of molecules. Polyester molecules are trapped in the network, which makes further reaction very difficult [15]. Therefore, at high conversion, the styrene reaction is more favorable than the polyester reaction. However, the homopolymerization rate of styrene is very low [7], so it is difficult to achieve a high final conversion especially at low temperatures. The reaction at later stage may be enhanced at the presence of comonomers that have a high copolymerization reactivity with styrene, such as acrylonitrile, methyl methacrylate, isoprene, etc.

In order to study the effect of comonomer on reaction rate and final conversion of UP/St/LPA resin systems, a series of experiments were carried out at 35 °C isothermally. The comonomer chosen was methyl methacrylate (MMA) because the copolymerization between MMA and styrene is much higher than that of styrene homopolymerization. The monomer reactivity ratios in copolymerization, i.e. the ratios of the rate constant for a given radical adding its own monomer to that for adding the co-monomer, in the styrene (M1)–methyl methacrylate (M2) system are: $r_1 = 0.28–0.59$ and $r_2 = 0.31–0.54$. Both r_1 and r_2 are less than 1, meaning that the radical prefers to add the co-monomer in the St/MMA copolymerization with a selectivity about 2 in this case [16,17].

The effect of MMA content on the reaction kinetics measured by both DSC and FTIR is shown in Fig. 2. The monomers, styrene and MMA, to unsaturated polyester vinylene double bond ratio remains at 2/1 for all of the samples. One can see that the reaction of UP/St/LPA systems slows down and the onset of auto-acceleration occurs at a later time as more MMA is added into the resin system. The highest reaction rates for different MMA contents are similar except for the system with a MMA/St molar ratio of 1. This system has a lower peak reaction rate and a longer reaction time at 35 °C. However, the final resin conversion is higher as more MMA is added into the UP/St/LPA systems.

MMA monomer contains 10–100 ppm monomethyl ethyl hydroquinone (MEHQ) as inhibitor while St monomer contains 10–15 ppm *tert*-butylcatechol (TBC) as inhibitor. The amount of MEHQ and TBC changes as more MMA is introduced into the resin system. Since each inhibitor has its own inhibition efficiency [18], this may result in a different reaction onset time. In order to keep a constant inhibitor content in the resin system, the inhibitors in St and MMA were removed. Solid UP resin and LPA were then dissolved in the inhibitor-removed monomers. Benzoquione (BQ) of 100 ppm was then added into the resin mixture during sample preparation in the DSC study to prevent premature reaction. Fig. 3 shows reaction profiles of the resin systems.



(a)

(b)

Fig. 2. Effect of comonomer (MMA) content on (a) reaction rate and (b) resin conversion of UP/St/LPA cured at 35 °C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

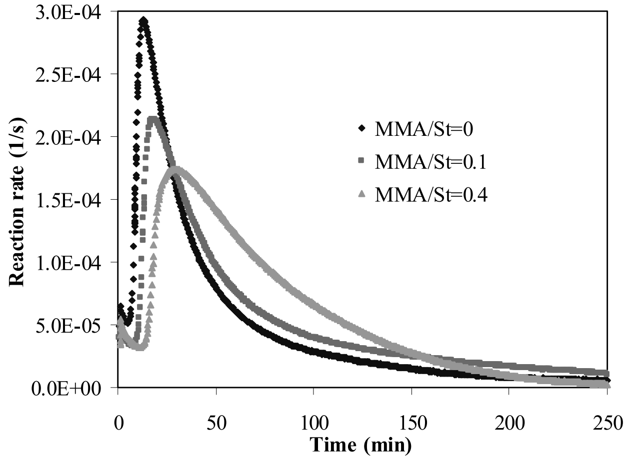


Fig. 3. Reaction rate profiles of UP/St/LPA resin systems with different comonomer (MMA) contents cured at 35 °C as inhibitor is removed from all reactants (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 100 ppm BQ).

The reaction of the UP/St/LPA systems still slows down and the onset of auto-acceleration occurs at a later time as the MMA in the resin system increases. This indicates that the type and amount of inhibitor in the reactants do not significantly influence the reaction trend in the resin system. Another possible factor is the reactivity difference between MMA and St and it could be the main reason.

The UP/St/LPA system with MMA is a very complicated reaction. There are three reactive components in the system, and the reactivity among them may affect the reaction rate and final structure of the cured resin. Fig. 4 shows the relative conversion profiles for St/UP C=C bond pair and St/MMA C=C bond pair at different MMA contents. Compared to the system without MMA, St C=C bond in the resin system with MMA shows relatively higher conversion when UP C=C bond reaches the same conversion, and up-bending of the curve at later stage becomes less obvious. The conversion of St C=C bonds is higher than that of MMA C=C bonds at early stage since the conversion of St C=C bonds is higher than the azeotropic polymerization line.

