Evaluation of Low-profile Additives in the Curing of Unsaturated Polyester Resins at Low Temperatures

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ABSTRACT

The effects of four low-profile additives (LPAs) namely poly (vinyl acetate) (PVAc), poly (methyl methacrylate) (PMMA), general purpose polystyrene (PS), and a high density polyethylene (HDPE) on the volume shrinkage of two series of unsaturated polyester (UP) resins with different chemical composition or structure have been investigated by volume shrinkage method. Different low cure temperatures from 25 to 70°C have been used to cure the specimens. Within limits of this study, it was found that shrinkage increases as the curing temperature increases. In addition, our studies show that there are two phase transitions for UP resins containing PVAc and PMMA cured at low temperatures. Adding LPAs to the neat UP resins can decrease the volume shrinkage to different extents, depending on the types of LPAs added and the kind of UP resin used. Results show that the nature of UP resin has a significant effect on the amount of volume shrinkage but, the trend is similar for each kind of LPAs. In both unsaturated polyester resins the best, second best, and worst shrinkage control obtained by adding PVAc, PMMA, and PS, respectively. But, surprisingly HDPE has a good shrinkage control effect at 70°C.

INTRODUCTION

It has been known that non-reacting thermoplastic polymers as low-profile additives (LPAs) can be used to control the shrinkage that occurs during the cure of unsaturated polyester (UP) resins. The high curing shrinkage of UP resins causes sink marks and irregularities on the surface of many shaped articles. Moreover, there is a tendency for the shaped articles to become warped or cracked [1].

Adding specific thermoplastic polymers such as poly vinyl acetate...
(PVAc), polystyrene (PS), polyethylene (PE), acrylic polymers, polyurethanes, and aliphatic polyesters in to the unsaturated polyester resins during the formulation of sheet moulding compounds (SMC) is a well-known industrial technology. Such thermoset-thermoplastic blends essentially made from UP, styrene monomer, and LPAs would lead to a reduction or even elimination of the shrinkage during the curing process [1-5]. Many researchers have investigated the shrinkage control of UP resins containing thermoplastics additives cured at low temperatures and pressures [6-13].

The development of composite manufacturing processes, such as resin transfer moulding (RTM) and vacuum infusion moulding processes, made low-shrinkage resins which can be processed at low temperatures attract considerable interest in the composite industry.

There are a number of theories that seek to explain the low-profile or anti-shrinkage action of LPAs [2, 6, 14-16]. But the one that is reported by Li and Lee [7, 8] seems to explain best the phenomenon relative to the unsaturated polyesters without any thermal effect. Although low profile additives and unsaturated polyester resins are generally incompatible, they all can be dissolved in styrene to form the one phase mixture, so LPAs are at least partly soluble in the uncured polyester/styrene solution. For LPAs like PVAc, such a mixture is stable before polymerization. For LPAs like poly (methyl methacrylate) (PMMA) and PS, such a mixture is unstable and phase separation may occur before the reaction.

As the polyester/styrene mixture cross-links, the thermoplastic polymer becomes incompatible or less soluble and partly comes out of solution, at least. This action causes the UP-rich and the LPA-rich phases. If micro voids can be formed in the LPA-rich phase or at the interface of the two phases, polymerization shrinkage can be reduced or eliminated without any thermal effect. In this case the appearance of sample (UP containing LPA) changes quickly from translucent to opaque. The measurements of the internal surface area of the cured samples and the results of the morphological investigation confirmed that the volume expansion and the change of opacity were caused by the formation of sample’s internal micro voids [8].

The curing reaction of a UP resin is a free-radical chain-growth cross-linking copolymerization between the styrene monomer and the UP molecules [17]. At the beginning of the reaction, UP-styrene copolymer micro gels are formed which are a groups of highly intra-cross-linked polyester chains. When the phase separation occurs, the micro gels coagulate to larger particle size in the range of micron. As the reaction continues, more and more particles are formed until they become cross-linked. During the micro gel step a macro gel structure is forming, thus the viscosity of the system that depends on the micro gel s concentration increases slightly. When the first particles were formed, they accelerate the increment in viscosity and when the cross-linking between the particles dominates the viscosity rises very rapidly until the gel point was achieved at the end of macro gelation.

