

# Effects of Nano-Scale Core-Shell Rubber on the Volume Shrinkage for Unsaturated Polyester

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## ABSTRACT

The effects of nano-scale poly (n-butyl acrylate) /poly (methyl methacrylate) types of core-shell rubbers (CSR) as low-profile additives (LPA) on the volume shrinkage and internal pigmentability of unsaturated polyester resins (UP) during the cure at 110°C were investigated. For ST/UP/CSR systems, adding a higher content of CSR may generally result in a lower volume shrinkage, or even an expansion after the cure. At a fixed CSR content, employing the MA-PG type of UP, with a higher molecular polarity than the MA-PA-PG type of UP, may generally lead to a lower volume shrinkage, where the microvoid formation and the relief of the polymerization shrinkage force caused by the rubbery core of the CSR are more favorable. The experimental results have been explained by an integrated approach of measurements for the static phase characteristics of the ST/UP/CSR system, reaction kinetics, cured sample morphology, and microvoid formation by using DSC, SEM, TEM, OM, and image analysis.

**Keywords:** unsaturated polyester resin (UP), nano-scale core-shell rubbers (CSR), low-profile additive (LPA), curing, volume shrinkage

## 1 INTRODUCTION

The large volume shrinkage of unsaturated polyester resins (UP) during the cure, typically ranging from 7-10% [1], is due to the extensive intramolecular or cyclization reactions of UP molecules and the formation of compact microgel structures [2] during the cure. Adding specific thermoplastic polymers as low profile additives (LPA) in the UP can lead to a reduction or even elimination of the polymerization shrinkage during the cure [3]. However, low-profile polyester molding compounds when formulated with pigments may usually exhibit an unacceptable hazing of the pigment's color. For the past 15 years, unique non-reactive [4] and reactive [5] LPAs for high temperature applications have been developed that give significantly improved deep color pigmentation while maintaining a smooth surface and zero shrinkage, yet the fundamental principle has not been treated until lately [6-7]. By employing non-reactive LPA [6], microvoids [8] can be generated during the cure, which can then compensate for the volume shrinkage. In contrast, by employing reactive

LPA [7], the intrinsic polymerization shrinkage may be reduced, which is due to the reduction in cyclization reaction of UP resin during the cure caused by the favorable intermolecular crosslinking reaction between UP and reactive LPA.

The objective of this work is to investigate the effects of nano-scale core-shell rubber (CSR) as an LPA on the volume shrinkage characteristics and internal pigmentability for styrene (ST)/UP/CSR ternary systems cured at high temperatures.

## 2 EXPERIMENTAL

### 2.1 Materials

The nano-scale core-shell rubbers (CSR), with poly(butyl acrylate) (PBA) as the core and poly(methyl methacrylate) (PMMA) as the shell, were synthesized by two-stage emulsion polymerizations [9-11]. The shells of the CSR were also modified by introducing either ethylene glycol dimethacrylate (EGDMA) as a crosslinking agent or ethyl acrylate (EA) as a comonomer. The properties of the three CSRs synthesized in this study, including BA/MMA-EGDMA (i.e. E1 type), BA/MMA (i.e. E0 type), and BA/MMA-EA(2) (i.e. E0-EA(2) type), are summarized in Table 1.

Two UP resins [12] were employed. One was made from maleic anhydride (MA), 1,2-propylene glycol (PG), and phthalic anhydride (PA) with a molar ratio of 0.63:1.20:0.37. The acid number and hydroxyl number were found to be 25.3 and 31.0 by end-group titration, which gives an  $M_n$  of 1990 g/mole. The other was made from MA and PG with a molar ratio of 1:1.15. The acid number and hydroxyl number were found to be 29.3 and 31.7 again by end-group titration, which gives an  $M_n$  of 1840 g/mole. On average, the number of C=C bonds for each UP molecule was 5.96 and 11.0 for the MA-PA-PG and MA-PG types of UP, respectively.

For the sample solution, 0%, 5% or 10% by wt. of CSR was added, while the molar ratio of styrene to polyester C=C bonds was fixed at MR = 2/1. The reaction was initiated by 1 wt. % of tert-butyl perbenzoate (TBPB). For the sample solution with pigments, 10% by weight of Bordeaux Red was added as pigments. All the cure reactions were carried out at 110°C isothermally for 1 hr.

### 2.2 Instrumentation and Procedure

The compatibility of ST/UP/CSR systems at 25°C and 110°C prior to reaction [12], cure kinetics of the ternary systems by DSC [13], cured sample morphology for the fractured surface by SEM [14], and cured sample morphology by optical microscopy (OM) [14] have been investigated. The relative quantity of microcracking in the morphology sample under OM was also measured by means of an image analyzer [14]. Volume shrinkage and color depth [4] of the cured sample were measured by density methods [14] and by using a chromameter (Minolta, CR-300) respectively.

