

Effects of Reactive Low-profile Additives on the Volume Shrinkage and Internal Pigmentability for Low-temperature Cure of Unsaturated Polyester

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ABSTRACT: The effects of reactive poly(vinyl acetate)-*block*-poly(methyl methacrylate) (PVAc-*b*-PMMA) and poly(vinyl acetate)-*block*-polystyrene (PVAc-*b*-PS) as low-profile additives (LPA) on the volume shrinkage characteristics and internal pigmentability for low-shrink unsaturated polyester resins (UP) during the cure at 30°C were investigated. These reactive LPAs, which contained peroxide linkages in their backbones, were synthesized by suspension polymerizations, using polymeric peroxides (PPO) as initiators. Depending on the LPA composition and molecular weight, the reactive LPA could lead to a reduction of cyclization reaction for UP resin during the cure, and would be favorable for the decrease of intrinsic polymerization shrinkage after the cure. The experimental results have been explained by an integrated approach of measurements for the static phase

characteristics of the styrene (ST)/UP/LPA system, reaction kinetics, cured sample morphology, and microvoid formation by using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), optical microscopy (OM), and image analysis. Based on the Takayanagi mechanical model, factors leading to both a good volume shrinkage control and acceptable internal pigmentability for the molded parts have been explored. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 967–979, 2006

Key words: reactive poly(vinyl acetate)-*block*-poly(methyl methacrylate); reactive poly(vinyl acetate)-*block*-polystyrene; low-profile additive (LPA); unsaturated polyester resins (UP); volume shrinkage; internal pigmentability

INTRODUCTION

Adding specific thermoplastic polymers as low profile additives, (LPA) in the unsaturated polyester resins (UP) can lead to a reduction or even elimination of the polymerization shrinkage during the cure.¹ For the past 35 years, extensive studies^{1–14} have been devoted to the employment of nonreactive LPAs, such as thermoplastic polyurethane (PU), poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), and polystyrene (PS), aimed at the compensation of volume shrinkage by effective microvoid and/or microcrack formation,^{3,4} to which the phase separation between LPA and crosslinked UP phases during the cure is a prerequisite. It is straightforward that the other approach to the volume shrinkage control during the cure would be reducing the intrinsic polymerization shrinkage since the total volume change is the sum-

of volume shrinkage and volume compensation.

The large volume shrinkage of UP resins during the cure, typically ranging from 7 to 10%,² is due to the extensive intramolecular or cyclization reactions of UP molecules and the formation of compact microgel structures¹⁵ during the cure. Minimizing intramolecular or cyclization reactions of UP molecules during the cure can then lead to the minimization of intrinsic polymerization shrinkage. Although some reactive LPAs, such as PVAc-*b*-PMMA and PVAc-*b*-Polystyrene (PS) with many peroxide linkages along the skeleton of LPA, were successfully developed^{16–18} to minimize the volume shrinkage of UP resins, yet the fundamental principles have not been treated in details.

Ujikawa et al.¹⁸ explained the volume shrinkage reduction for the ST/UP/reactive LPA system by the formation of the microvoids during the cure (i.e., the increase of the free volume in the system), which is essentially the same as the explanation for the volume shrinkage control generally accepted for the ST/UP/nonreactive LPA system.^{3,4,13,14} This is, however, different from the viewpoint proposed for the ST/UP/reactive LPA system in this work.

Low-profile polyester molding compounds when formulated with pigments may usually exhibit an un-

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TABLE I
Raw Materials and Reaction Temperature History Used in the Synthesis of Reactive LPAs

LPA codes	MMA (g)	ST (g)	VAc (g)	ATPPO ^a	CTA (g)	PVOH solution (g) ^b	Reaction temp history (°C)
VAc- <i>b</i> -MMA16K(25)	40	–	10	5	0.48	400 ^c	60–70 ^d
VAc- <i>b</i> -MMA17K(32)	35	–	15	5	0.42	400	60–70 ^d
VAc- <i>b</i> -MMA33K(5)	45	–	5	5	0.27	400	60–70 ^d
VAc- <i>b</i> -MMA38K(15)	45	–	5	5	0.135	400	60–70 ^d
VAc- <i>b</i> -ST22K(10)	–	45	5	5	0.135	400 ^c	80–70 ^e
VAc- <i>b</i> -ST14K(14)	–	40	10	5	0.24	400	80–70 ^e

^a The weight ratio of ATPPO (polymeric peroxide) to monomer is 1:10.

^b The PVOH aqueous solution contained 0.5% by weight of PVOH ($M_n = 88,000$ g/mol), and the weight ratio of water to monomer is 8:1 for the reaction system.

^c For either of the two stages of suspension polymerization, 400 g of 0.5 % by wt of PVOH aqueous solution was employed (see text).

^d The MMA homopolymerization was carried out at 60°C for 3 h, followed by the VAc/MMA copolymerization at 70°C for another 5 h.

^e The ST homopolymerization was carried out at 80°C for 3 h, followed by the VAc/ST copolymerization at 70°C for another 5 h.

acceptable hazing of the pigment's color. This appears to be largely the results of the refractive index difference between the air/solid interface that occurs with microvoiding.¹⁹ In recent years, unique nonreactive LPAs for high temperature applications have been developed²⁰ that give significantly improved deep color pigmentation while maintaining a smooth surface and zero shrinkage, yet the fundamental principle has not been studied. Most recently, interest in the development of low shrinkage UP resins for low temperature applications has grown considerably in the industry, which has attracted some research attention.^{21,22}

The objective of this work is to investigate the effects of reactive vinyl acetate-based block copolymer types of LPA on the volume shrinkage characteristics and internal pigmentability for styrene(ST)/UP/LPA ternary systems cured at low temperatures. Using an integrated approach combining the static ternary phase characteristics of ST/UP/LPA at 25°C, cured sample morphology, reaction kinetics, microvoid formation, and property measurements, factors leading to both good volume shrinkage control and acceptable internal pigmentability for the molded parts are discussed.

EXPERIMENTAL

Reactive LPA

The reactive poly(vinyl acetate)-*b*-poly(methyl methacrylate) (PVAc-*b*-PMMA), and poly(vinyl acetate)-*b*-polystyrene (PVAc-*b*-PS) types of LPAs were synthesized by suspension polymerizations.^{16,23,24} Self-synthesized polymeric peroxides (PPO), *n*-dodecyl mercaptan (Acros), and poly(vinyl alcohol) (PVOH, $M_n = 88,000$ g/mol, Acros) were used as initiator,

chain transfer agent (CTA), and suspending agent, respectively. The first series of LPA was made from vinyl acetate (VAc, Acros) and methyl methacrylate (MMA, Acros), and the second series of LPA from vinyl acetate and styrene (ST, Acros). The raw materials and reaction temperature history used in the synthesis of the six LPAs for this study are summarized in Table I. These LPAs are reactive since there are peroxide linkages in their backbones, which are capable of thermal decomposition during cure, and may participate in the free radical crosslinking copolymerizations for the ST/UP/LPA system.

Synthesis of polymeric peroxides

A five-neck 0.5-L jacketed glass vessel reactor equipped with a thermometer, a stirrer, and a water pump was used in the synthesis of polymeric peroxides (PPO). A temperature-controlled circulation water bath (Haake F3C) was also employed to control the reaction temperature by water flowing through the jacket. Into the first reactor, there were charged 109.8 g (0.6 mol) of adipoyl chloride (AC, Merck) and 45 g (0.3 mol) of triethylene glycol (TEG, Acros). The reaction was then carried out under agitation (a stirring speed of 400 rpm) at a reaction temperature of 50°C, and maintaining a pressure of 40–50 mmHg (to eliminate HCl for the facilitation of polymerization) for 3 h, whereby a dark brown viscous liquid of triethylene glycol-bis (adipoyl chloride) (ATCI) was produced.

