Shrinkage, Cure Characterization and Processing of Unsaturated Polyester Resin Containing PVAc Low-profile Additive

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ABSTRACT

With the development of composite manufacturing processes, such as low-pressure compression moulding of sheet moulding compounds (SMC), resin transfer moulding (RTM) and vacuum infusion moulding processes, low-shrinkage resin which can be processed at low temperatures have attracted considerable interest in composite industry. In this paper the effect of polyvinyl acetate (PVAc) as a low profile additive (LPA) on shrinkage control of an iso unsaturated polyester resin has been investigated and cure behaviour, morphology and mechanical properties of this system has been studied. Our studies show that the maximum exothermic temperature and the rate of cure decreases with increasing the PVAc concentration. The PVAc content has a significant effect on the resin viscosity. It was found that there are two transitions for UP resin containing PVAc cured at low temperatures. The PVAc content is effective for shrinkage control only in a concentration between these two transitions. Experimental results showed that the mechanical properties of this system decreases by increasing the PVAc content.

Key Words:
Shrinkage; unsaturated polyester; polyvinyl acetate; curing; composite.

INTRODUCTION

Even though unsaturated polyester resins, UP, showed considerable utility in the composite industries; their growth into many potentially high-volume applications was restricted by a number of problems. These are poor surface appearance, fibre pattern show trough, warpage of moulded parts and inability to mould close tolerances, internal cracks and voids, particularly in thick sections and a notable depression sink on the surface opposite thick section such as reinforcing ribs and bosses. The
cause of these problems can be traced to the high curing shrinkage occurring during the copolymerization of unsaturated polyester resin with the cross-linking styrene monomer [1]. The resin volume shrinkage causes the compound to pull away from the surface of the mould and shrink away from the fibrous reinforcement. This reduces the accuracy of mould surface reproduction and reveals fibre pattern at the surface. Stresses created by non-uniform shrinkage cause warpage and internal cracks, and prohibit moulding to close tolerance [1]. This shrinkage is normally 7-10% in the curing of a typical unsaturated polyester resin [2]. Low profile additives (LPA) are thermoplastic materials that generally serve as non-reactive additives in the unsaturated polyester and vinyl ester resins. LPA has been found to be highly effective in eliminating the curing shrinkage of UP resins. They are initially soluble or form a stable dispersion in the styrene and resin mixture before cure, but become incompatible with the cured resin during the curing process. Common LPA includes polyvinyl acetate, polymethyl methacrylate, thermoplastic polyurethane and polyesters.

The effect of LPA type, molecular weight and its concentration on resin shrinkage, surface quality and dimensional control of moulded polymer composites have been studied by many researchers [3-5]. The effects of cure conditions on LPA behaviour, including temperature, pressure and thermal history, have also been investigated [6-8]. Most studies on LPA mechanism have focused on curing process at high temperatures, since UP resins containing LPA have found most of their applications in the high temperature and pressure process such as compression moulding of sheet moulding compounds (SMC) and compression or injection moulding of bulk moulding compounds (BMC).

Recently, because of the growing interest of manufacturing processes, such as low-pressure/low-temperature SMC moulding, Resin transfer moulding (RTM) and vacuum infusion moulding, low-shrinkage moulding compounds with the ability to be processed at low temperature and low pressure have attracted considerable interest in industry [9-10].

Since the resin thermal histories in the high-temperature and low-temperature processes are totally different, the performance of LPA may vary from process to process. The volume change of the moulded material during moulding can be divided into three stages: thermal expansion during heating, polymerization shrinkage and thermal expansion/contraction during curing, and further thermal contraction demoulding and cooling. To achieve the maximum shrinkage control in high temperature processes, a large thermal expansion of the LPA during heating and reaction and micro-void formation during cooling are essential. In contrast, in low-temperature processes, there is a little temperature variation during curing and the curing cycle is usually long. Obviously, thermal expansion of LPA can no longer be counted for these moulding processes. It is interesting, therefore, to investigate the mechanism and performance of low profile additives for low temperature curing process that has not been studied extensively.