### 3 RESULTS AND DISCUSSION

The molecular polarity of UP resin and the shell of CSR was evaluated in terms of the calculated dipole moment per unit volume [12],  $\mu/V^{1/2}$  (Table 2). It was higher for the MA-PG type of UP than the MA-PA-PG (0.0867 vs. 0.0811). Also, the molecular polarity of UP resin was higher than that of the shell of CSR.

In general, the higher the polarity difference per unit volume between UP and the shell of CSR, the less compatibility for the ST/UP/CSR system at 25°C prior to reaction. Data in Table 2 reveal that at a fixed CSR, the ST/UP/CSR system containing MA-PG type of UP resin would lead to a lower compatibility than that of the ST/UP/CSR system containing MA-PA-PG type of UP resin. This is generally in agreement with the static phase characteristics data for the uncured ST/UP/CSR systems at 25°C (Table 3), where the MA-PG system containing either E0 or E0-EA(2) would phase separate and the MA-PA-PG system would not.

At a fixed CSR the phase separation time for the uncured ST/UP/CSR systems at 25°C and 110°C was generally shorter for the MA-PG system than the MA-PA-PG system. For both the MA-PG and the MA-PA-PG systems, increasing the mixing temperature from 25°C to 110°C could shorten the phase separation time. However, the degree of phase separation, as revealed by the weight percent of upper layer solution (i.e.  $w_0$ ), was reduced for the MA-PG systems containing E0 or E0-EA(2). This is in contrast to the MA-PG system containing E1 and the MA-PA-PG systems containing E1 or E0-EA(2).

During the cure at 110°C, SEM micrographs at 5000 X showed that both the neat MA-PA-PG and the neat MA-PG systems containing no CSR exhibited a flake-like microstructure (not shown). For the MA-PA-PG systems, adding a CSR at either 5 wt. % or 10 wt. % level can cause a less compatible ST/UP/CSR system with a two-phase microstructure, which consisted of a flake-like continuous phase and a CSR-dispersed phase (not shown). Also, at a fixed CSR content, the E1 system was the least incompatible, as evidenced by the smallest average area for the dispersed phase, followed by the E0 system and the E0-EA(2) system, which showed the same trend as that of predicted compatibility for the uncured ST/UP/CSR systems (Table 2). Moreover, for a fixed type of CSR,

adding a higher content of CSR may lead to the more incompatibility of the ST/UP/CSR system, again as evidenced by the larger average area for the CSR-dispersed phase.

During the cure at 110°C, SEM micrographs at 5000 X (not shown) show that for the ST/UP/5%E1 and the ST/UP/10%E1 systems, the MA-PA-PG systems were more compatible than the MA-PG systems, where the latter system possessed a larger average area for the dispersed phase with globule morphology inside.

During the cure at 110°C, OM micrographs at 500 X (not shown) show that for the ST/UP/E0 and the ST/UP/E0-EA(2) systems, the MA-PA-PG systems were again more compatible than the MA-PG systems, where the latter system possessed a larger number of the dispersed phase.

For the cured CSR-containing UP resin systems with their characteristic morphologies, their mechanical behavior can be approximately represented by the Takayanagi models [15], where arrays of weak CSR (R) and stiff styrene-crosslinked polyester (P) phases are employed (not shown). For all of the six ST/UP/CSR systems, the two-phase microstructure can be represented by a P-(P-P-S) model (not shown).

The volume shrinkages of the neat UP resins were about 9.0% (MA-PA-PG type) and 10.8% (MA-PG type). For ST/UP/CSR systems, adding a higher content of CSR may generally result in a lower volume shrinkage, or even an expansion (for MA-PG systems containing 10% E0 or 5% E0-EA(2)) after the cure. At a fixed CSR content, employing the MA-PG type of UP, which is more reactive, more flexible, and with a higher molecular polarity than the MA-PA-PG type of UP, could result in the more incompatibility of the ST/UP/CSR system during the cure, and may lead to a lower volume shrinkage. Apparently, pertinent incompatibility of the ST/UP/CSR system during the cure is indispensable for good volume shrinkage control. For the MA-PA-PG systems, adding 10% E0-EA(2) as an LPA would lead to the best volume shrinkage control ( $\Delta V/V_0 \cong -5.7\%$ ). In contrast, for the MA-PG systems, adding 5% E0 or 10% E0-EA(2) as an LPA would lead to the most effective volume shrinkage control ( $\Delta V/V_0 \cong -1.5\%$  to  $-1.7\%$ ).