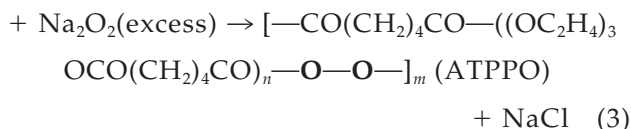


Into a second five-neck 0.5-L jacked glass reaction vessel, there was charged 231.8 g of 5.1 wt % aqueous solution of sodium peroxide (0.295 mol of NaOH) first. After the vessel temperature was controlled at 5°C, 12.14 g of 35 wt % of aqueous solution of hydrogen peroxide (0.125 mol of H₂O₂) was added to the reactor for the production of Na₂O₂, where a nitrogen sparge rate of 40 mL/min and a stirring speed of 450 rpm were maintained.



After 10 min of reaction time, 50 g of ATCl (0.113 mol) obtained in the above reaction was charged into the second reaction vessel through a feeding funnel at an addition rate of 1 g/min. After the completion of the feeding, the reaction was maintained at 5°C for another 30 min to complete the reaction of producing polymeric peroxides, ATPPO.

ATCl



The resultant precipitate was poured out, followed by washing with water three times, filtration, and vacuum-drying at room temperature overnight. The obtained white solid was then dissolved in 2.6 times by wt of chloroform, the resultant solution was poured into 11.4 times by wt of methanol for the purification by recrystallization, and stored in a refrigerator overnight. After the separation by filtration under suction and vacuum-drying at room temperature overnight in a vacuum oven, a purified ATPPO white solid was obtained.

Synthesis of reactive PVAc-*b*-PMMA and PVAc-*b*-PS types of LPA

For the synthesis of reactive PVAc-*b*-PMMA and PVAc-*b*-PS types of LPA, a two-stage reaction was adopted.

For the first stage reaction, into a five-neck 2-L glass vessel reactor provided with a stirrer, an N₂ inlet, a reflux condenser, a thermocouple, and a temperature controller, there were charged 400 g of 0.5% by wt aqueous solution of poly(vinyl alcohol) and a solution which was prepared by mixing monomers (MMA or ST), CTA, and ATPPO as shown in Table I. The reactants were mixed at room temperature for 30 min under a nitrogen sparge rate of 40 mL/min and a stirring speed of 500 rpm, and then heated up to reaction temperatures. The polymerization was carried out at 60°C (for MMA) or 80°C (for ST) isother-

mally for 3 h. The polymerization product was poured out, followed by washing with hot water (70–80°C) three times in a hot plate, with stirring to effectively remove the suspending agent adsorbed on the polymer, filtration under suction, and vacuum-drying overnight, whereby a white granular reactive homopolymer (PMMA or PS) bearing peroxide linkages on its backbone was obtained.

For the second stage of reaction, 400 g of 0.5% by wt aqueous solution of poly(vinyl alcohol), monomer 2 (*i.e.*, VAc), and the reactive homopolymer obtained in the first stage of reaction, which was used as an initiator, were charged into a five-neck 2-L glass vessel reactor. (No additional ATPPO was added.) After thorough mixing, suspension polymerization was carried out at 70°C for 5 h, where the pretreatment and purification procedures were essentially the same as those of the first stage reaction described earlier. A random block copolymer, PVAc-*b*-PMMA or PVAc-*b*-PS, could then be obtained, where the PMMA or the PS segment, with peroxide linkages on it, was reactive, while the PVAc segment was nonreactive.

The properties of the reactive LPAs synthesized in this study are summarized in Table II.

UP resins

The UP resin²⁶ was made from maleic anhydride (MA), 1,2-propylene glycol (PG), and phthalic anhydride (PA) with a molar ratio of 0.62:1.25:0.38. The acid number and hydroxyl number were found to be 28.5 and 31.1 by end-group titration, which gives an M_n of 1860 g/mol.

Preparation of sample solutions

For the sample solution, 10% by wt of LPA was added, while the molar ratio of styrene to polyester C=C bonds was fixed at MR = 2/1. The reaction was initiated by an amine-accelerated system with 3% by wt of benzoyl peroxide (BPO; an initiator, Lucidol W-75, Akzo), 0.3% *N,N*-dimethyl aniline (DMA, a promoter, Akzo), and 0.6% *p*-*tert*-butyl catechol (NLC-10, an inhibitor, Akzo). For the sample solution with pigments, 10% by wt of Bordeaux Red was added as pigments. All the cure reactions were carried out at 30°C isothermally for 2 h.

Phase characteristics

To study the compatibility of ST/UP/LPA systems before reaction, 20 g of sample solutions were prepared in 100 mL separatory glass cylinders, which were placed in a constant-temperature water bath at 25°C. The phase separation time was recorded and the mixture of each layer was separated and weighed.

TABLE II
LPAs Used in This Study

LPA codes	Monomer	Molar comp. ^a	M_n^b	M_w^b	PD ^b	T_g (°C) ^c	No. of —O—O— per LPA ^f
Reactive LPAs							
VAc- <i>b</i> -MMA16K(25)	VAc, MMA	0.25:0.75	16,000	38,000	2.4	62 (24, 82) ^d	0.29
VAc- <i>b</i> -MMA17K(32)	VAc, MMA	0.32:0.68	17,000	37,000	2.2	52 (23, 90) ^d	0.34
VAc- <i>b</i> -MMA33K(5)	VAc, MMA	0.05:0.95	33,000	87,000	2.6	60 (34, 98) ^d	0.41
VAc- <i>b</i> -MMA38K(15)	VAc, MMA	0.15:0.85	38,000	149,000	3.9	76 (46,104) ^d	0.62
VAc- <i>b</i> -ST22K(10)	VAc, ST	0.10:0.90	22,000	110,000	5.0	81 (28,107) ^e	0.11
VAc- <i>b</i> -ST14K(14)	VAc, ST	0.14:0.86	14,000	79,000	5.6	-	0.15
Non-reactive LPAs							
PVAc109K ¹³	VAc		109,000	166,000	1.52	20.4	

^a By ¹H NMR.

^b By GPC (g/mole).

^c By DSC.

^d The medium transition temperature (i.e., 62, 52, 60, or 76°C) is the T_g for the random block copolymer of VAc and MMA, while the lower (i.e., 24, 23, 34, or 46°C) and higher (i.e., 82, 90, 98, or 104°C) transition temperatures are the T_g for the PVAc and PMMA segments, respectively.

^e The medium transition temperature (i.e., 81°C) is the T_g for the random block copolymer of VAc and ST, while the lower (i.e., 28°C) and higher (i.e., 107°C) transition temperature are the T_g for the PVAc and PS segments, respectively.

^f The average no. of peroxide groups in the reactive LPA as measured by the iodine titration.²⁵

Cure kinetics

For the cure kinetic study, 6–10 mg sample solution was placed in a hermetic aluminum sample pan. The isothermal reaction rate profile at 30°C was measured by a DuPont 9000 differential scanning calorimeter, and the final conversion of total C=C bonds was calculated.^{27,28}

Scanning electron microscopy

In the morphological study, the fractured surface of the sample, which was cured at 30°C for 2 h in a stainless steel mold with inner trough dimensions of 17 × 1.4 × 0.35 cm³, was observed by a Hitachi SEM, with accelerating voltage of 20 kV at 1000 and 5000×.

Microvoids

The morphology of the sample during cure was also observed by means of an optical microscope (OM). One drop of sample (about 0.8 mg) was placed between two microscope cover glasses, which was then inserted into a hot stage (Mettler, FP82HT). The cured sample at 30°C was chilled in liquid nitrogen, and was subsequently observed at room temperature under an optical microscope, using transmitted light at magnifications of 100–400×.

The relative quantity of microcracking in the morphology sample under OM was measured by means of an image analyzer.^{5,9} Since the samples were of uniform thickness, the fraction of the image area which was black (due to light scattering by the microcracks)

would be proportional to the volume of the microcracks in the sample.

