

Effects of Poly(vinyl acetate) and Poly(methyl methacrylate) Low-Profile Additives on the Curing of Unsaturated Polyester Resins. I. Curing Kinetics by DSC and FTIR

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SYNOPSIS

The effects of two low-profile additives (LPA), poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) on the curing kinetics during the cure of unsaturated polyester (UP) resins at 110°C were investigated by using a differential scanning calorimeter (DSC) and a Fourier transform infrared spectrometer (FTIR). The effects of temperature, molar ratio of styrene to polyester C=C bonds, and LPA content on phase characteristics of the static ternary systems of styrene-UP-PVAc and styrene-UP-PMMA prior to reaction were presented. Depending on the molar ratio of styrene to polyester C=C bonds, a small shoulder or a kinetic-controlled plateau in the initial portion of the DSC rate profile was observed for the LPA-containing sample. This was due to the facilitation of intramicrogel crosslinking reactions since LPA could enhance phase separation and thus favor the formation of clearly identified microgel particles. FTIR results showed that adding LPA could enhance the relative conversion of polyester C=C bonds to styrene throughout the reaction. Finally, by use of a microgel-based kinetic model and static phase characteristics of styrene-UP-LPA systems at 25°C, the effects of LPA on reaction kinetics regarding intramicrogel and intermicrogel crosslinking reactions, relative conversion of styrene to polyester C=C bonds, and the final conversion have been explained. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the curing of unsaturated polyester (UP) resins, about 7% of volume shrinkage would result.¹ Although the addition of fillers and glass fiber reinforcements into UP resins could reduce the volume shrinkage, such problems as a wavy surface or fiber pattern appearance in molded parts, inability to mold to close tolerances, warpage of molded parts, internal cracks and voids, etc. due to the polymerization shrinkage would not be totally excluded. To overcome these problems, low-profile additives (LPA) have been widely used in the sheet molding compound (SMC) and bulk molding compound (BMC) formulations for the past 25 years, resulting in a low-shrinkage or even a zero-shrinkage molding compound.

These LPAs are usually specific thermoplastic polymers, such as poly(vinyl acetate), poly(methyl

methacrylate), thermoplastic polyurethane, polystyrene, and so on, the amount of which is 2–5% by weight of the molding compound or 7–20% by weight of the organic resins alone. Among the extensive studies^{1–8} on the mechanism of volume shrinkage compensation caused by low-profile additives, it is now generally agreed that during the reaction the LPA and crosslinked UP phases must phase-separate first. The subsequent microvoid formation at the interface between the LPA and the crosslinked UP phases as well as inside the LPA phase due to the microstress cracking that is initiated at the interface between LPA and crosslinked UP phases could then lead to the volume shrinkage compensation.

Considerable research has been devoted to the effects of LPA on the reaction kinetics in the cure of UP resins solely by using differential scanning calorimetry (DSC).^{8–14} All of the results showed that adding LPA could reduce the reaction rate as well as the total heat of reaction. The detailed reaction kinetics regarding the conversions of styrene and polyester C=C bonds has never been reported.

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In this work, the measurement of reaction kinetics was carried out for the low-shrink UP resins at various molar ratios of styrene to polyester C=C bonds by DSC and Fourier transform infrared (FTIR) spectroscopy. The effects of poly(vinyl acetate) and poly(methyl methacrylate) LPAs on the reaction kinetics during the entire reaction are discussed.

EXPERIMENTAL

Materials

The unsaturated polyester resin obtained from a local company contains isophthalic acid, fumaric acid, and propylene glycol with a molar ratio of 1 : 1.70 : 2.73 by $^1\text{H-NMR}$ analysis. The acid value and the hydroxyl number of the resin were found to be 24.5 and 27.8, respectively, by end-group titration, which gives a number-average molecular weight of 2140 g/mol. On the average, the calculated number of C=C bonds in each polyester molecule is 7.72. The styrene content in UP resin was determined by evacuating styrene monomers in the vacuum oven at room temperature, and 36.4% of styrene was found therein. The initial viscosity of the resin was measured to be 719 cP. Based on the characterization results, extra styrene was added to the resin so that the molar ratio (MR) of styrene to polyester C=C bonds was adjusted to be MR = 2/1 in the preparation of the sample solutions. Sample solutions with MR = 1/1, 3/1, and 6/1 were also prepared.