The objective of this study is to investigate the effect of polyvinyl acetate (PVAc) performance as a low-profile additive at low-temperature cure of an unsaturated polyester resin.

**EXPERIMENTAL**

**Materials**

The unsaturated polyester resin used in this study was BUSHEPOL 751129 from Bushehr Chemical Industry containing 40% by weight of styrene. The thermoplastic additive was polyvinyl acetate [18948-0] from Aldrich Co. with medium molecular weight and it was used in the form of 38% solution in styrene. An amount of 1.5% MEKP (Peroxir KP50) from Iran Peroxide Co. and 0.3% cobalt naphthanate (commercial grade) were used as the low temperature catalyst and accelerator, respectively.

**Instruments and Procedures**

For the characterization of UP resin, samples were dissolved in CDCl₃ solvent, and then identified by 500MHz ¹H NMR (Bruker DRX500 Avance) for its molar composition, degree of isomerization from maleate to fumarate and the percentage of Ordelt reaction due to C=C saturation by glycols in the synthesis of resin. Acid number (AN) was measured according to ASTM D1639 and the hydroxyl number (HN) was also measured [11]. The number of average molecular weight of resin was then calculated by \( \overline{M}_n = 2 \times 56100/(AN+HN) \).
Viscosity measurement of all formulation was made by a rotational viscometer (model ST Digit R). Gel time and exotherm peak were measured according to ASTM D2471-99. For linear shrinkage measurement of UP resins containing LPA the ASTM D2566-86 standard was used. The linear shrinkage ($S_l$) was changed to the volume percentage ($S_v$) according to the following equation:

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

For the mechanical tests, dumb-bell-shaped specimens based on ASTM D638-2a type V were used to determine the tensile properties of polyester matrices on the MTS 10/M Universal Testing Machine at a constant cross-head speed of 2 mm/min. The Izod impact test was also carried out based on ASTM D256 method A by using Zwick impact tester.

For the morphological study, Cambridge S-360 scanning electron microscope (SEM) with accelerating voltage of 20 kV was used to investigate the fracture surface of each sample of impact test at magnifications of 1000 to 5000.

**RESULTS AND DISCUSSION**

**Characterization of UP Resin**

The characterization of UP resin has been made by $^1$H NMR. The results of this study are presented in Table 1. These include molar composition of UP resin, degree of isomerization from maleate ($\delta = 6.2-6.3$ ppm) to fumarate ($\delta = 6.9-7.1$ ppm), percentage of Ordelt reaction ($\delta = 2.8-3.1$ ppm) (which reduces the degree of C=C unsaturation of UP resins and decreases the cross-link density), degree of unsaturation and average number of C=C bond per UP resin. These results show that the molar ratio (MR) of styrene to polyester C=C bonds of this resin is 2.7.

**Preparation of Styrene/UP/LPA Solutions**

In general, according to the literature [12], there would be an optimal initial molar ratio of styrene to polyester C=C bonds at MR=2/1, either below or above which would cause inferior mechanical properties. However, in styrene/UP/PVAc systems, there is a significant increase of viscosity with increasing PVAc content. Figure 1 shows the variation of viscosity with PVAc content at different molar ratios. For all samples, at fixed MR, as the PVAc increased, the viscosity increased as well. This is due to the fact that the PVAc has the higher molecular weight in comparison to the

<table>
<thead>
<tr>
<th>Specification</th>
<th>BUSHEPOL 751129</th>
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<tbody>
<tr>
<td>Composition</td>
<td>MA, IPA, PG, DEG$^a$</td>
</tr>
<tr>
<td>Mole ratio of UP resin$^b$</td>
<td>1:1,15:1:14:1.44</td>
</tr>
<tr>
<td>Total weight (g)</td>
<td>467.92</td>
</tr>
<tr>
<td>Acid number (mgKOH/g)</td>
<td>18.3</td>
</tr>
<tr>
<td>Hydroxyl number (mgKOH/g)</td>
<td>22.5</td>
</tr>
<tr>
<td>$M_n$</td>
<td>2750</td>
</tr>
<tr>
<td>No. of C=C bonds per UP molecule</td>
<td>5.88</td>
</tr>
<tr>
<td>Viscosity$^c$ (cp)</td>
<td>750</td>
</tr>
<tr>
<td>Degree of unsaturation (%)</td>
<td>47</td>
</tr>
<tr>
<td>Ordelt reaction (%)</td>
<td>$\approx 0$</td>
</tr>
<tr>
<td>Isomerization (%)</td>
<td>98</td>
</tr>
<tr>
<td>Volume shrinkage (%)</td>
<td>6.12</td>
</tr>
</tbody>
</table>