It should be noted that⁵ the absolute quantity of microcracking cannot be measured by the image analyzer system since overlapping cracks cannot be distinguished and cracks normal to the incident light do not scatter light. Other methods for estimating the relative microcrack fraction includes the Brunauer–Emmett–Teller (BET) surface area measurement technique demonstrated by Kinkelaar et al.,²⁹ but their results were far from satisfactory when the microvoid size in the ST/UP/LPA cured systems was less than 0.1 μm.

Suspene *et al.*⁶ reported that the microvoids for the cured ST/UP/LPA ternary system can be identified qualitatively by the white image seen from the TEM micrograph. TEM combined to image analysis would possibly be allowed to give interesting additional information.

Recently, in a study of carbon black-filled polyethylene conductive composites, Oakey et al.³⁰ demonstrated that atomic force microscopy (AFM) can be used to identify void size and absolute volume fraction of voids through a comparison of complementary height and phase images. Also, in the investigation of microvoids in polyacrylonitrile fibers, Thunemann and Ruland³¹ used a small-angle X-ray scattering technique (SAXS) for the quantitative description of orientation, length, diameter, and relative volume of microvoids. In our laboratory, research has been under way for the direct measurement of microvoids by AFM and SAXS techniques.

Volume change and calorimetric measurements

Density measurements⁹ at room temperature were employed for obtaining volume shrinkage data for isothermally cured specimens at 30°C. About 10 g of degassed sample solution was placed into a 10-mL density bottle, and its density at 25°C before reaction, ρ_1 , was measured. The density of the sample cured isothermally at 30°C was also determined at 25°C as ρ_2 by an immersion method using distilled water. The volume shrinkage can then be calculated by $(1/\rho_2 - 1/\rho_1)/(1/\rho_1)$.

Measurements of color depth²⁰ at room temperature for the corresponding cured specimens were carried out by using a chromameter (Minolta, CR-300). Ten measurements of L^* value as a color depth index were taken for both sides of the specimen respectively. The higher the L^* value, the lower the color depth, and the hazing phenomenon of the cured specimen is more pronounced, leading to a worse internal pigmentability. In this study, an L^* value within 30 was recognizably dark red in tint, and can be employed as the acceptable upper bound for good internal pigmentability.

RESULTS AND DISCUSSION

Synthesis of reactive LPA

The reactivity of LPA synthesized would depend on the number of peroxide groups in its skeleton, which may be influenced by the reaction temperature history (Table I). In this work, the polymeric peroxide, ATPPO (see eq. (3)), was employed as the initiator, whose half-life of thermal decomposition ($t_{1/2} = 10$ h at 61.3°C as determined by DSC at a heating rate of 1.25°C/min and assuming a first-order kinetics) exhibited similar activity to that of the conventional peroxides, such as lauroyl peroxide ($t_{1/2} = 10$ h at 62°C) and benzoyl peroxide ($t_{1/2} = 10$ h at 72°C),³² for the initiation of vinyl monomer polymerization. In the synthesis of reactive LPA, including VAc-*b*-MMA and VAc-*b*-ST, the peroxide linkages in the ATPPO, the PMMA segments, and the PS segments would be capable of thermal decomposition to generate free radicals during the 8-h reaction for the two isothermal stages at 60 and 70°C (for VAc-*b*-MMA), or at 80 and 70°C (for VAc-*b*-ST). Therefore, either the higher the reaction temperature or the longer the duration of reaction time, the number of peroxide linkages survived in the reactive LPA at the end of synthesis would be smaller, leading to a less reactive LPA. For the reactive LPA in this work, the average number of peroxide linkages per LPA molecule was measured to be 0.1–0.6 by the iodine titration method²⁵ (Table II).

For the VAc-*b*-MMA and VAc-*b*-ST random block copolymers, the introduction of VAc can alter the glass transition temperature (T_g) and molecular polar-

ity in comparison with PMMA or PS. This may then change the miscibility of the ST/UP/LPA ternary system.

Characterization of ATPPO and LPA

Oshibe and Yamamoto²³ pointed out that the polycondensate ATCI obtained in eq. (1) is a mixture A(TA)_{*n*}, with *n* ranges from 0 to 6. Their thin layer chromatography (TLC) and ¹H nuclear magnetic resonance (¹H NMR) analysis showed that as *n* equals to 1 (i.e., ATA), the weight distribution of the polycondensate reaches a maximum. Therefore, the average molecular weight of the repeating unit for ATPPO in eq. (3) would be 404 g/mol by assuming *n* equals to 1. Since the number-average and weight-average molecular weights of the ATPPO synthesized in this work were measured to be 5000 and 12,800 g/mol by GPC, on average, there were 12.4 peroxide groups in each ATPPO molecule.

The molar compositions of VAc-*b*-MMA and VAc-*b*-ST types of LPA as shown in Table II were identified by ¹H NMR, where the peak intensities of —OCH₃ ($\delta = 3.4$ – 3.6) for MMA, —O—CH< ($\delta = 4.0$ – 4.2) for VAc, and ortho proton ($\delta = 6.4$ – 6.8) for ST were selected for the calculations. (A two-dimensional HETCOR experiment³³ of NMR was also carried out to confirm the peak assignment mentioned earlier.)

The number-average molecular weight, M_n , as measured by GPC, for the six reactive LPAs fell in the range of 14,000–38,000 g/mol, while the polydispersity (PD) ranged from 2.2 to 5.6 (Table II).

DSC results in Table II showed that for the VAc-*b*-MMA and the VAc-*b*-ST types of LPA, more than one T_g can be measured (except for the VAc-*b*-MMA14K(14) system, where no T_g can be identified.), where the medium transition temperature (i.e., 62, 52, 60, 76, or 81°C) is the T_g for the random block copolymer, VAc-*b*-MMA or VAc-*b*-ST, while the lower (e.g., 24°C for VAc-*b*-MMA16K(25)) and higher (e.g., 82°C for VAc-*b*-MMA16K(25)) transition temperatures are the T_g for the PVAc and PMMA (or PS) segments, respectively. The introduction of VAc monomer in the PMMA or PS backbone can lead to a decrease of the stiffness of polymer chain and, in turn, a decrease in T_g .

Compatibility of styrene/UP/LPA systems prior to cure

The molecular polarity of UP resin and LPA was evaluated in terms of the calculated dipole moment per unit volume,²⁶ $\mu/V^{1/2}$, by using the Debye's equation³⁴ and group contribution methods.^{34,35} In general, the higher the polarity difference per unit volume between UP and LPA, the less compatibility for the ST/UP/LPA system at 25°C prior to reaction. Data in

TABLE III
Calculated Molar Volumes and Dipole Moments for UP and LPA, Phase Characteristics for ST/UP/LPA
Uncured Systems at 25°C, and Final Conversions of Total C=C Bonds as Measured by DSC for ST/UP/LPA
Systems Cured at 30°C

UP or LPA	μ^a	V^b	μ'^c	$\mu'_{UP}\mu'_{LPA}$	t_p (25) ^d	w_u (%) ^e	α^f
Neat UP resin							
MA-PG-PA	3.13	1,389	0.0840		—		61.3
Reactive LPAs							
VAc- <i>b</i> -MMA16K(25)	8.37	12,950	0.0736	0.0104	∞^g	—	64.4
VAc- <i>b</i> -MMA17K(32)	8.67	13,710	0.0741	0.0099	∞	—	62.4
VAc- <i>b</i> -MMA33K(5)	11.86	26,930	0.0722	0.0118	∞	—	66.0
VAc- <i>b</i> -MMA38K(15)	12.81	30,900	0.0729	0.0111	390	32.3	76.9
VAc- <i>b</i> -ST22K(10)	2.97	18,190	0.0220	0.0620	130	40.5	81.9
VAc- <i>b</i> -ST14K(14)	2.90	11,550	0.0270	0.0570	161	35.1	75.7
Non-reactive LPAs							
PVAc109K ¹³	23.53	86,510	0.0800	0.0040	∞	—	73.0 ^h

^a Dipole moment (Debye/mol^{1/2}).