In this study, two LPAs including poly(vinyl acetate) (PVAc, LP40A, Union Carbide) and poly(methyl methacrylate) (PMMA) were employed. The number-average molecular weights for PVAc and PMMA were measured to be 42,000 and 34,000, respectively, by vapor pressure osmometry (VPO). For the sample solution with LPA, 10% by weight of LPA was added, while the molar ratio of styrene to polyester C=C bonds was still adjusted to be MR = 1/1, 2/1, 3/1, or 6/1. The reaction was initiated by 1% by weight of tert-butyl perbenzoate (TBPB) at 110°C. All the materials were employed as received without further purification.

Instrumentation and Procedure

Phase Characteristics

Most LPAs are incompatible with UP. When a common solvent such as styrene is added to form a polymer-polymer-common solvent system, the LPA and UP usually cannot coexist in a homogeneous

phase. For a given UP with known chemical nature and molecular weight dissolving in styrene with a fixed ratio, the addition of a third component, LPA, into the UP solution beyond a certain percent generally leads to the formation of two phases in equilibrium. The exact percentage of LPA depends on the chemical nature and the molecular weight of the LPA chosen, the molar ratio of styrene to UP C=C bonds for the given UP solution, and the temperature.

To study the compatibility of two different types of LPA (i.e., PVAc and PMMA) with the UP solution in styrene prior to reaction (i.e., the uncured UP resin), several sample solutions with known compositions of styrene-UP-LPA were prepared in 50-mL separatory funnels, which were then placed in a constant-temperature bath. After a phase equilibrium was reached, the mixture of each layer could be separated and weighed. Composition of samples from upper and bottom layers could also be determined by using FTIR.^{8,15} The static ternary phase diagrams (i.e., for the unreacted ternary systems) of styrene-UP-PVAc and styrene-UP-PMMA at 25°C (i.e., mixing temperature) and at 110°C (i.e., cure temperature) were made.

Differential Scanning Calorimetry

The reaction kinetics were measured by a DuPont 9000 differential scanning calorimeter with a 910 pressurized DSC cell at atmospheric pressure. All the reactions were conducted in hermetic aluminum sample pans with sample weights ranging from 6 to 10 mg. Isothermal reaction rate vs. time profiles were measured at 110°C. Isothermal DSC runs were ended when there was no further exotherm. Samples were then reheated from room temperature to 210°C in the scanning mode with a heating rate of 2.5°C/min to determine the residual reactivity left in the isothermally cured samples. Resins were also cured in the scanning mode at 2.5°C/min heating rate. The total heat of reaction was calculated from the area under the scanning DSC curve. If we make three assumptions that density and heat capacity of the resin change little with reaction from liquid to solid within the temperature range used, that heats of polymerization associated with styrene and polyester C=C bonds are approximate, and that the reaction can be complete as long as the temperature is high enough for a long period of time, the rate of overall reaction can be directly converted from the rate of heat release measured by DSC as follows:¹⁶

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_T} \frac{d\Delta H_t}{dt} \quad (1)$$

and

$$\alpha = \frac{1}{\Delta H_T} \int_0^t \frac{d\Delta H_t}{dt} dt = \frac{\Delta H_t}{\Delta H_T} \quad (2)$$

where $d\alpha/dt$ and α are the overall reaction rate and total conversion at a given time, ΔH_t is the heat release before the time t , and ΔH_T is the total heat release, which is usually taken as the heat release from direct scanning DSC run (i.e., $\Delta H_T = \Delta H_S$).

Fourier Transform Infrared Spectroscopy

In this study, a FTIR spectrometer (Digilab, FTS-40) with a resolution of 4 cm^{-1} in the transmission mode was also used for on-line conversion measurements of styrene and polyester C=C bonds during the reaction. One drop of sample solution about 0.8 mg was pasted between two potassium bromide plates, which were then transferred to a liquid sampling cell, TFC (Temperature-Controlled Flow-Through Cell, Harric Scientific) where the possible evaporation loss of volatile species, such as styrene monomers, during the measurement could be prevented. As soon as the TFC was mounted on a sample holder located in the IR chamber, isothermal reaction of the sample was measured continuously at 110°C under atmospheric pressure during the entire course of the reaction. Four consecutive 1-s scans were taken at each sampling time, and their average was transformed into a frequency-domain spectrum. The sampling interval was 45 s. Measurement was ended when there were no changes in absorbance peak areas. All IR spectra were expressed in absorbance where individual reaction conversion of styrene and polyester C=C bonds could be determined as a function of time.