In room temperature processes, without any external heating source, polymer chains become diffusion controlled. This impedes unsaturated polyester resins from achieving final conversion, i.e., low styrene residue when cured at low temperatures. It is found by many investigators that the degree of improvement in shrinkage control is dependent on the structure, molecular weight, and the amount of LPA used and the structure of UP resin employed [2, 7, 8, 15, 18-21].

In the previous paper [13], we discussed the morphological and mechanical properties of poly(vinyl acetate) low profile system. In this paper, the performance of four thermoplastic additives namely PVAc, PMMA, PS, and high density polyethylene (HDPE) and the effect of their concentrations are investigated on shrinkage control of two unsaturated polyester resins at curing temperatures ranging from 25 to 70°C.

**EXPERIMENTAL**

**Materials**

Two unsaturated polyester resins namely Bushepol 751129 (iso type) and Bushepol 751212 (ortho type) used in this study were supplied by Bushehr chemical Industries. Four LPAs including; PVAs (medium molecular weight by Aldrich), PMMA (medium molecular weight by Aldrich), PS (1540/1 general purpose by Tabriz Petrochemical Co.), and HDPE (3840 UA by Tabriz Petrochemical Co.) were used in this work. PVAc, PMMA, and PS were used in the form of 38, 33 and 40% solution in styrene, respectively. HDPE Was
used in the form of powder with the size of 100 µ.

The polymeric additive solutions were mixed thoroughly with unsaturated polyester resins in the desired weight ratio so that the molar ratio (MR) of styrene to unsaturated polyester resins C=C bonds was fixed to 4/1. Tables 1 and 2 present the compositions used in this work. All the samples being tested were formulated to provide the MR of 4/1.

An amount of 1.5% methyl ethyl ketone peroxide, (MEKP) (Peroxir KP50, from Iran Peroxide Co.) and 0.3% cobalt naphthenate (commercial grade) were used as the low temperature initiator and promoter, respectively.

**Instruments and Procedures**

Detailed characterization of UP resins identified by 500MHz $^1$HNMR (Bruker DRX500 AVANCE) to determine their molar composition [22, 23]. Acid number (AN) and hydroxyl number (HN) were measured according to ASTM D 1639. The number of average molecular weight of resin ($M_n$) was then calculated by the following equation [24]:

$$M_n = 2 \times \frac{56100}{(AN+HN)}$$

Cure exotherm peaks were measured according to ASTM D 2471-99. The polyester resin containing cobalt (II) promoter and various type of thermoplastic additives were mixed with the appropriate amount of initiator at ambient temperature and the mixture rapidly mixed for one minute. Approximately 70 g of this mixture was poured into a paper cup (4 cm diameter and 7 cm deep) at ambient temperature. The height of mixture in the paper cup was 5 cm. The time-temperature data was measured by placing a thermocouple connected to a digital thermometer in the center of the isolated paper cup.

For linear shrinkage measurement of UP resin containing LPA the ASTM D 2566-86 standard was used. The linear shrinkage ($S_l$) was changed to the volume percentage ($S_v$) according to the following equation:

$$S_v = (1+S_l)^3-1$$

Cambridge S-360 scanning electron microscope (SEM) with accelerating voltage of 20 kV was used to investigate the gold coated fractured surface of each sample of Izod impact test at magnification of 1000x and 5000x.

**RESULTS AND DISCUSSION**

**Characterization of Unsaturated Polyester Resins**

Detailed characterizations of UP resins are presented in Table 3. These include molar composition of UP resins,
degree of isomerization from maleate to fumarate, degree of unsaturation, and the average number of C=C bonds per UP molecule. With the variation of unsaturated polyester resin type, the reactivity of the resin and the degree of unsaturation can be varied [2]. Table 3 shows that the unsaturation and the reactivity of ortho resin are lower than the iso type therefore, the shrinkage of ortho resin is lower than of the iso resin (5.12 versus 6.12%).