^b Molar volume (cm³/mol).

^c Dipole moment per unit volume ($=(\mu^2/V)^{1/2}$; Debye/cm^{3/2}).

^d Phase separation time (min) at 25°C (*i.e.* t_p (25)).

^e Weight percent for the upper layer solution after a phase equilibrium at 25°C (%).

^f Cure conversion of total C=C bonds (%) for ST/UP/LPA systems as measured by DSC at 30°C.

^g One phase after 1440 min.

^h Cured at 110°C isothermally for 1 h (1% by wt of *tert*-butyl perbenzoate, TBPB, was used as an initiator).

Table III reveal that the ST/UP/LPA system containing VAc-*b*-MMA would be theoretically more compatible than that containing VAc-*b*-ST. Also, adding an LPA with a higher content of relatively polar vinyl acetate (VAc) monomer, as compared with the relatively nonpolar methyl methacrylate or styrene (MMA or ST) monomer, would lead to a higher compatibility of the ST/UP/LPA ternary system. This is generally in agreement with the static phase characteristics data for the uncured ST/UP/LPA systems at 25°C (Table III), where the degree of phase separation, as revealed by the relative weight of upper layer solution, was less for the VAc-*b*-MMA systems than the VAc-*b*-ST systems. Also, the degree of phase separation was more noticeable for the VAc-*b*-ST22K(10) system than the VAc-*b*-ST14K(14) system.

Cured sample morphology, cure kinetics, and compatibility of cured ST/UP/LPA ternary systems

During the cure at 30°C, SEM micrographs (Fig. 1) show that the VAc-*b*-MMA systems were generally more compatible than the VAc-*b*-ST systems (it was not clear for Fig. 1(b) though), where a more conspicuous two-phase microstructure containing a flake-like continuous phase and an LPA-rich dispersed phase was observed for the latter systems. This is due to a higher polarity difference between UP and LPA for the VAc-*b*-ST systems (Table III).

Also, for a fixed type of LPA (VAc-*b*-MMA or VAc-*b*-ST) and with a similar molecular weight range of LPA ($M_n = 16K-17K$, $M_n = 33K-38K$, or $M_n = 14K-22K$), adding an LPA with the lower molecular polar-

ity (also with a lower reactivity due to the lower concentration of —O—O— groups per LPA shown in Table II), such as VAc-*b*-MMA16K(25), VAc-*b*-MMA33K(5), and VAc-*b*-ST22K(10), can cause a globular continuous phase for the ST/UP/LPA system during the cure (see Figs. 1(a), 1(c), and 1(e)), which is in contrast to a flake-like continuous phase generated (see Figs. 1(b), 1(d), and 1(f)). For ST/UP/LPA systems, the microgel particles generated during the cure may be better segregated by the less polar and less reactive LPAs, leading to a globule morphology. In contrast, the microgel particles may be capable of overlapping with each other via the intermolecular crosslinking reaction with the more polar and more reactive LPAs, leading to a two-phase microstructure containing a flake-like continuous phase and an LPA-dispersed phase, where the number and size of the dispersed phase becomes smaller.

Isothermal DSC rate profiles for the ST/UP/LPA sample solution at 30°C (Fig. 2) showed that for a fixed type of LPA and with a similar molecular weight range of LPA, the VAc-*b*-MMA17K(32), the VAc-*b*-MMA33K(5), and the VAc-*b*-ST14K(14) systems were less compatible than their counterparts (*i.e.*, the VAc-*b*-MMA16K(25), the VAc-*b*-MMA38K(15), and the VAc-*b*-ST22K(10) systems, respectively), which is in agreement with that revealed by SEM micrographs (Fig. 1). This can be evidenced by the fact that the less compatible ST/UP/LPA system during the cure would exhibit dual reaction peaks in the DSC rate profile, where the former peak is due to the major continuous phase and the latter one due to the LPA-

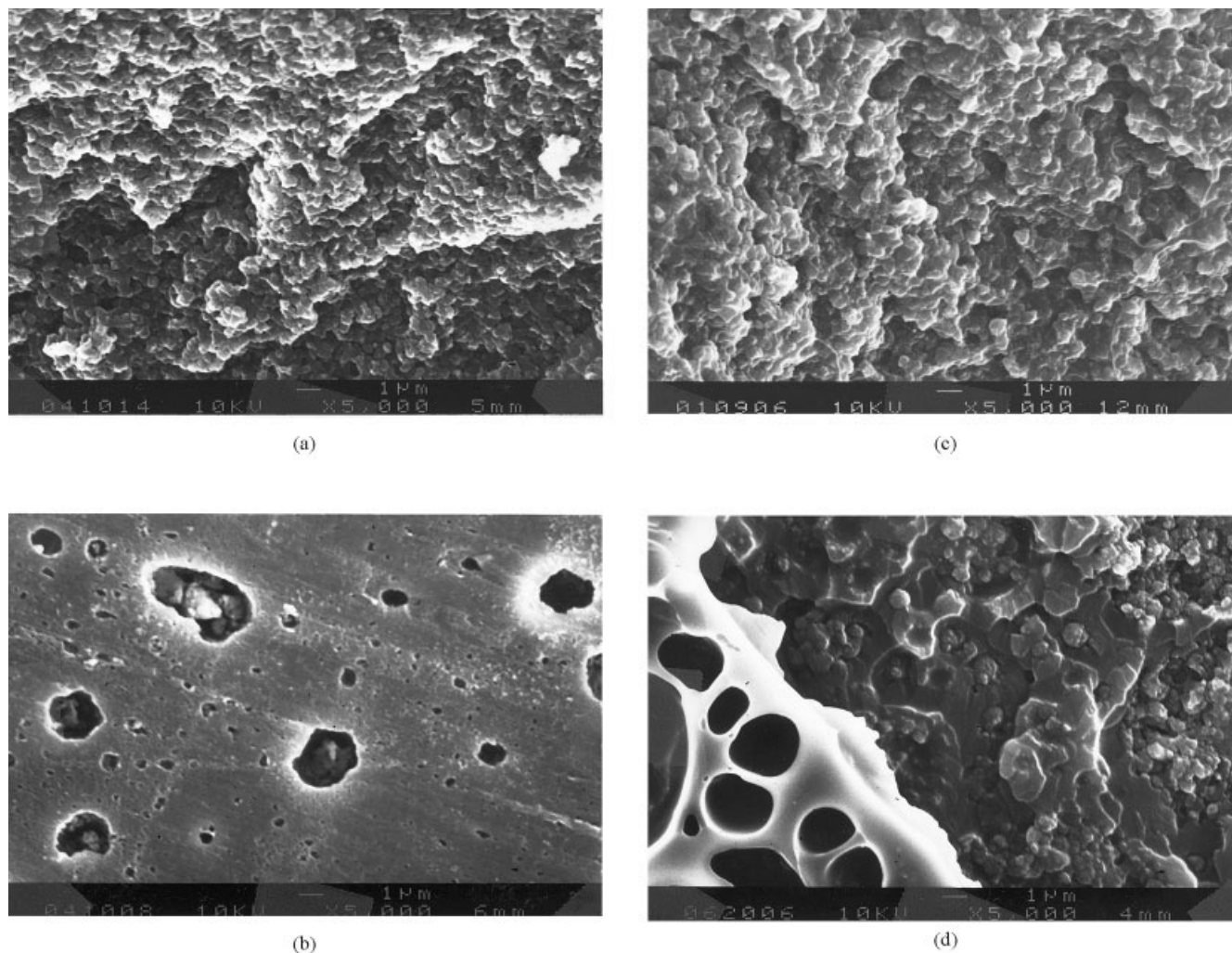


Figure 1 Effects of LPA types on the cured sample morphology under SEM. (a) VAc-*b*-MMA16K(25), (b) VAc-*b*-MMA17K(32), (c) VAc-*b*-MMA33K(5), (d) VAc-*b*-MMA38K(15), (e) VAc-*b*-ST22K(10), (f) VAc-*b*-ST14K(14), and (g) PVAc109K. The system of ST/UP/LPA containing 10% PVAc109K was cured at 110°C isothermally for 1 h, followed by a post cure at 150°C for another hour.