CONVERSION CALCULATION

In the analysis of IR spectra, all the absorbances were based on peak areas. Changes of absorbance at 912 cm^{-1} (C—H out-of-plane bending in $\text{CH}_2=\text{CHR}$ for styrene) and 982 cm^{-1} (C—H out-of-plane bending in $\text{CHR}=\text{CHR}$ for polyester) were employed to calculate conversions of styrene and polyester vinylene groups, respectively. The absorbance at 1730 cm^{-1} (C=O stretching) was picked as an internal standard. The absorbance at 695 cm^{-1} (C—H out-of-plane bending in benzene ring of styrene) was also measured to correct for styrene loss. However, by using the TFC, no styrene

loss was found during the continuous monitoring of the sample reaction. Since the peaks at 982 and 992 cm^{-1} (C—H out-of-plane bending in $\text{CH}_2=\text{CHR}$ for styrene) overlapped, a simple subtraction method was used to separate the individual peaks.^{17,18}

For the sample solution with LPA, the peak at 1019 cm^{-1} due to PVAc and the peak at 986 cm^{-1} due to PMMA, respectively, overlapped with the peak at 982 cm^{-1} due to polyester vinylene groups. Besides, the peak at 940 cm^{-1} due to PVAc and the peak at 912 cm^{-1} due to PMMA, respectively, overlapped with the peak at 912 cm^{-1} due to styrene (see Fig. 1). To allow for conversion calculations for styrene and polyester vinylene groups, a subtraction method has been derived to separate the individual peaks¹⁵ and will be presented below.

Styrene-UP-PVAc System

The percentage of styrene consumption, which includes reaction conversion and evaporation loss, can be calculated as:

$$\alpha'_S = 1 - \left(\frac{\bar{A}_{912+940}^t - \bar{A}_{940}^t}{\bar{A}_{912+940}^0 - \bar{A}_{940}^0} \right) \quad (3)$$

where \bar{A}^0 and \bar{A}^t are the normalized absorbance of the functional group before the reaction and after a reaction time t based on the absorbance peak at 1730 cm^{-1} (i.e., $\bar{A}^t = A^t/A_{1730}^t$ and $\bar{A}^0 = A^0/A_{1730}^0$), which is contributed by both UP and PVAc, i.e., $A_{1730} = A_{1730(\text{PES})} + A_{1730(\text{PVAc})}$, $A_{912+940}$ is the peak area at 912 and 940 cm^{-1} together, and the absorption peak at 940 cm^{-1} is contributed by both UP¹⁸ (OH out-of-plane bending in polyester terminal groups) and PVAc [see Fig. 1(a)], i.e., $A_{940} = A_{940(\text{PES})} + A_{940(\text{PVAc})}$. Since the absorption peak at 940 cm^{-1} is due to inert functional groups, $\bar{A}_{940}^t = \bar{A}_{940}^0$ during the reaction, which can be calculated from FTIR spectrum for styrene-UP-PVAc system before reaction after the removal of styrene monomers or by applying the additivity rule of Beer's law for UP and PVAc at 940 and 1730 cm^{-1} .

Since the C—H out-of-plane bending at 695 cm^{-1} due to isophthalic acid (IPA) in UP resin can be neglected,¹⁸ the percentage of styrene due to evaporation and the styrene conversion can thus be calculated as:

$$\alpha''_S = 1 - \left(\frac{\bar{A}_{695}^t}{\bar{A}_{695}^0} \right) \quad (4)$$