**Effect of PVAc and Resin Type on Shrinkage Control**

Figure 1 shows the volume shrinkage profile of several samples cured at 25, 50, and 70°C for isophthalic and orthophthalic resins with PVAc as low-profile additive. For isophthalic resin whatever the PVAc content is, the shrinkage increases as the cure temperature increases from 25 to 70°C. Since the conversion increases at 50 and 70°C therefore, shrinkage also increases.

Figure 1 clearly demonstrates that there are an upper and a lower concentration limit for the PVAc to be effective in the shrinkage control, especially at 50 and 70°C. We observe an optimum PVAc concentration corresponding to the minimum shrinkage. The minimum values are 6, 6.6, and 8% at 25, 50, and 70°C for iso resin, respectively. The appearance of the cured samples within this range is also quite different from those that are outside the range. The formers are stark white (opaque), whereas the laters are translucent.

Figure 1 also shows that the behaviour of PVAc with orthophthalic resin is similar to that with isophthalic resin except its effective concentration range at 25°C is higher. According to this figure, the PVAc concentration should eventually reach an optimum amount for best shrinkage control, only at 25 and 70°C, and with the addition of more PVAc the amount of volume shrinkage should be lessen. At 25°C curing temperature, the 8%wt of PVAc take the maximum effectiveness in shrinkage control for the ortho resin. At 70°C the effective range lies between 6 and 8%.

Figures 2, and 3 show the SEM images of fractured surfaces of the cured UP resins containing PVAc. Morphological studies of the surface of the cured samples show that increasing the PVAc concentration in the UP resin would cause the sample morphology to change from the flake-like to partially flake-like and partially particulate, then to complete particulate structure.

Continues particulate structure allows the formed micro voids to cover the entire sample which effectively reduce the sample shrinkage. This kind of morphology has been reported before [8, 18]. The morphological

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**Table 3. Molecular characterization of unsaturated polyester resins used in this work.**

<table>
<thead>
<tr>
<th>Kind of resin</th>
<th>Iso unsaturated polyester resin</th>
<th>Ortho unsaturated polyester resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition&lt;sup&gt;a&lt;/sup&gt;</td>
<td>MA:IPA:PG:DEG</td>
<td>MA:PA:PG:DEG</td>
</tr>
<tr>
<td>Styrene monomer (%)</td>
<td>37.5</td>
<td>34</td>
</tr>
<tr>
<td>Acid number (AN)</td>
<td>18.3</td>
<td>20.4</td>
</tr>
<tr>
<td>Hydroxyl number (HN)</td>
<td>22.5</td>
<td>31.7</td>
</tr>
<tr>
<td>M&lt;sub&gt;n&lt;/sub&gt;</td>
<td>2750</td>
<td>2154</td>
</tr>
<tr>
<td>No. of C=C bond per UP molecule</td>
<td>5.88</td>
<td>4.55</td>
</tr>
<tr>
<td>Isomerization (%)</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>Unsaturation (%)</td>
<td>47</td>
<td>44</td>
</tr>
<tr>
<td>Density (25°C, g/cm³)</td>
<td>1.119</td>
<td>1.142</td>
</tr>
<tr>
<td>Viscosity&lt;sup&gt;c&lt;/sup&gt;, cP</td>
<td>750</td>
<td>830</td>
</tr>
<tr>
<td>Volume shrinkage (%)</td>
<td>6.12</td>
<td>5.12</td>
</tr>
</tbody>
</table>

<sup>a</sup> measured by <sup>1</sup>H NMR: MA, IPA, PG, PA and DEG are standing for maleic anhydride, isophthalic acid, propylene glycole, phtalic anhydride and diethylene glycole, respectively;
<sup>b</sup> calculated by end group titration method;
<sup>c</sup> determined at 25°C using spindle R3.
transitions of ortho UP/PVAc system are similar to that of iso UP/PVAc system. In other words, the change of thermoplastic concentration results in a similar change in the microstructure.