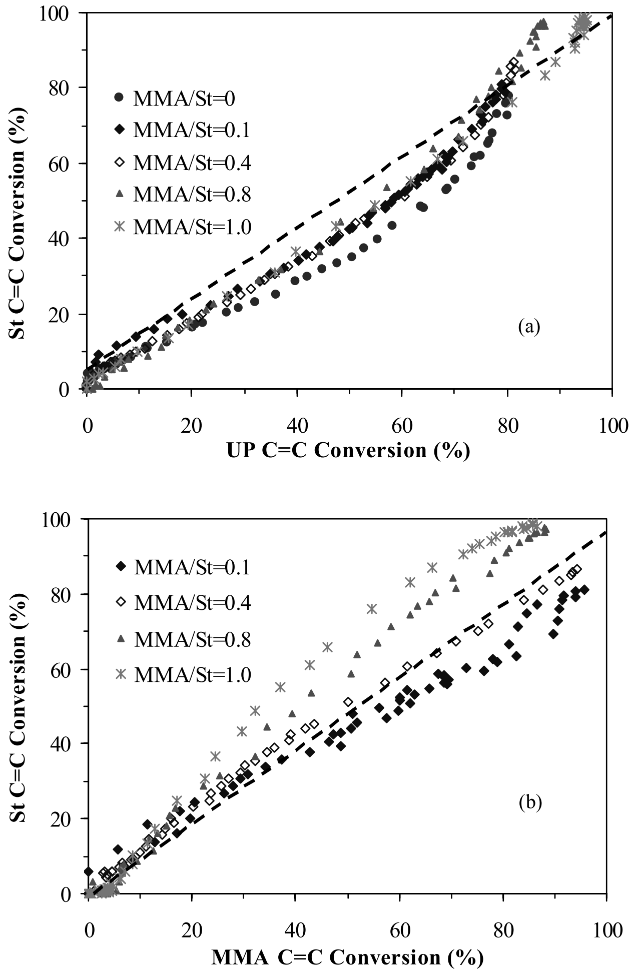


Fig. 4. Relative conversion of (a) St vs. UP and (b) St vs. MMA C=C bond of UP/St/LPA resin systems with different MMA contents cured at 35 °C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

Table 2 summarizes the residual St, MMA, and UP content of UP/St/LPA systems with different MMA contents cured at 35 °C. The residual St content decreases from more than 10 to 0.3% as the MMA content in the system increases. The final UP residue also decreases, except for the system with a MMA/St molar ratio of 0.1. On the other hand, more residual MMA is found in the cured sample when the MMA content increases. However, the total amount of styrene and MMA residue decreases.

Unsaturated polyester used in this study is a step growth product of maleic anhydride (MA) and propylene glycol (PG). The conventional polyesterification procedures lead to substantial isomerization of maleate to fumarate. From the literature, there is 95% fumarate structure in PG-MA type of unsaturated polyester resins [19]. Therefore, it is reasonable to assume that the reactivity of UP vinylene is close to that of diethyl fumarate (DEF). The monomer reactivity ratios among St, MMA, and DEF are given in Table 3 [17]. As can been seen from this table, the homopolymerization rate of unsaturated polyester molecules (DEF C=C bonds) is very low and UP C=C bonds can polymerize with St and MMA much easier. In fumarate/MMA C=C bond pair, it was found that the fumarate content in the copolymer of DEF and MMA is much lower than that in the initial feed through ^{1}H NMR study [20]. Since r_2 ($M_2 = \mathrm{MMA}$) is larger than 1, MMA prefers homopolymerization than copolymerization with the fumarate UP resin. Therefore, UP C=C bonds would react more favorably with St when MMA is introduced into the resin system. This results in a higher St conversion than MMA as shown in Fig. 4(b).