rich dispersed phase. (see curves 3 and 4 in Fig. 2). Also, a relatively lower peak reaction rate would be an indication of the lower compatibility for the ST/UP/LPA system during the cure.¹³ (compare curves 6 and 7 in Fig. 2)

For the ST/UP/LPA sample solution containing reactive LPA, isothermal DSC conversion profiles at 30°C (Fig. 3) showed that for a fixed type of LPA and with a similar molecular weight range of LPA, the less compatible systems (i.e., the VAc-*b*-MMA17K(32), the VAc-*b*-MMA33K(5), and the VAc-*b*-ST14K(14) systems) possessed a lower cure conversion than their counterparts (i.e., the VAc-*b*-MMA16K(25), the VAc-*b*-MMA38K(15), and the VAc-*b*-ST22K(10), systems, respectively). This is ascribed to the fact that the molar ratio of styrene to polyester C=C bonds (MR) in the major continuous phase of styrene-crosslinked polyester would be less deviated from (less than) an MR of 2:1 for the more compatible ST/UP/LPA system dur-

ing the cure, and better styrene swelling effect on the microgel structure in the major continuous phase could lead to a higher final cure conversion²⁷ therein, and, in turn, a higher overall cure conversion.

Relationship between morphologies and mechanical properties—The Takayanagi models

For the cured LPA-containing UP resin systems with their characteristic morphologies shown in Figures 1(a)–1(g), their mechanical behavior can be approximately represented by the Takayanagi models,^{36,37} where arrays of weak LPA (R) and stiff styrene-crosslinked polyester (P) phases are indicated (Fig. 4). The subscripts 1, 2, and 3 for P phases are employed due to the distinction of styrene and UP compositions as a result of phase separation during cure, and the quantities λ , φ , ξ , and ν or their indicated multiplications indicate volume fractions of each phase.

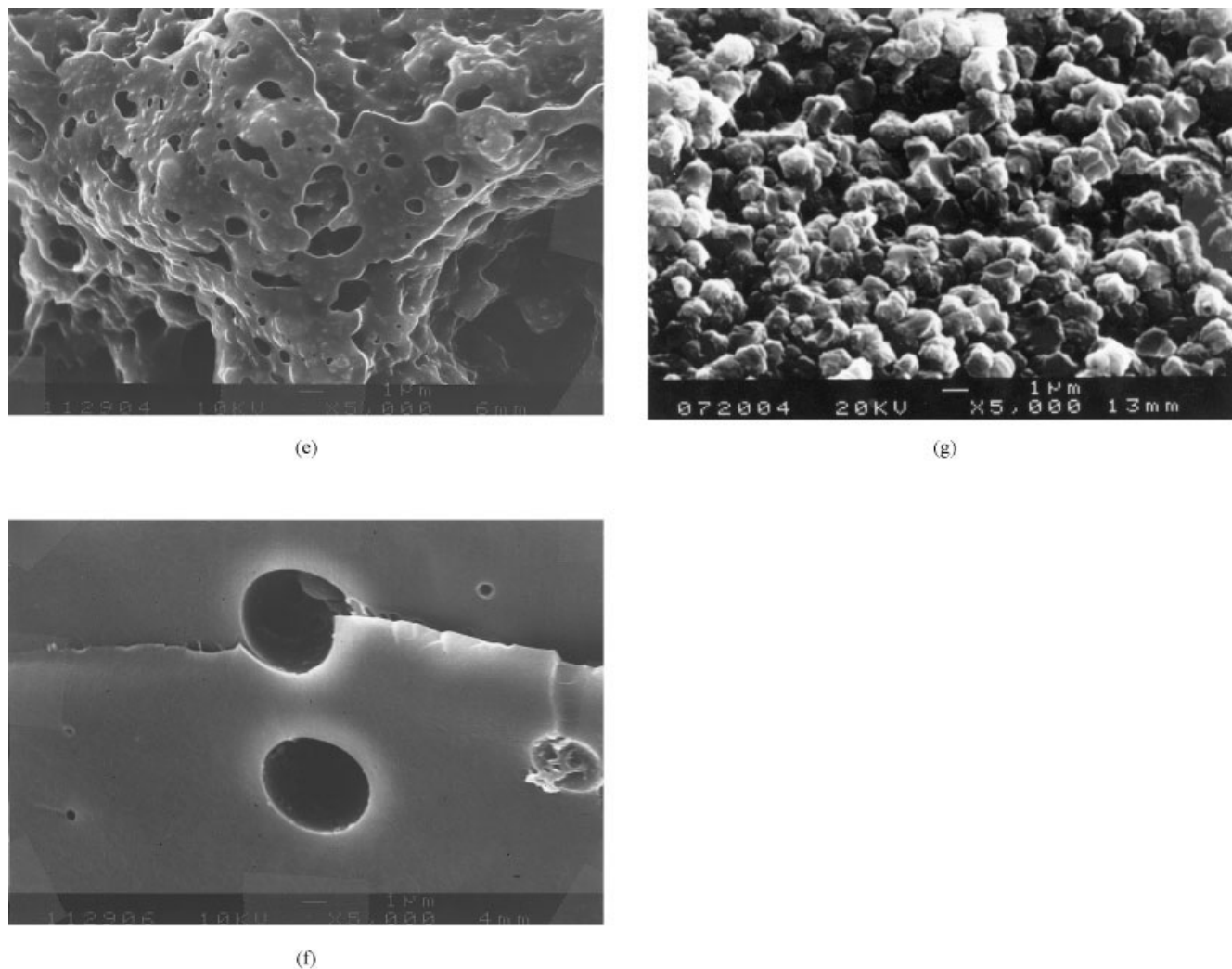


Figure 1 (Continued from the previous page)

For the systems shown in Figures 1(a), 1(c), and 1(g), the microgel particles (phase P_1) are surrounded by a layer of LPA (phase R). Between the LPA-covered microgel particles, there are some lightly styrene-crosslinked polyester chains and polystyrene chains (taken both together as phase P_2), with different compositions of ST and UP from those in phase P_1 , dispersed in the LPA phase (phase R). Hence, the characteristic globule microstructure may be represented by the P-P-S model as shown in Figure 4(a), which is a parallel combination of the three elements, i.e., P_1 , R, and P_2 -R in series. In contrast, for the system shown in Figures 1(b), 1(d)–1(f), the microstructure consists of a stiff continuous phase of styrene-crosslinked polyester (phase P_1) and a weak globule LPA-dispersed phase, whose globule morphology can also be represented by a P-P-S model. Hence, the upper bound of mechanical behavior for the overall morphology can be represented by a P-(P-P-S) model as shown in Figure 4(b), which is simply a parallel combination of the continuous phase P_1 and the dispersed phase denoted by a (P-P-S) model.

Volume shrinkage and internal pigmentability

The volume shrinkage of the neat UP resin was about 8.3%, while adding different reactive VAc-*b*-MMA and VAc-*b*-ST types of LPAs can generally reduce the volume shrinkage to about -3.9 to -7.4% (Table IV). For the ST/UP/LPA system with a similar molecular weight range of LPA added ($M_n = 16\text{K}–17\text{K}$, $M_n = 33\text{K}–38\text{K}$, or $M_n = 14\text{K}–22\text{K}$), the less compatible ternary system during the cure may generally lead to a lower volume shrinkage (except for the VAc-*b*-ST22K(10) system). However, the VAc-*b*-ST22K(10) system, which was more compatible than the VAc-*b*-ST14K(14) system, would be the most effective for the volume shrinkage control. ($\Delta V/V_0 \cong -3.9\%$)

In light of the fact that the VAc-*b*-MMA system is more compatible than the VAc-*b*-ST system, volume shrinkage data in Table IV reveal that either a very compatible or a very incompatible ST/UP/LPA system could not result in a good volume shrinkage control.