The effects of shell chemical structure of CSR on  $L^*$  value as the index of internal pigmentability for ST/UP/CSR systems after the cure generally shows reverse trend to those on the fractional volume shrinkage. (The higher the  $L^*$  value, the worse the internal pigmentability.) Since an  $L^*$  value within about 30 can be employed as the acceptable upper bound for good internal pigmentability in this study, all of the MA-PA-PG systems and ST/UP(MA-PG)/10% E0-EA(2) system exhibit good internal pigmentability (Table 5). Among the six ST/UP/CSR systems, the ST/UP(MA-PG)/10% E0-EA(2) system has provided the best volume shrinkage control ( $\Delta V/V_0 \cong -1.7\%$ ), and achieved acceptable internal pigmentability ( $L^* \cong 29-30$ ).

Pattison et al. [8] have proposed that as the crosslinking of LPA-containing UP resins proceeds, strain due to polymerization shrinkage develops in the system, particularly at the interface of LPA phase (phase R) and crosslinked UP phase (phase P). This strain can increase to the point that stress cracking propagates through the weak LPA phase, relieving this strain, forming microcracks and/or microvoids, and compensating for the overall volume shrinkage by the microcrack or microvoid space. However, unlike the ST/UP/LPA systems containing nonreactive LPAs [6], such as poly(vinyl acetate), for the ST/UP/CSR systems, the relative volume fraction of microvoid data shown in Table 6 could not fully explain the experimental results, where the system with a smaller volume fraction of microvoids, such as the ST/UP(MA-PG)/5% E0 system, would not necessarily lead to a higher volume shrinkage, and vice versa.

The microvoid formation is intimately connected with the internal pigmentability [4]. As incident light enters an internally pigmented part of the cured ST/UP/CSR system, the intensity of reflective light to the pigment can be greatly reduced due to the severe light scattering which may occur at the solid/air (microvoid) interface inside the parts, leading to the hazing of a pigment's color. In theory, the higher the volume fraction of microvoids, the worse the internal pigmentability. For the ST/UP/CSR systems, the relative volume fraction of microvoid data shown in Table 6 generally agreed with the experimental results, where the MA-PA-PG system with a smaller volume fraction of microvoids would lead to a better internal pigmentability (i.e. a lower  $L^*$  value).

Besides microvoid formation, the intrinsic polymerization shrinkage is also important in determining the volume shrinkage control during the cure of ST/UP/CSR system. It is inferred that the relief of the polymerization shrinkage force caused by the rubbery core of the CSR, which can lead to the less compact microgel structures and a decrease of intrinsic polymerization shrinkage during the cure, are more favorable for the MA-PG system. This is the reason why the ST/UP(MA-PG)/5%E0 system, with a smaller volume fraction of microvoids ( $\cong 3.3\%$ ), could lead to a very good volume shrinkage control.

In addition to the volume fraction of microvoids, the average size of microvoids is also influential for the internal pigmentability. For the ST/UP(MA-PG)/5%E0 system, it is inferred that the average size of microvoids generated during the cure would be close to the wavelength of visible light ( $\lambda = 0.45 - 0.75\mu\text{m}$ ), where the light scattering at the solid/air (microvoid) interface could be more pronounced, leading to a worse internal pigmentability.

#### 4 CONCLUSIONS

For ST/UP/CSR systems, the microvoid formation can affect both the volume shrinkage control and internal pigmentability for the cured sample. The intrinsic

polymerization shrinkage may be reduced by employing CSR as an LPA, where the relief of the polymerization shrinkage force caused by the rubbery core of the CSR can lead to the less compact microgel structures and a decrease of intrinsic polymerization shrinkage. At a fixed CSR content, the more incompatible MA-PG system may lead to a much lower volume shrinkage after the cure than the MA-PA-PG system. In this work, the ST/UP(MA-PG)/10% E0-EA(2) system has achieved a very good volume shrinkage control and acceptable pigmentability ( $\Delta V/V_0 \cong -1.7\%$  and  $L^* \cong 29-30$ ).

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CSR codes	Simple codes	monomers	Molar comp. of monomers	$T_g(C)^\text{a}$	$D_n(\text{nm})^\text{b}$
BA/MMA-EGDMA	E1	Core: BA Shell: MMA, EGDMA	Core:0.773 Shell:0.990:0.010	-44.8, 9.7, 118.2	43.6
BA/MMA	E0 <sup>c</sup>	Core: BA Shell: MMA	Core:0.781 Shell:1.000	-	40.3
BA/MMA-EA(2)	E0-EA(2) <sup>d</sup>	Core: BA Shell: MMA, EA	Core:0.727 Shell:0.930:0.070	-	40.2

a: by TSC (Methods of Thermally Stimulated Currents); the low, medium, and high transition temperatures are the  $T_g$ 's for the core (i.e. PBA), the interlayer (i.e. PBA-g-PMMA),

and the shell (i.e. lightly EGDMA-crosslinked PMMA) of the CSR, respectively.

b: by DLS (Dynamic Light Scattering).

c: The molar composition of BA and MMA, for the CSR was measured to be 0.903: 1.000 by  $H^1$ -NMR.

d: The molar composition of BA, MMA, and EA for the CSR was measured to be 0.937: 0.984: 0.016 by  $H^1$ -NMR.