In this study, the monomer (both St and MMA) double bonds to unsaturated polyester double bonds ratio was fixed at 2.0. Adding MMA into the resin system results in a lower St/UP double bond ratio (decreases from 2/1 to 1/1). As shown in Fig. 5, the St C=C bond conversion at the same UP conversion increases before UP conversion reaches 50%, but the final St C=C bond conversion remains nearly the same as St/UP double bond ratio decreases from 3 to 1. Similar results were also reported in the literature [21–23]. Therefore, a decreased initial St content would not substantially reduce St residue. After reaction becomes

Table 2
Final individual and overall conversion and residual content in UP/St/LPA systems with different MMA contents cured at 35 °C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ)

MMA/St (molar ratio)	α_T (%)	α_{St} (%)	α_{UP} (%)	α_{MMA} (%)	Residue (wt%)		
					St	UP	MMA
0.0	78.7	77.8	80.6	–	12.3	8.0	–
0.1	80.8	81.1	78.9	88.2	9.6	8.7	0.6
0.4	86.3	86.8	81.2	94.3	5.3	7.8	0.9
0.8	90.9	97.2	86.4	88.2	0.9	5.7	2.8
1.0	93.1	98.8	95.0	85.6	0.3	2.1	3.9

Table 3
Monomer reactivity ratios [17]

Monomer 1	Monomer 2	r_1	r_2
DEF	St	0.02–0.11	0.29–0.63
DEF	MMA	0.04–0.05	2.1–40.3
St	MMA	0.28–0.59	0.31–0.54

diffusion control, the copolymerization between UP and St becomes more difficult since UP C=C bonds or radicals are bonded to the network structure. The remaining reaction would mainly be St homopolymerization if there were no MMA in the resin system. Since copolymerization between St and MMA is much easier than St homopolymerization, the presence of MMA would reduce residual St content.

Besides the reason mentioned above, the addition of MMA into the resin system may affect the flexibility of the polymer network. T_g of the post-cured samples with various amount of MMA after cured at 35 °C isothermally was compared in Fig. 6 because resin system can achieve higher final conversion with high MMA content and T_g depends greatly on the resin conversion [25,26]. As shown in Fig. 6, the T_g of post-cured samples decreases with an increase in MMA content in the resin system, except that T_g of the sample with a MMA/St molar ratio of 0.1 is lower than the sample of a MMA/St ratio of 0.4. It has been reported in the literature that introducing MMA segments into polystyrene would influence T_g of the MMA/St random copolymer [24]. When the MMA molar fraction in St/MMA monomer mixture is less than 0.6, the T_g of the random copolymer shows a negative deviation and the copolymer chain tends to be more flexible [24]. With the MMA/St molar ratio ranges from 0 to 1.0 in this study, molar fraction of MMA is from 0 to 0.5 if considering the mixture of St and MMA only. The molar fraction of MMA remains less than 0.6 till UP C=C bond conversion reaches 80% as shown in Fig. 7, which may lead to a lower T_g of the network compared to the system with only styrene as the cross-linking monomer. This may result in higher chain mobility in the network structure during reaction, consequently, reaction is relatively easy to go further after it becomes diffusion control and a higher final conversion can be achieved. The detailed mechanism needs further investigation.

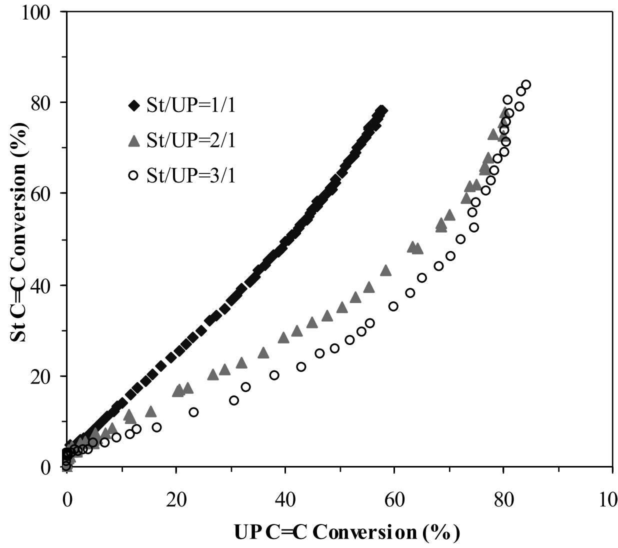


Fig. 5. Relative conversion of St vs. UP C=C bond of UP/St/LPA resin systems with different St/UP C=C bond ratios cured at 35 °C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

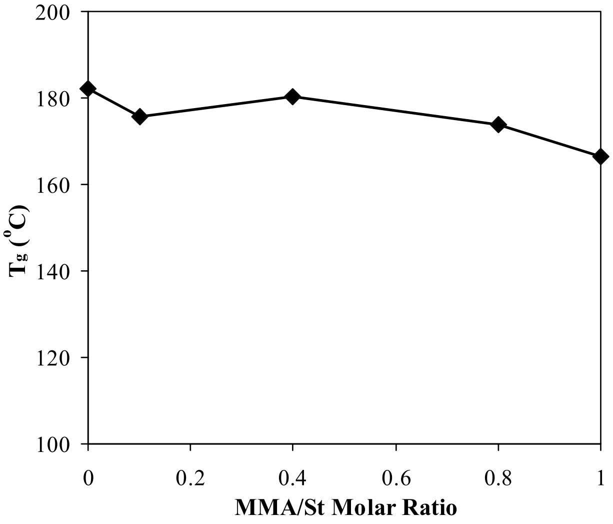


Fig. 6. Glass transition temperature (T_g) as a function of MMA content in UP/LPA/St resin systems (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