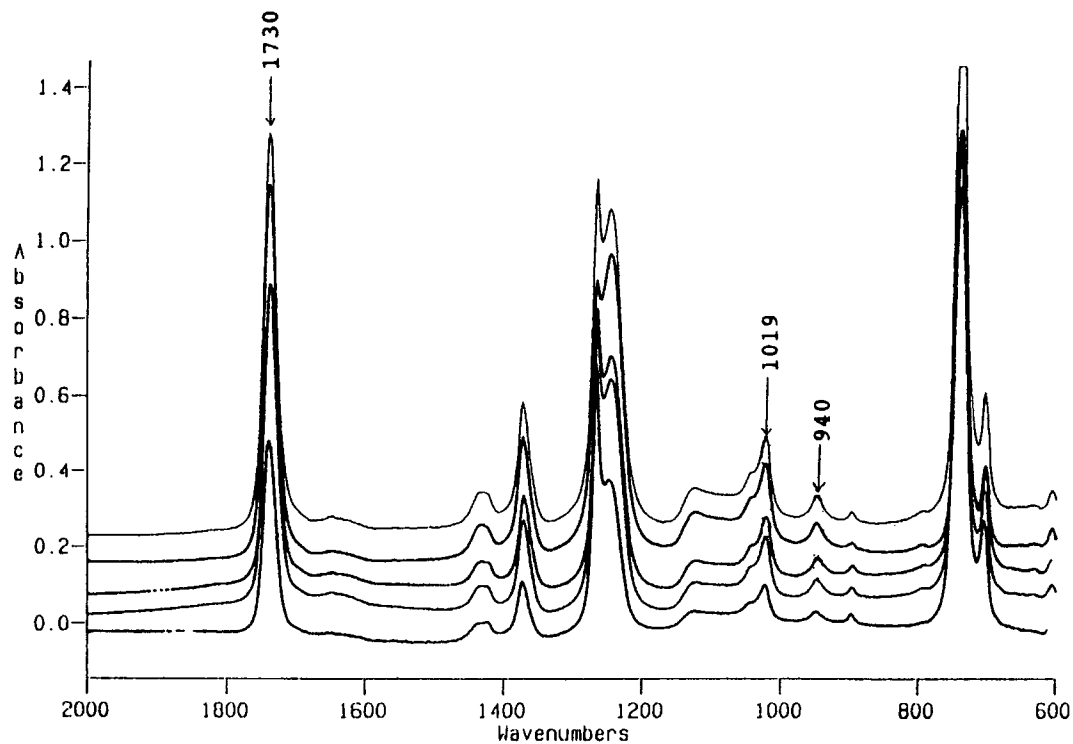


Figure 1 (a) FTIR spectra for varied concentrations of PVAc solution in dichloromethane.

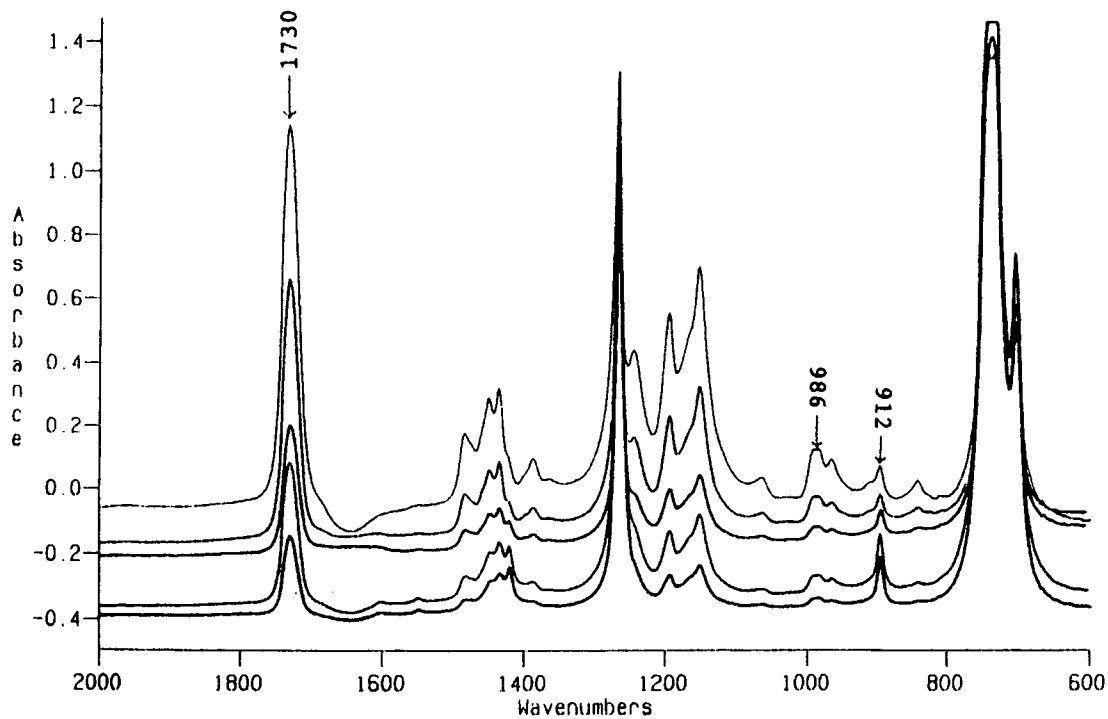


Figure 1 (b) FTIR spectra for varied concentrations of PMMA solution in dichloromethane.

and

$$\alpha_S = \alpha'_S - \alpha''_S \quad (5)$$

For $\alpha''_S = 0$ in this study, $\alpha_S = \alpha'_S$.