Table 1: CSR used in this study

UP or Shell of CSR	dipole moment per unit volume $\mu' (= (\mu^2/V)^{1/2})$ (debye/cm <sup>3/2</sup> )	$\mu'_{MA-PG}$ $\mu'_{shell\ of\ CSR}$	$\mu'_{MA-PA-PG}$ $\mu'_{shell\ of\ CSR}$
(a)UP resin			
MA-PG type of UP	0.0867	-	-
MA-PA-PG type of UP	0.0811	-	-
(b) Shell of CSR			
MMA-EGDMA	0.0723	0.0144	0.0087
MMA	0.07218	0.01452	0.00882
MMA-EA(2)	0.07217	0.01453	0.00883

Table 2: Calculated dipole moments for UP and the shell of CSR

CSR added	Simple codes	$t_p(25)^a$ (min)	$w_u(25)^b$ (%)	$t_p(110)^a$ (min)	$w_u(110)^b$ (%)	$\alpha(\%)^c$
Neat UP (MA-PG)						-
BA/MM A-EGDMA	E1	$\infty^d$	-	90	76	-
BA/MM A-	E0	90	39	10	31	-
BA/MM A-EA (2)	E0-EA(2)	120	33	10	26	-
Neat UP (MA-PA-PG)						62.2
BA/MM A-EGDMA	E1	$\infty^d$	-	180	69	76.6
BA/MM A-	E0	$\infty^d$	-	$\infty^d$	-	-
BA/MM A-EA (2)	E0-EA(2)	$\infty^d$	-	60	65	-

a: phase separation time (min) at 25 (i.e.  $t_p(25)$ ) and 110°C (i.e.  $t_p(110)$ ); b: relative wt. of upper layer (%) at 25 (i.e.  $w_u(25)$ ) and 110°C (i.e.  $w_u(110)$ ); c: final cure conv. of total C=C bonds at 110°C by DSC; d: one phase (after 1440 min).

Table 3: Phase separation characteristics for ST/UP/10%CSR uncured systems at 25 and 110°C, and final conversions of total C=C bonds by DSC for ST/UP/10%CSR systems cured at 110°C

CSR added	Wt% of CSR	UP type	
		MA-PG	MA-PA-PG
Neat UP		-10.8(0.35) <sup>a</sup>	-9.01(0.15) <sup>a</sup>
E1	5	-6.62(0.35)	-7.79(0.12)
	10	-4.07(0.28)	-7.90(0.07)
E0	5	-1.54(0.15)	-8.36(0.14)
	10	5.38 <sup>b</sup> (0.06)	-8.55(0.09)
E0-EA(2)	5	1.99 <sup>b</sup> (0.32)	-8.81(0.04)
	10	-1.67(0.19)	-5.66(0.11)

a: The values in parentheses represent the estimated standard errors; b: volume expansion.

Table 4: Volume shrinkage (%),  $\Delta V/V_0$ , for ST/UP/CSR systems cured at 110°C

CSR added	Wt% of CSR	UP type			
		MA-PG		MA-PA-PG	
		Upper	Lower	Upper	Lower
Neat UP		28.17(0.15) <sup>a</sup>	27.90(0.27)	25.67(0.18) <sup>a</sup>	25.32(0.12)
E1	5	34.09(0.15)	29.92(0.06)	24.22(0.15)	23.67(0.02)
	10	38.70(0.17)	36.21(0.21)	24.54(0.11)	24.91(0.05)
E0	5	40.20(0.19)	28.65(0.13)	26.53(0.12)	25.07(0.12)
	10	37.20(0.22)	30.92(0.94)	25.29(0.09)	24.70(0.08)
E0-EA(2)	5	31.18(0.09)	28.02(0.14)	25.09(0.07)	24.19(0.08)
	10	30.07(0.05)	28.53(0.23)	24.90(0.05)	24.56(0.25)

a: The values in parentheses represent the estimated standard errors.

Table 5: Internal pigmentability index,  $L^*$ , for both sides of molded parts for ST/UP/CSR cured systems

CSR added	Wt% of CSR	UP type	
		MA-PG	MA-PA-PG
Neat UP		-	-
E1	5	10.7	2.09
	10	32.6	1.58
E0	5	3.33	4.92
	10	7.07	3.02
E0-EA(2)	5	15.8	4.22
	10	7.25	1.92

Table 6: Relative volume fraction (%) of microvoids,  $v_m$ , for ST/UP/CSR cured systems