3.2. Volume shrinkage

The effect of the MMA content on volume shrinkage in UP/St/LPA systems is shown in Fig. 8. In the absence of LPA, the volume shrinkage of the resin system depends on the polymerization shrinkage of monomer. The volume

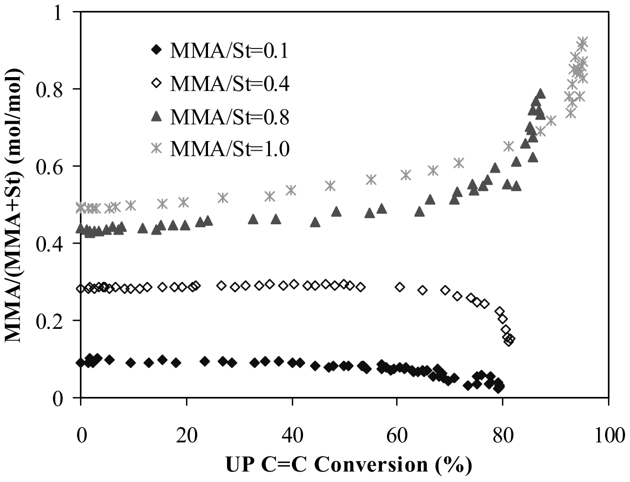


Fig. 7. MMA molar fraction based on St and MMA only vs. UP C=C bond conversion in the UP/St/LPA resin systems with different MMA contents cured at 35 °C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

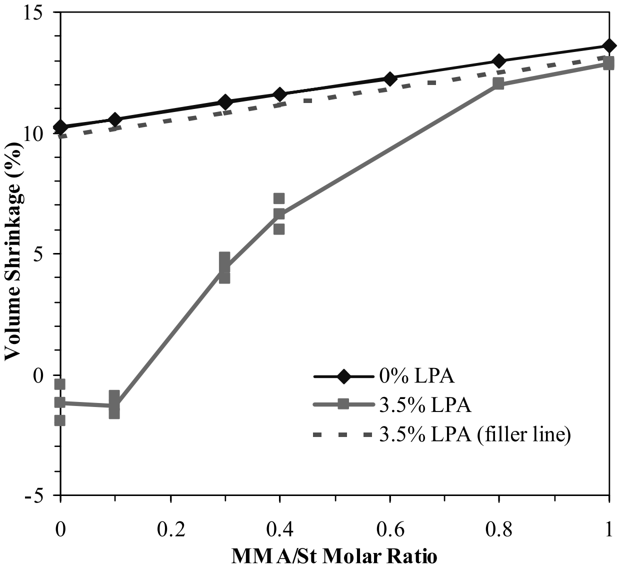


Fig. 8. Final shrinkage vs. MMA content in UP/LPA/St resin systems cured at 35 °C (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

shrinkage of the resin system increases with more MMA added into the resin system. This may result from the addition of MMA into the polyester network structure, which increases the compactness of the St/MMA cross-linked UP network because MMA has closer polarity to the polyester molecule than St. Since styrene has a polymerization shrinkage of 15% and MMA has a shrinkage of 20% [19], larger polymerization shrinkage of MMA than St may also contribute to the higher volume shrinkage. In the presence of LPA, the volume shrinkage of the resin system with the MMA/St molar ratio of 0.1 is nearly the same as the system without any MMA. The LPA is more effective on shrinkage control since the intrinsic volume shrinkage of the resin system (the volume shrinkage of the resin system without LPA) is higher when compared with the system without any MMA (as shown in Fig. 8). The performance of LPA becomes less effective when the MMA/St molar ratio is higher than 0.1 and LPA eventually functions like a filler when the MMA/St molar ratio reaches 0.8. This can be explained by the phase behavior of the UP resin system with LPA. The LPA used in this study is poly(vinyl acetate) that has a dipole moment of 1.6. When there is no MMA in the UP/LPA/St resin system, the highly polar UP resin (dipole moment of 2.0–2.5) becomes less polar (dipole moment less than 1.0) during curing due to polymerization and the introduction of the non-polar polystyrene segment (dipole moment of 0.3) into the network. LPA with a dipole moment of 1.6 tends to phase out during curing [27]. However, in the presence of MMA, the polarity of the cured unsaturated polyester resin may not decrease as much as in the system without MMA, since MMA is more polar than styrene and PMMA has a dipole moment of 1.3. Consequently, LPA may be more compatible with the resin system and phase separation is less likely to take place. As more MMA is added, the cured sample changes from opaque to translucent or even transparent, and the volume shrinkage increases substantially.