The effects of LPA chemical structure on L^* value as the index of internal pigmentability for ST/UP/LPA

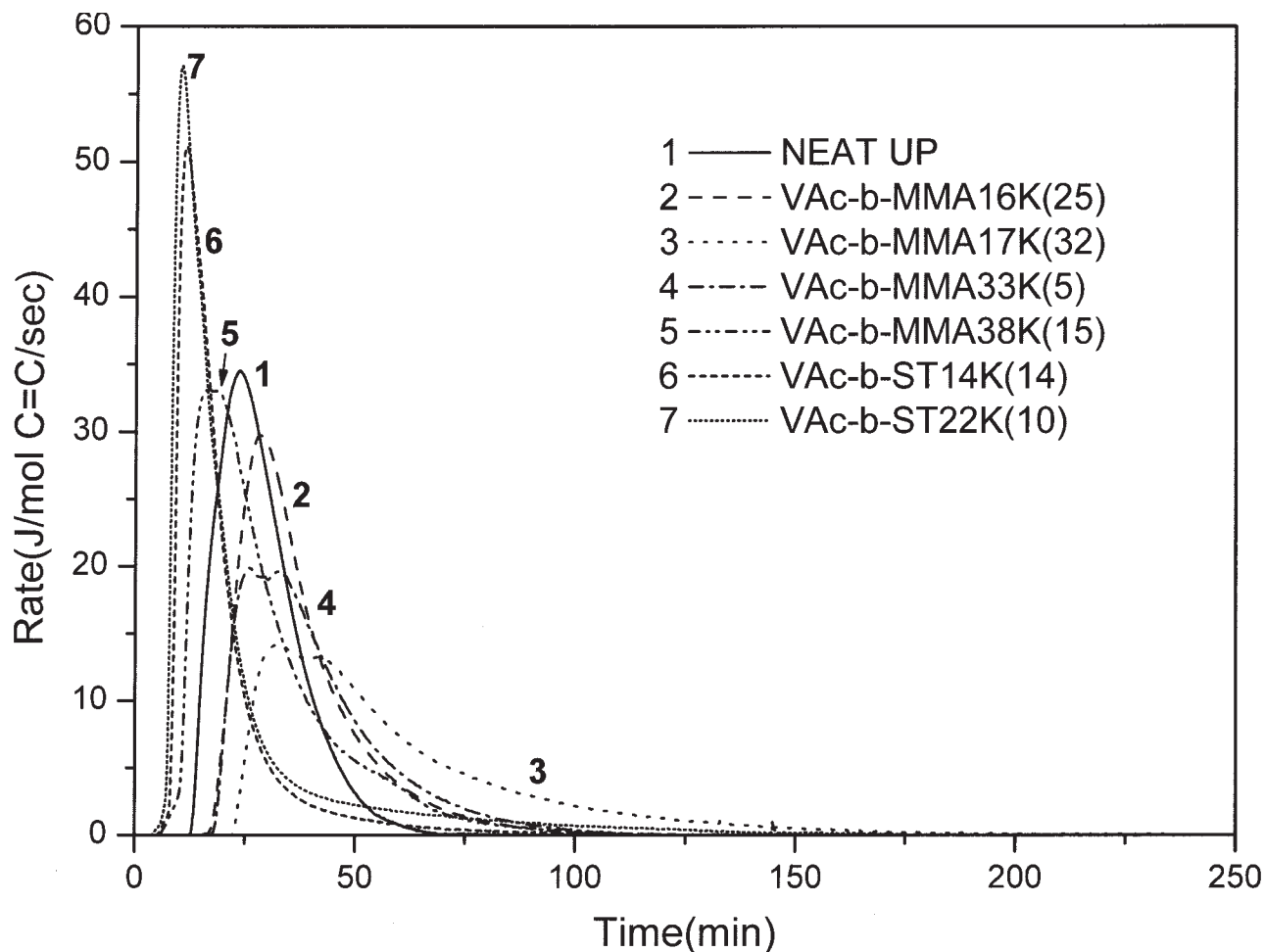


Figure 2 The effects of the reactive LPA on the DSC reaction rate profile at 30°C for ST/UP/LPA systems.

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, except the VAc-*b*-MMA33K(5) system, all of the systems exhibit good internal pigmentability (Table IV).

Effects of microvoid formation on volume shrinkage

Pattison et al.^{3,4} 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 or microvoids or both, and compensating for the overall volume shrinkage by the microcrack or microvoid space. However, unlike the ST/UP/LPA systems containing nonreactive LPA,¹³

such as poly(vinyl acetate), for the ST/UP/LPA systems containing reactive LPAs, the relative volume fraction of microvoid data shown in Table IV could not fully explain the experimental results, where the system with a smaller volume fraction of microvoids, such as the VAc-*b*-ST22K(10), would not necessarily lead to a higher volume shrinkage, and vice versa. This is in contrast to the ST/UP/LPA system containing a nonreactive LPA, such as PVAc109K, which may lead to a higher relative volume fraction of microvoids ($v_m = 49\%$) after the cure at 110°C, and, in turn, a good volume shrinkage control ($\Delta V/V_0 = -2.1\%$). (see Table IV)

Effects of microvoid formation on internal pigmentability

The microvoid formation is intimately connected with the internal pigmentability.²⁰ As incident light enters an internally pigmented part of the cured ST/UP/LPA system, the intensity of reflective light to the pigment can be greatly reduced due to the severe light scattering which may occur at the sol-