In the ortho UP/PVAc system, the first and the second phase transitions take place at 8 and 12% of PVAc, respectively which are higher than that of iso UP/PVAc system. This results may arising from decreasing the unsaturation (44 vs. 47%) in the UP resin. The reasons for this observation are not clear and it requires further investigations.

As one of the most effective low shrinkage additives, PVAc enhances the intramolecular reactions of UP and the micro gel formation during curing. More important, PVAc can act as a segregating agent for the micro gels. When the micro gel phase migrates from the PVAc-containing mixture, a layer of PVAc covers the micro gel particles and prevents the particles from merging. As a result partially interconnected UP resin particles are formed [16]. It was also found, that by etching the surface (Figure 3) PVAc resides mostly in the open surfaces of the particles.

The results show that the structure and composition of UP resin, PVAc concentration, and isothermal reaction temperature have influence on the volume shrinkage of the UP/styrene/PVAc systems. Cao and Lee [10] have investigated the shrinkage control behaviour of UP/styrene/LPA systems cured at different temperatures. Their experimental results show that by increasing the curing temperature from 35 to 100°C the size of the particulate region becomes smaller. The various morphological structures result in different interface areas, strongly affecting the shrinkage control. Our results in Figure 1 show that in the intermediate cure temperature (50°C) and for ortho unsaturated polyester resin, PVAc does not affect the shrinkage control significantly.

**Effect of PMMA on Shrinkage Control**

Figure 4 shows the volume shrinkage profile of samples containing isophthalic resin with PMMA as low profile additive cured at 25, 50, and 70°C. PMMA Does not show any effectiveness in shrinkage control at 25 and 50°C and the appearance of the cured samples are also translucent. However, at 70°C, there is two transition in shrinkage control at 6 and 12% of PMMA.

The above results show that PMMA does not have a good performance at low temperature cure. The cause of this effect relates to the lower coefficient of thermal expansion of PMMA in comparison with PVAc [2].

Huang and Liang [15] have found that the volume fraction of micro crack for the UP/styrene/PVAc is
Figure 2. The SEM micrographs of iso UP resin sample cured at 25°C, containing a: 0% PVAc, b: 3.5% PVAc, c: 6% PVAc, and d: 10% PVAc at two different magnifications (the right images with 5000x and the left images with 1000x).
higher than the UP/styrene/PMMA. Their experimental results generally support the volume shrinkage mechanism of strain relief through stress cracking, and the greater micro crack formation would give less volume shrinkage.

The literatures [6,18] show that the mixture of PMMA and UP resins tends to separate into two layers before any polymerization. The rate of phase separation and two phase region area decrease with increasing temperature. Interfacial area resulted from phase separation is an important, but not probably the only factor for shrinkage control. The several properties of LPA such as glass transition temperature, thermal expansion coefficient, and polarity may all play significant roles on its behaviour.

The time to reach the maximum temperature (exotherm peak) for the PVAc/UP and PMMA/UP systems is shown in Figures 5 and 6. The system containing PMMA as LPA took much longer time to reach its exotherm peak. The micro void and micro crack formation for volume shrinkage compensation are influenced by the relative reaction rate in the LPA-rich and the UP-
rich phases, which also depends on the resin and LPA structure, the reaction temperature, and curing agent [10]. The results of gel time measurements (Figures 5 and 6) determined that the gelation of the UP/styrene/ PVAc occurs earlier. This causes the earlier onset of micro void formation and volume shrinkage, which, in turns gives better shrinkage control.

**Effect of PS and HDPE on Shrinkage Control**

Figure 7 shows volume shrinkage profile of samples of orthophthalic resin system containing general purpose polystyrene as low-profile additives cured at 25 and 70°C. Shrinkage was measured at 0, 3.5, 6, 8, and 10 wt% polystyrene concentration. It is shown that polystyrene does not have a low profile effect at 25°C and only acts as filler. However at higher temperature (70°C) it has a better effect on shrinkage control and increased it by increasing its concentration.