The morphology of samples cured at 35 °C with different MMA content is shown in Fig. 9. The morphology of the sample without any MMA is a two-phase co-continuous structure. 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). A similar two-phase structure is observed when the MMA/St molar ratio is 0.1 in the resin system. The particle diameter is still in the range of 1–5 μm and is loosely packed. The domain size in the sample with the MMA/St molar ratio of 0.4 is much smaller than the sample with the MMA/St molar ratio of 0.1. Further increase in the MMA content results in a very uniform and flat-like morphology. It clearly demonstrates that the system becomes more compatible when more MMA is added. Since a strong phase separation between the LPA-rich and the UP-rich phases during curing is necessary for stress cracking and micro-void formation [28], the effect of volume shrinkage control of the resin system turns to be less effective when more MMA is added into the resin system.

3.3. SCRIMP molding

In order to understand the performance of the resin system with a comonomer MMA in the real molding process, a series of low temperature Seemann composite resin infusion molding process (SCRIMP) experiments were carried out using a glass mold at 35 °C as shown in Fig. 10. Three layers of dry stitched E-glass fiber mats (QM6408 from Brunswich Technologies, Inc.) were laid upon a glass plate mold. Q6408 is a non-bindered and quadraxial mat, which is composed of five layers, i.e. 0°, 90°, +45°, −45° continuous E-glass fiber and one layer of 50 mm chopped E-glass fiber. Each layer was 150 mm long and 125 mm wide except for the bottom layer fiber mat, which was 25 mm longer to control the minimum mold filling time. The fiber stack was covered by a transparent polyester film to form a vacuum bag whose outer edges were sealed by tacky tape. A resin inlet and a vacuum outlet on opposite ends of the mold were also formed.

Before mold filling, vacuum was applied through the outlet, forcing the bag to press tightly against the fiber stack. The liquid resin with the curing agent was degassed to remove trapped air and then introduced into the fiber stack under vacuum through a supply line. The gel time of each resin system was determined when there was no liquid resin dropping off from the outlet. During molding, reaction exotherm was recorded by a DianaChart recorder through a thermocouple placed in the center of the fiber stack. A linear variable differential transformer (LVDT) was placed on the top of the fiber stack to monitor the dimension change of the molded panel. The residual reactivity of the molded composite parts was examined 24 h after molding by DSC