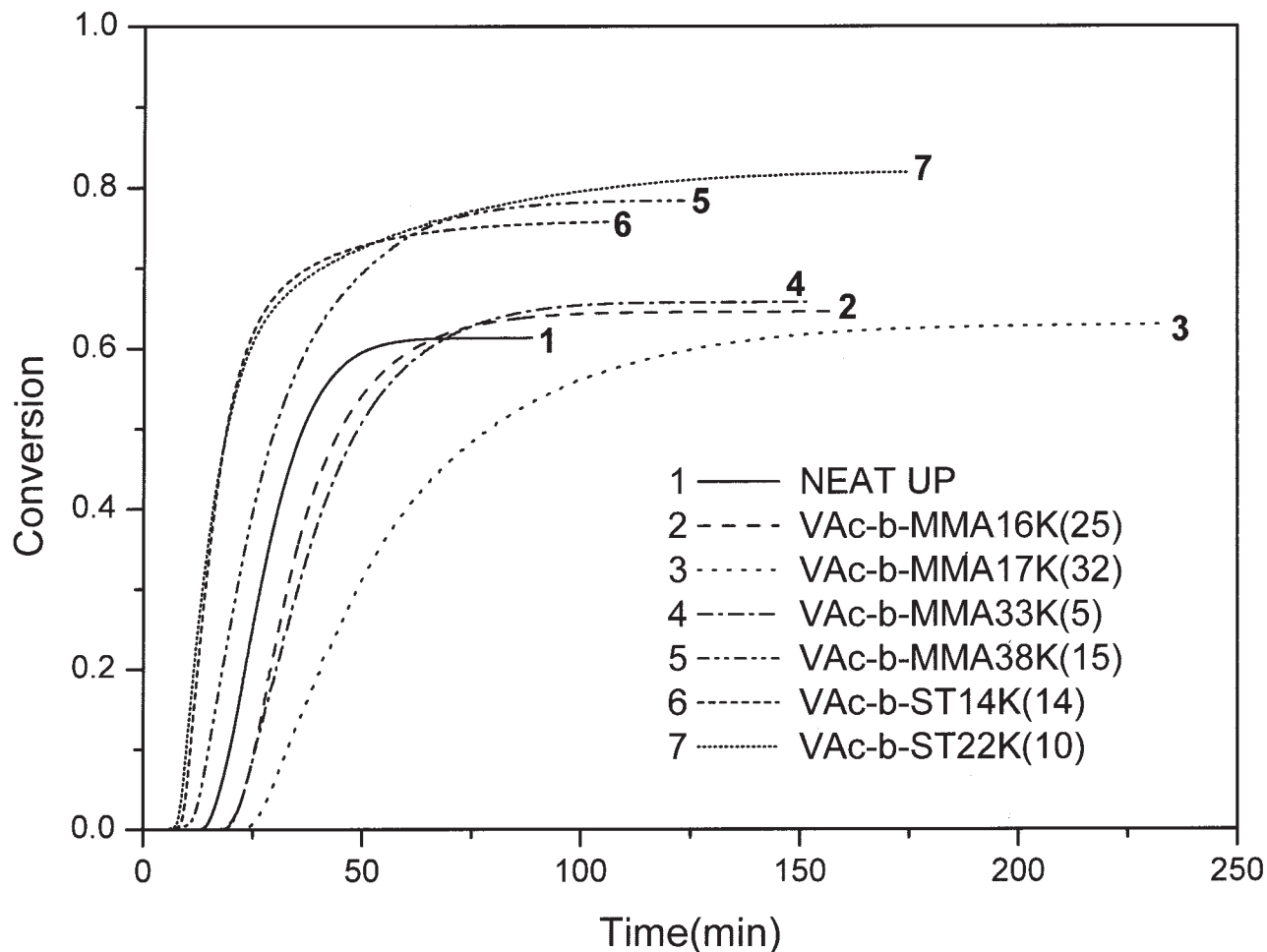


Figure 3 The effects of the reactive LPA on the DSC conversion profile at 30°C for ST/UP/LPA systems.

id/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/LPA systems containing reactive LPAs, the relative volume fraction of microvoid data shown in Table IV generally agreed with the experimental results, where the system with a larger volume fraction of microvoids, such as the VAc-*b*-MMA33K(5) system, would lead to a worse internal pigmentability (i.e., a higher L^* value).

The large difference of L^* value between the upper side and the bottom side of the VAc-*b*-MMA33K(5) system (21.2 vs. 38.7) can be due to the nonhomogeneous volume and/or size distribution of microvoids throughout the part (Fig. 1(c)) caused by the phase separation during cure. For the VAc-*b*-MMA systems, the L^* value was always higher (i.e., worse internal pigmentability) for the bottom side, which reveals that either the volume fraction or the average size of microvoids was larger for the bottom side than for the upper side.

Effects of intrinsic polymerization on volume shrinkage

Besides microvoid formation, the intrinsic polymerization shrinkage is also important in determining the volume shrinkage control during the cure of ST/UP/LPA system. Based on our experimental data of SEM micrographs, the reactive LPA with a lower reactivity and a lower molecular polarity, such as VAc-*b*-ST22K(10), could lead to expansion effects on the styrene-crosslinked polyester microgel structure (Fig. 1(e)). This is ascribed to the reduction in cyclization reaction of UP resin during the cure, caused by the intermolecular reaction between UP and reactive LPA, as well as the repulsive forces between chain segments of UP and LPA within the microgel structures. A lower intrinsic polymerization shrinkage could then result (see Fig. 5).

In the design of reactive PVAc-*b*-PMMA and PVAc-*b*-PS types of LPA, the less polar PMMA or PS segment, with peroxide linkages on it, was reactive, while the more polar PVAc segment was nonreactive. In the

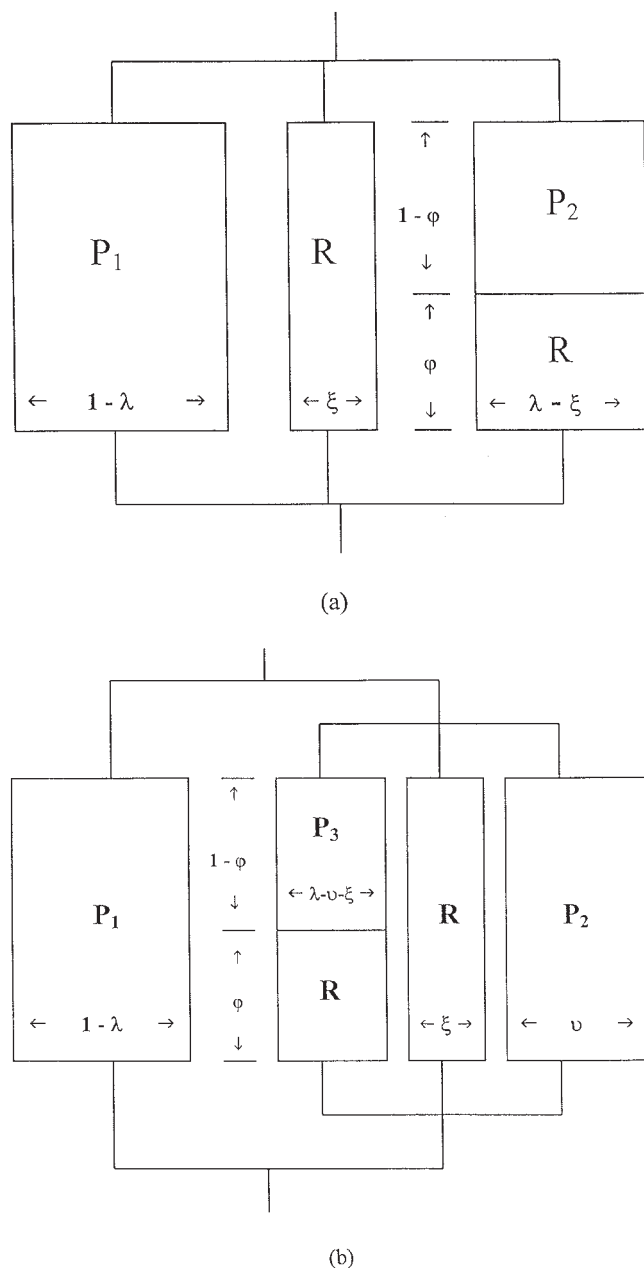


Figure 4 The Takayanagi models for mechanical behavior of cured LPA-containing UP resin systems. (a) parallel-parallel-series (P-P-S) model, and (b) parallel-parallel-parallel-series (P-P-P-S) model. The area of each diagram is proportional to a volume fraction of the phase.

subsequent curing of ST/UP/LPA system, the styrene-crosslinked polyester microgel particles, with the less polar PMMA or PS segment of the LPA covalently bonded to their surfaces, tend not to overlap with each other (see Fig. 5) due to the incompatibility between UP and PMMA (or PS), and could thus facilitate the reduction of polymerization shrinkage due to the expansion effect of the microgel structure. (The microgel structure (large circle in Fig. 5) is composed of tens and hundreds of primary microgel particles (small

circle in Fig. 5) with unsaturated C=C double bonds at their surfaces.)

This expansion effect, hence, depends on three factors, namely, the repulsive forces between chain segments of UP and LPA (F_{rep}), reactivity of LPA (k_{LPA}), and the LPA molecular weight (MW_{LPA}). Firstly, F_{rep} can be controlled by the polarity difference per unit volume between UP and LPA, $\Delta\mu'$. On one hand, increasing $\Delta\mu'$ can lead to a larger F_{rep} , and a lower volume shrinkage ($\Delta V/V_0$) during the cure would result due to a greater expansion effect of reactive LPA on microgel. On the other hand, increasing $\Delta\mu'$ can also result in a faster phase separation rate for ST/UP/LPA system during the cure. LPA concentration inside the microgels (i.e., large circle in Fig. 5), C_{LPA} , would then be decreased, leading to a higher $\Delta V/V_0$ caused by a smaller expansion effect of reactive LPA on microgel. The two opposing effects of repulsive force and phase separation should be adjusted to achieve a satisfactory $\Delta V/V_0$.