Polystyrene has less compatibility with uncured unsaturated polyester resin because of different dipole moments (dipole moment = 0.3) which is relatively non-polar. Therefore, as the polyester cross-links, the polar thermoplastics such as PVAc and PMMA have greater driving force on being incompatible and available for reaction-induced micro void formation to compensate polymerization shrinkage [2]. Because of greater compatibility of polystyrene systems, it is believed that these composites can accept internal pigmentation and yield uniform colours, while use of more polar additives normally will not allow this approach.

We observed the change of transparency of the UP/styrene/PS system at constant temperature (25°C) from transparent to cloudy for all PS concentrations. The cured sample containing a relatively non-polar LPA such as PS tends to exhibit a two-phase microstructure. The segregation effect of such LPA on the micro gel particles generation during the cure is also less profound, and results in a lower volume frac-

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**Figure 4.** Volume shrinkage profile vs. PMMA concentration for Iso UP resin at MR=4/1 cured at different temperatures.

**Figure 5.** The cure exotherm peaks of iso UP resin systems containing different amount of PVAc.

**Figure 6.** The cure exotherm peaks of iso UP resin systems containing different amount of PMMA.
Volume shrinkage of UP resin containing PS (Figure 7) decreases with increasing polystyrene content nearly in a linear manner. Hung and Liang [15] have measured volume shrinkage in the cure of UP resins containing PS. They suggested that both the occupied volume of the dispersed phase after the cure and the segregation effect of PS in micro gel particles generated there would also increase with increasing PS concentration, resulting in favorable effects on micro void formation and volume shrinkage control.

The amount of volume shrinkage in our experiments is less than that of Huag and Liang’s, because the LPA works well in the maleic anhydride-propylene glycol type UP resins, whereas for the UP resins containing orthophthalic or isophthalic acid units, thermoplastics are less effective.

Figure 8 shows the volume shrinkage of low-profile system with orthophthalic resin containing high density polyethylene (HDPE) powder as low-profile additive cured at 25 and 70°C. Particle size and distribution have a great effect on the performance of HDPE powder. When particle size of powder is bigger, the particles migrate to surface of system and do not act effectively in shrinkage control. Polyethylene powder with particle size of 100 micron selected and used in this work.

Figure 8 shows that polyethylene does not have a low-profile effect on shrinkage control at 25°C, but shows a good effect in shrinkage control at 70°C. Comparing the experimental results for the investigated thermoplastics, the final shrinkage is markedly higher for the UP/styrene/HDPE system at 70°C. According to literatures [25, 26], micro cracking would occur when the stress generated by the polymerization shrinkage is greater than the strength possessed by the material at the interface or in the LPA-rich phase. The former depends on the copolymerization between UP and styrene, whereas the latter should be a function of the modulus of the material at the interface or in the LPA-rich phase, the stress relaxation behaviour of the material, and the phase structure. Although, shrinkage control behaviour of HDPE is unclear, but it may be related to the strength of this thermoplastic particles, which decreases with increasing temperature.

**CONCLUSION**

In the cure of low-profile unsaturated polyester resins at low temperature (<70°C) increasing LPA concentration reduces the volume shrinkage after the cure. There are an upper and a lower concentration limit (two transitions) for the polar LPAs (PVAc and PMMA) that are
effective in shrinkage control. These thermoplastics are effective for shrinkage control only in the concentration range between the two transitions. The range depends on the thermoplastic type, UP resin type and reaction temperature. With increasing the degree of C=C unsaturation per molecule and reactivity of resins (iso and ortho), we observed an increase in the volume shrinkage. Non-polar LPAs (PS and HDPE) do not act effectively in shrinkage control at 25°C. However it appears that they show a good effect in shrinkage control at 70°C but with different mechanisms.

REFERENCES