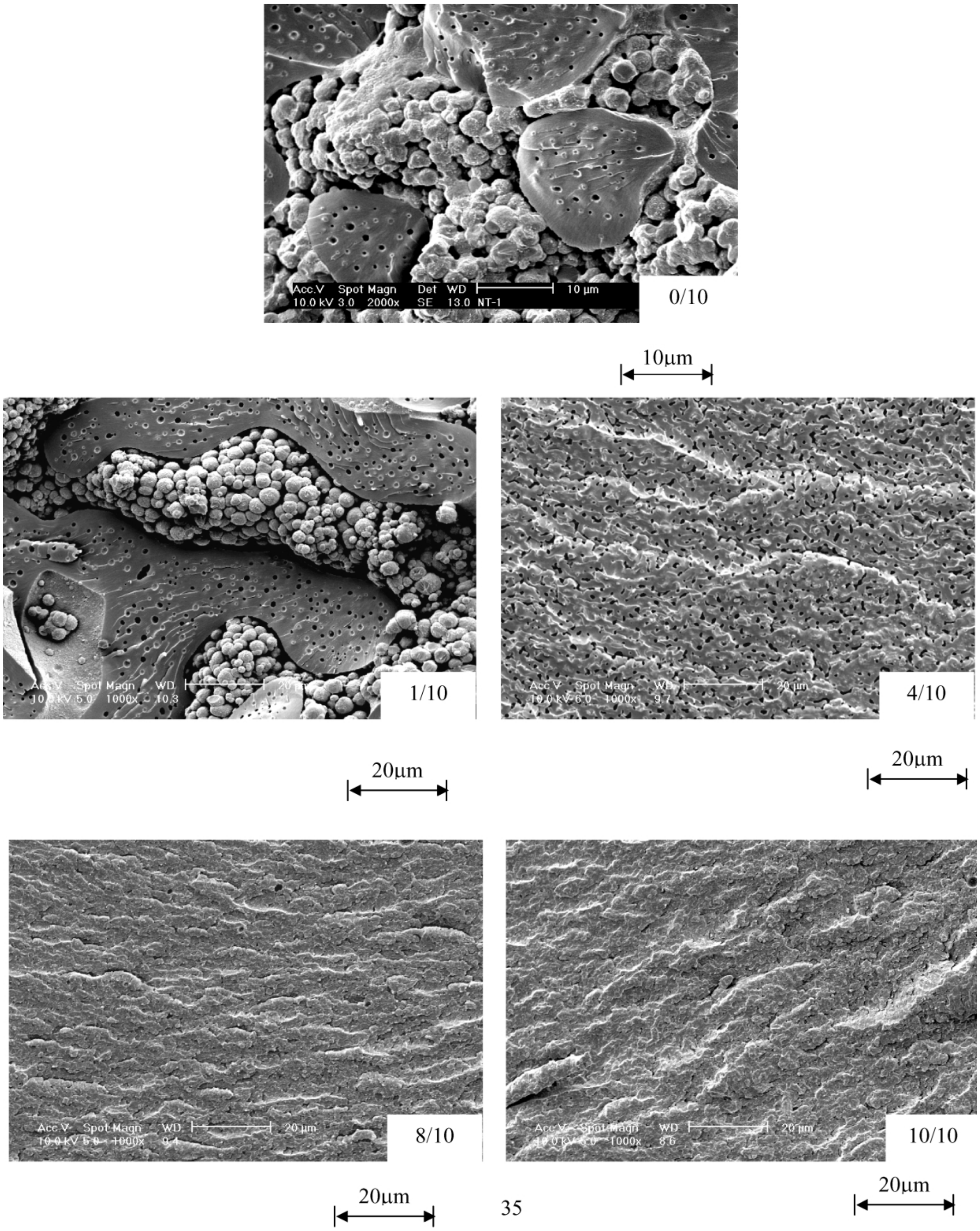


Fig. 9. Morphology of samples with different MMA/St double bond ratios cured at 35 °C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

in the scanning mode of 5 °C/min from room temperature to 300 °C, based on a total reaction exotherm of the corresponding resin system according to a DSC kinetics study (the summation of reaction exotherm from the both isothermal run and residual scanning). Three samples were taken at the surface of each part and the average value was calculated. It was found that the calculated conversion (i.e. residual heat) varied with ± 3%.

Fig. 11 shows the molding results of the resin system without any MMA. At time zero the mold filling started and the time to complete mold filling was about 5 min. The resin started as a clear solution, then turned cloudy indicating

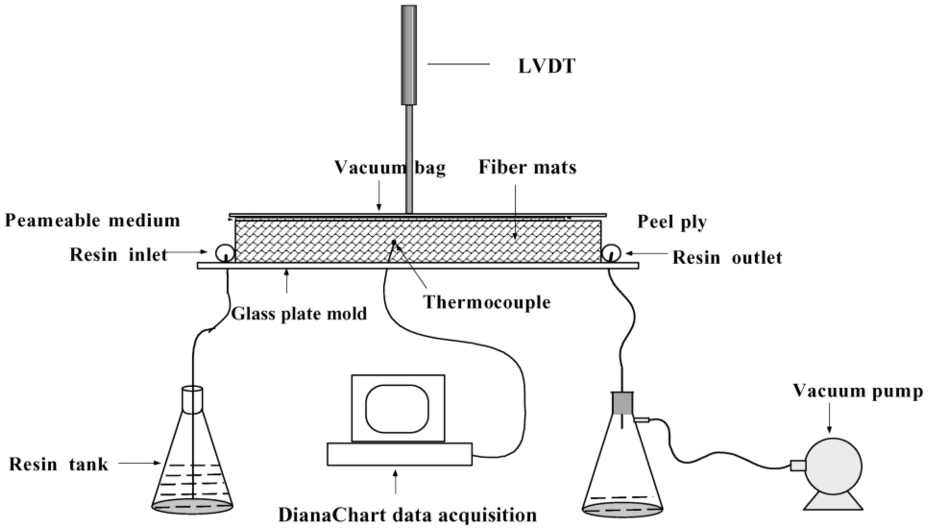


Fig. 10. Schematic of experimental set-up for SCRIMP.

phase separation. The resin gelled after phase separation at 90 min, which then led to an increase in temperature due to reaction exotherm. In the meantime, the LVDT position increased, indicating a thinner molding panel because of polymerization shrinkage. At 140 min, the temperature reached the maximum value (i.e. 38.2 °C), then started to decline because of heat loss to the surroundings. The LVDT position kept increasing until 163 min. At about 175 min, a white spot could be seen in the molded panel and it eventually expanded to the whole panel area. The LVDT position then started to decrease suggesting expansion. The whitening of the molded panel is believed to be a result of micro-void formation in the resin phase. Similar temperature and LVDT profiles were observed in other experiments, except that the panel did not turn white in some cases.