(a) MA, IPA, PG and DEG stand for maleic anhydride, isophthalic acid, propylene glycole and diethylene glycole, respectively.
(b) measured by $^1$H NMR
(c) at 25°C using spindle R3

![Figure 1. Viscosity variations with PVAc content at different mole ratios.](image-url)
liquid UP resin. On the other hand, as MR increases, the styrene content of the solution increases and it reduces the viscosity of the solution. Figure 1 shows that the rate and the amount of viscosity increment depend on the PVAc content and MR ratios. In this investigation, all the samples being tested were formulated to provide a molar ratio of 4 in order to be suitable for low pressure and temperature moulding processes. In these processes like RTM, it is necessary to have a low viscosity resin system to be able to be injected. From the mechanical point of view it is necessary to choose the lower MR ratio [12], therefore, we choose the molar ratio of 4 for the formulation of all samples.

**Cure Characteristic**

Figure 2 shows the exotherm peaks of UP resin solutions containing different amount of PVAc. It is seen that the addition of low profile additive slows down the rate of cure because of the dilution of the resin by additional styrene originally present in the solution of low profile additive.

When the MR is kept constant, there is no significant influence of the LPA on the cure kinetics. Slower reaction rates may be ascribed to the fractionation of the initiator (used in small amount) in the PVAc-rich phase segregated during the polymerization.

In the cure of UP resins with LPA, micro-gel particles generated are allowed to be clearly identified. This is due to the fact that a layer of LPA could cover the surface of the micro-gel particles as a result of the phase separation of micro-gel particles from the unreacted resin matrix containing LPA. The segregating effect of LPA on micro-gel particles could enhance the subsequent intra micro-gel cross-linking reaction [13].

**Shrinkage Control**

Figure 3 shows the volume shrinkage profile of several samples cured at 25, 50 and 70 C. It is seen that the amount of shrinkage strongly depends on the resin conversion. In other words, a higher conversion would result in a higher amount of shrinkage. Since the conversion increases at 50 and 70 C, therefore, shrinkage would also increase as well. Figure 3 clearly demonstrates that there are an upper and a lower concentration limit for the PVAc to be effective for shrinkage control. The optimum thermoplastic concentration for the shrinkage compensation lies in the early part of this range. The appearance of the cured samples within this range is also quite different from those outside the range. The former is stark white (opaque), while the appearance of the later is translucent.

Figure 3 shows that at 25 C curing temperature, the sample without the PVAc additive has a final shrinkage of 6.7%. When the concentration level of PVAc was low, namely 2 or 3.8%, the final shrinkage decreased slightly and the PVAc simply may be acted as filler. At 6% of PVAc there was a large drop of final shrinkage, and the shrinkage decreased to 3.9%. However, when the PVAc concentration was further increased, the efficiency of shrinkage control of PVAc decreased.

The shrinkage control of PVAc for the samples that cured at 50 and 70 C is similar to those cured at 25 C. But, at 10% PVAc level, its low profile effect signif-

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**Figure 2.** The cure exotherm peaks of resin systems containing different amounts of PVAc.

**Figure 3.** The final shrinkage of UP resin containing different amounts of PVAc cured at various temperatures.
significantly reduced. The reason behind this kind of behaviour can be explained through their morphology and it is explained in the next section.