Secondly, k_{LPA} depends on the average number of peroxide groups in the LPA backbone, n_{-O-O-} . On one hand, increasing n_{-O-O-} may enhance k_{LPA} , and the reduction for cyclization of UP resin during cure can be facilitated, leading to a decrease in $\Delta V/V_0$. On the other hand, increasing n_{-O-O-} may also increase the probability of intramolecular reaction of reactive LPA, and the intermolecular reactions between UP and reactive LPA may be curtailed, resulting in an increase in $\Delta V/V_0$ due to a smaller expansion effect of reactive LPA on microgel. Hence, optimum n_{-O-O-} would exist for achieving a satisfactory $\Delta V/V_0$.

Thirdly, decreasing MW_{LPA} may lower the phase separation rate for ST/UP/LPA system during the cure. LPA concentration inside the microgels (i.e., large circle in Fig. 5), C_{LPA} , would then be increased, leading to a smaller $\Delta V/V_0$ caused by a greater expansion effect of reactive LPA on microgel.

This is the reason why the VAc-*b*-ST22K(10) system, with the largest $\Delta\mu'$ value of 0.0620 (Table III) among the LPAs, the smallest n_{-O-O-} value of 0.11 (Table II), and an M_n of 22,000 g/mol, could lead to both a very good volume shrinkage control and acceptable internal pigmentability despite its smaller volume fraction of microvoids ($\sim 1.3\%$).

Factors in good volume shrinkage control and acceptable internal pigmentability

Either the higher volume fraction of microvoids or the lower intrinsic polymerization is required for a good volume shrinkage control for the ST/UP/LPA systems. The nonreactive PVAc109K system cured at 110°C pertains to the former case, whereas the reactive VAc-*b*-ST22K(10) system cured at 30°C is categorized as the latter case (Table IV).

TABLE IV
Volume Shrinkage Data, $\Delta V/V_0$, L^* Value as the Index of Internal Pigmentability for Both Sides of Molded Parts, and Volume Fraction of Microvoids, v_m , for ST/UP/LPA Systems after Isothermal Cure at 30°C

LPA added	$-\Delta V/V_0$ (%)	L^*		v_m (%)
		upper side	bottom side	
Neat UP resin	8.30 (0.15) ^a	21.94 (0.05) ^a	22.32 (0.09)	–
Reactive LPAs				
VAc- <i>b</i> -MMA16K(25)	7.31 (0.08)	22.91 (0.76)	24.43 (0.72)	1.36
VAc- <i>b</i> -MMA17K(32)	6.75 (0.13)	24.05 (0.06)	25.94 (0.63)	1.04
VAc- <i>b</i> -MMA33K(5)	5.49 (0.18)	21.19 (0.12)	38.66 (0.12)	9.42
VAc- <i>b</i> -MMA38K(15)	7.38 (0.20)	22.25 (0.19)	22.93 (0.18)	2.51
VAc- <i>b</i> -ST22K(10)	3.93 (0.14)	26.53 (0.38)	25.33 (0.40)	1.33
VAc- <i>b</i> -ST14K(14)	6.93 (0.24)	23.57 (0.10)	23.40 (0.13)	1.13
Non-reactive LPAs				
PVAc109K ¹³	-2.1 ^b	24.94 (0.06)	24.93 (0.08)	48.97

^a The values in parentheses represent the estimated standard errors for the experimental averages.

^b Cured at 110°C isothermally for 1 h.

In addition to the volume fraction of microvoids, the average size of microvoids is also influential for the internal pigmentability. For the VAc-*b*-MMA33K(5) system, it is inferred that the average size of micro-

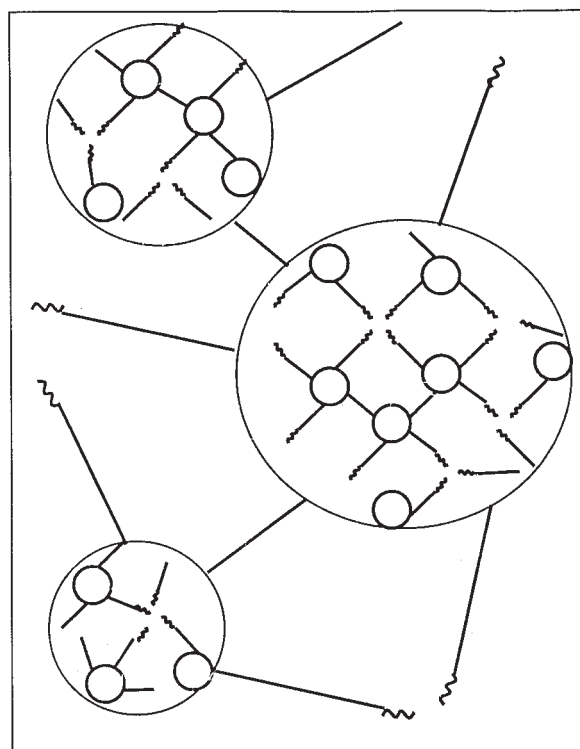
voids generated during the cure would be close to the wavelength of visible light ($\lambda = 0.45\text{--}0.75\ \mu\text{m}$), where the light scattering at the solid/air (microvoid) interface could be more pronounced, leading to a worse internal pigmentability.

Among the six ST/UP/LPA systems containing reactive LPAs, the VAc-*b*-ST22K(10) system has provided a very good volume shrinkage control ($\Delta V/V_0 \cong -3.9\%$) and achieved acceptable internal pigmentability ($L^* \cong 25\text{--}27$). Despite its relatively lower volume fraction of microvoids ($\sim 1\%$), it is inferred that the average size of the microvoids should be smaller than $0.05\text{--}0.1\ \mu\text{m}$, which is about 1/10 to 1/5 of the wavelength of visible light, so that the light scattering caused by the microvoids would be insignificant and the haziness of a pigment's color could be minimized.

CONCLUSIONS

For ST/UP/LPA systems, the microvoid formation can affect both the volume shrinkage control and internal pigmentability for the cured sample. Higher volume fraction of microvoids is favorable for the reduction of volume shrinkage, whereas the smaller average size of microvoids, as compared with $0.45\text{--}0.75\ \mu\text{m}$ for the wavelength of visible light, is indispensable for an acceptable pigmentability of cured samples.

Besides microvoid formation, the intrinsic polymerization shrinkage is also important in determining the volume shrinkage control during the cure of ST/UP/LPA system. The intrinsic polymerization shrinkage may be reduced by employing reactive PVAc-*b*-PS types of LPA with peroxide groups in their backbone, which could lead to expansion effects on microgel structures during cure. This is ascribed to the reduction in cyclization of UP resin during the cure, caused







 : nonreactive PVAc segment  : primary microgel particle
 : reactive PMMA segment or PS segment  : microgel particle

Figure 5 Schematic diagram showing the expansion effect of reactive LPA on the microgel structure during the cure of ST/UP/LPA systems.

by the intermolecular reaction between UP and reactive LPA, as well as the repulsive forces between chain segments of UP and LPA within the microgel structures. In this work, by employing MA-PG-PA type of UP resin (molar ratio of MA and PA \cong 0.62:0.38), and the reactive VAc-*b*-ST22K(10) type of LPA ($\Delta\mu' = 0.0620$ debye/cm^{3/2}, $n_{\text{O-O}} = 0.11$, $M_n = 22,000$ g/mol, $T_g = 81^\circ\text{C}$, and the molar ratio of VAc and ST \cong 0.10:0.90) under an isothermal cure at 30°C , a very good volume shrinkage control ($\Delta V/V_0 \cong -3.9\%$) and acceptable pigmentability ($L^* \cong 25\text{--}27$) for the molded parts have been achieved.

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