The effect of the comonomer MMA on the SCRIMP molding of UP resins, i.e. the phase separation time (t_p), gel time (t_g), and final conversion (α_f), is summarized in Table 4. As seen in this table, the final resin conversion increases when more MMA is added into the resin system, which is consistent with the kinetics study.

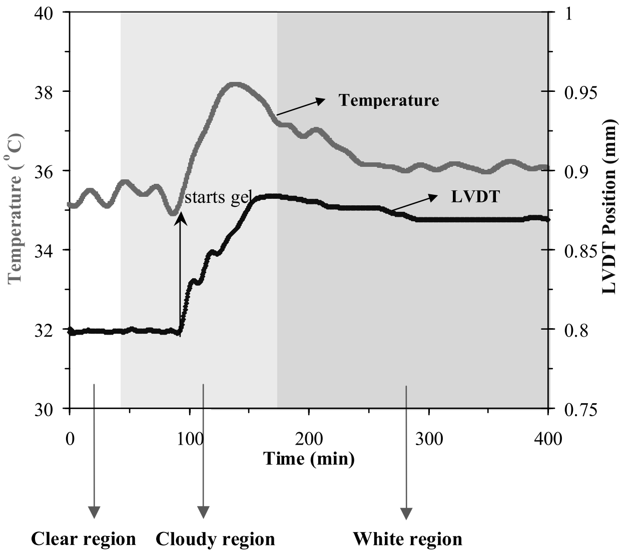


Fig. 11. Temperature and LVDT profiles during SCRIMP molding (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

The onset of phase separation was noted by the onset of turbidity (i.e. cloudy point), while the gel point was determined when the resin stopped to flow. It is interesting to note that an increase in the amount of MMA leads to a later phase separation and a delayed gelation. Moreover, the length of the phase separation period of resin systems with MMA is longer than that of resin systems without MMA, except when the MMA to St molar ratio is 0.1. The time difference ($t_g - t_p$) of resin systems without any MMA was about 55 min, while for resin systems with the MMA to St molar ratio of 0.6 the time difference was 69 min. A larger ($t_g - t_p$) generally provides more time for phase separation and a better shrinkage control of resins with LPA [29]. However, the shrinkage of the resin system with a longer phase separation period is worse under this curing condition, which is indicated by a large volume shrinkage. A possible explanation is that the phase separation is influenced by both the thermodynamics of the resin system and phase separation kinetics. For the curing condition used in this

Table 4
SCRIMP molding of UP/St/LPA systems with different MMA contents at 35 °C (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ)

LPA (%)	MMA , St	t_p (min)	t_g (min)	Δt (min)	α_f (%)	S_f (%)	R_a (μm)
0	0	–	83	–	81.2	10.2	0.74
3.5	0	35	90	55	78.5	− 1.2	0.34
3.5	0.1	38	84	46	80.8	− 1.3	0.13
3.5	0.4	79	142	63	82.1	6.6	0.67
3.5	0.6	87	156	69	86.8	8.3	0.94

t_p: phase separation time; t_g: gel time; Δt: time period between t_p and t_g; α_f: final conversion; S_f: volume shrinkage of resin system.

study, the phase separation period ($t_g - t_p$) is at least 55 min, which may be sufficiently long for phase separation. Thermodynamics (compatibility of the resin system) then becomes a determining factor. An increase in the MMA content results in a more uniform and flat-like morphology, which suggests poor phase separation and consequently, a poor shrinkage control of the resin system.