**Morphology**

The scanning electron microscopy (SEM) micrographs of the fracture surface of cured samples are shown in Figure 4a-4d. The surface morphology of the sample without PVAc was found to be planed flake-like (Figure 4a). At low PVAc concentration such as 3.5%, a two-phase structure was found as presented in Figure 4b. The dispersed phase consists of small droplets with diameter ranging from 1 to 3 µm. The droplets are PVAc-rich phase, while the flake-like region is UP-rich phase. The raising of PVAc concentration to 6%, a major structure change occurred (Figure 4c). The PVAc-rich phase (particulate) and the UP-rich phase (flake-like) became co-continuous. At 10% concentration of PVAc (Figure 4d) particles were fused together, this indicates that micro-cracks did not occur in those areas. Accordingly, the shrinkage control efficiency decreased. The surface morphology of the sample was single-phase, homogeneous and particulate-like. The fusion among the particles was very severe and the shrinkage control efficiency totally disappeared.

The above results reveal that increasing the PVAc concentration in the UP resin systems would cause changes of the sample morphology from the flake-like to partially flake-like and partially particulate, and then to complete particulate structure. A continuous (or co-continuous) particulate structure allows the formed micro-voids to cover the entire sample, which effectively reduces the shrinkage of specimen. The loss of the shrinkage control effect of PVAc takes place when particles fused together at high PVAc concentrations. A severe fusion of particles reduces the possibility of micro-void formation at the particle interface.

**Mechanical Properties**

**Impact Strength**

Figure 5 shows the effect of PVAc concentration on the impact strength of cured samples at a fixed MR of 4/1. The impact strength decreased with increasing PVAc concentration. However, the decrease of impact strength is not significant at low concentration of PVAc. It is interesting that the impact strength at 3.5% PVAc content has high variations. It would be attributed to the fact that the PVAc is close to the rubbery state under the test condition at 25°C. The dispersed micro-voids would be as usual during the cure at the interface between the PVAc and the cross-linked UP phases as well as inside the PVAc phase. Since the micro-voids could lead to a crack tip blunting effect [14] releasing the stress severity at the crack tip and delaying the crack propagation could improve the impact strength. On the other hand, since the crack would eventually propagate through the voided plane during the impact testing of specimens, an excessive higher volume fraction of micro-voids (at higher concentration of PVAc) could cause an adverse effect on the impact strength.

**Tensile Strength**

Figure 6 shows the effect of PVAc concentration on the tensile strength of cured samples at a fixed MR of 4/1. The tensile strength decreased with increasing PVAc concentration. This may be due to the fact that micro-void formation may act as stress concentrator and this phenomenon reduces the tensile strength. On the other hand, PVAc might have a plasticizing effect which reduces the tensile strength. Figure 6 also shows that at each amount of PVAc, except at 10%, the scattering of results are rather high. This may be ascribed to the morphology of these systems that described before.

**Tensile Modulus**

Tensile modulus represents the extent of resistance to deformation for a sample in the initial stage of tensile test, during which the sample would be unbroken. It would be connected with the degree of tightness of the network rather than the degree of cross-linking of the sample.

Figure 7 shows that the tensile modulus decreased with increasing PVAc concentration. Although the trend is the same as that of the tensile strength, the reason behind this may be different. Increasing PVAc content could reduce volume fraction of the major continuous phase, leading to a lower tensile modulus. The plasticizing effect of PVAc also might be the reason behind this reduction.
Figure 4. SEM Micrographs of UP resin containing various amounts of PVAc cured at 25 °C at two different magnifications.

(a) 0% PVAc

(b) 3.5% PVAc

(c) 6% PVAc

(d) 10% PVAc
CONCLUSION

Results show that the addition of PVAc to the UP resin increases the viscosity of these systems. The rate and amount of viscosity increment depends on the PVAc content and molar ratio of styrene to polyester C=C bonds. Our studies show that the maximum exotherm temperature and the rate of cure decrease with increasing the concentration of LPA, but the gel time increases. Addition of 6% PVAc decreases the volume shrinkage of UP resin from 6.7 to 3.9%. However, when the PVAc concentration was further increased, the efficiency of shrinkage control decreased. Results demonstrate that there are an upper and a lower concentration limit for PVAc to be effective for shrinkage control. Results also show that the mechanical properties of cured resin decreases with increasing PVAc concentration. This may be regarded to the micro-void formation that is revealed by scanning electron microscope or plasticizing effect of PVAc.

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