3.4. Properties of SCRIMP molded composites

Surface appearance of all composites panels reveals that the samples with a MMA/St molar ratio of less than 0.1 are much better than other samples. These panels have fewer fiber read-outs and a shiny surface indicated by a clear reflection image of fluorescent light bulbs off the surface. The other samples have a rougher surface and the fiber filament can be seen clearly on the composite surface. The composite panel with a MMA/St molar ratio of 0.6 appears transparent. The surface roughness R_a is used to quantify the effect of MMA on the surface quality. The results are given in Table 4. As the MMA content increases, the surface roughness of UP composites with LPA exhibits a decrease first, followed by an increase and reaching a minimum value at the MMA/St molar ratio of 0.1. The surface of the composite panel with a MMA to St molar ratio of 0.6 is even rougher than the system without LPA. These results correlate quite well with the volume shrinkage results of resin systems without any fiber reinforcement. To characterize the flexural properties of the composites, a three-point bending test was carried out. The species size, span length and cross-head were determined according to the sample thickness. Fig. 12 shows the flexural strength of composites under different conditions. As shown in this figure, the flexural strength rises as the MMA content in the resin system increases, except when the MMA/St ratio equals 0.1. This could be attributed to the fact that increasing the MMA content could elevate the final conversion of the cured resin system, leading to a favorable effect on the flexural strength. The slightly lower flexural strength of the composite with a MMA/St ratio of 0.1 is the result of final conversion and morphology from Table 2 and Fig. 9. Compared to the resin system without any MMA, the system at this MMA content has a similar morphology of two-phase co-continuous structure (Fig. 9). Since the volume shrinkage is lower, this sample has a higher volume fraction of micro-void. Since the crack would eventually propagate through the voided plane during the flexural testing of specimens, this higher volume fraction of micro-void could cause an adverse effect on flexural strength. For the composite without any MMA, a decrease in flexural strength was observed when compared with the neat resin system without any LPA. The flexural strength decreases from 458 to 409 MPa. The presence of LPA and the micro-void formation inside the composite panel could explain the decrease in strength. However, the composites with 3.5% LPA and a MMA/St molar ratio higher than 0.4 are stronger than the neat resin composite.

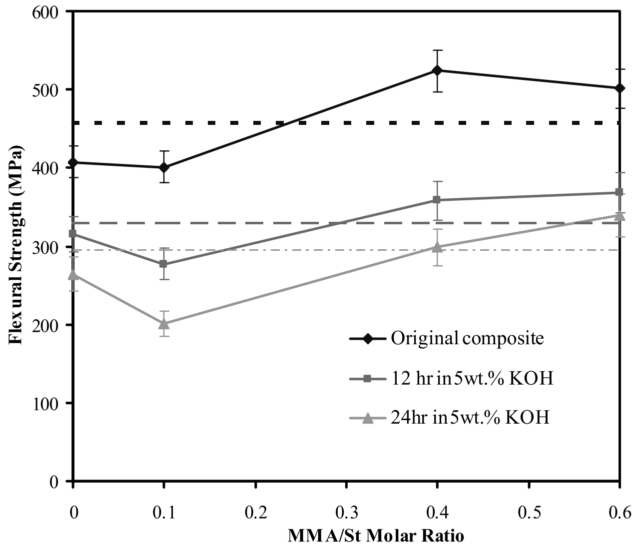


Fig. 12. Comparison of flexural strength of SCRIMP molded composites under different conditions (3.5% LPA). Dashed lines are the results of composites without any LPA and MMA. - - - Original; – – – 12 h in 5 wt% KOH; — - — - — - 24 h in 5 wt% KOH.

In order to characterize the corrosion resistance of composite, SCRIMP panels with different MMA content were soaked in the boiled KOH solution for a certain time and flexural strength was then measured afterward. The flexural strength decreases for all of the samples after 12 and 24 h in a boiling 5% KOH solution. The strength of the system with the MMA/St ratio larger than 0.4 is still higher than the composites with or without LPA in the absence of MMA. Therefore, the addition of MMA can improve the mechanical properties and corrosion resistance of unsaturated polyester composites. However, the volume shrinkage control and surface quality of composites suffer.

4. Conclusions

The residual styrene, volume shrinkage, and mechanical properties of unsaturated polyester resin with a low profile additive cured with a comonomer MMA were investigated. In the study of reaction kinetics, both DSC and FTIR were employed to obtain the overall and individual reaction rate and conversion profiles. It was found that the final conversion and residual styrene could be improved greatly by introducing the comonomer MMA into the resin system. The relative reaction profiles of styrene, MMA and UP C=C bonds suggests that a higher consumption rate of St occurs compared to the system without MMA, indicating a favorite copolymerization of St and MMA.

The study on shrinkage shows that MMA has a negative effect on shrinkage control of UP/ST/LPA system because the system becomes more compatible with the addition of MMA, indicated by a uniform and flat-like morphology. Consequently, phase separation becomes more difficult, leading to poor shrinkage control. The surface quality and the flexural property of unsaturated polyester resin depend strongly on the volume shrinkage and final conversion of the resin system.

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