Another conversion, α_p , can be defined as the peak area change at 982 and 992 cm^{-1} :

$$\alpha_p = 1 - \left(\frac{\bar{A}_{982+992+1019}^t - \bar{A}_{1019}^t}{\bar{A}_{982+992+1019}^0 - \bar{A}_{1019}^0} \right) \quad (6)$$

where the absorption peak at 1019 cm^{-1} due to inert functional groups is assumed to be mainly contributed by styrene (ST) monomers¹⁸ (C—H in-plane bending in benzene ring) and PVAc (C—O—C stretching), as shown in Figure 1(a), i.e., $\bar{A}_{1019}^t = \bar{A}_{1019}^0(\text{PVAc}) + \bar{A}_{1019}^0(\text{ST}) (1 - \alpha''_S)$. For $\alpha''_S = 0$, $\bar{A}_{1019}^t = \bar{A}_{1019}^0$.

To determine α_p , \bar{A}_{1019}^0 (i.e., $\bar{A}_{1019}^0(\text{PVAc}) + \bar{A}_{1019}^0(\text{ST})$) should be known. First, by preparing monomer-dichloromethane solutions of known concentration for polyester and styrene, respectively, calibration curves could be established to calculate the B value ($= a_{982}/a_{992}$), where a_i is the absorptivity, which is characteristic of absorbing species, i . The B value calculated is 1.08; \bar{A}_{1019}^0 can now be calculated as:

$$\bar{A}_{1019}^0 = \bar{A}_{982}^0 \frac{B_1}{BI} \quad (7)$$

where \bar{A}_{982}^0 can be calculated in a manner similar to \bar{A}_{940}^0 as mentioned earlier, $I = (C_E/C_S)_0$, the units for C_{E0} and C_{S0} being grams of polyester/ cm^3 and grams of styrene/ cm^3 , respectively, before the reaction, and $B_1 = \bar{A}_{1019}^0/\bar{A}_{992}^0 = [a_{1019}(\text{PVAc}) C_{0(\text{PVAc})} + a_{1019}(\text{ST}) C_{0(\text{ST})}]/a_{992}(\text{ST}) C_{0(\text{ST})}$. The B_1 value can be calculated from the calibration curves for PVAc at 1019 cm^{-1} and for styrene at 1019 and 992 cm^{-1} .

With α'_S and α_p , the conversion of C=C bonds in polyester can then be calculated by the same formula^{17,18} derived for the neat UP resin system without LPA:

$$\alpha_E = 1 - \frac{1}{BI} [(1 - \alpha_p)(1 + BI) - (1 - \alpha'_S)] \quad (8)$$

Finally, the overall conversion of C=C bonds can be expressed as:

$$\alpha_T = \frac{\alpha_S + I'\alpha_E}{1 + I'} \quad (9)$$

where $I' = (C'_E/C'_S)_0$, and the units of C'_{E0} and C'_{S0} are moles of C=C bonds for polyester/ cm^3 and moles of C=C bonds for styrene/ cm^3 , respectively, before the reaction.

Styrene-UP-PMMA System

The conversion calculation formulas remain essentially the same except that Eqs. (3) and (6) should be written as the following forms:

$$\alpha'_S = 1 - \left(\frac{\bar{A}_{912+940}^t - \bar{A}_{940}^t - \bar{A}_{912(\text{PMMA})}^t}{\bar{A}_{912+940}^0 - \bar{A}_{940}^0 - \bar{A}_{912(\text{PMMA})}^0} \right) \quad (10)$$

and

$$\alpha_p = 1 - \left(\frac{\bar{A}_{982+986+992+1019}^t - \bar{A}_{1019}^t - \bar{A}_{986(\text{PMMA})}^t}{\bar{A}_{982+986+992+1019}^0 - \bar{A}_{1019}^0 - \bar{A}_{986(\text{PMMA})}^0} \right) \quad (11)$$

where the absorption peak at 1730 cm^{-1} is now contributed by both UP and PMMA, $\bar{A}_{940}^t = \bar{A}_{940}^0$ (solely due to UP), $\bar{A}_{912(\text{PMMA})}^t = \bar{A}_{912(\text{PMMA})}^0$, $\bar{A}_{1019}^t = \bar{A}_{1019}^0 (1 - \alpha''_S)$ (solely due to styrene), and $\bar{A}_{986(\text{PMMA})}^t = \bar{A}_{986(\text{PMMA})}^0$.

RESULTS

Phase Characteristics

The compatibility of the static ternary systems of styrene-UP-PVAc and styrene-UP-PMMA prior to reaction is presented in Table I. For MR = 2/1 used in typical SMC formulations, at 25°C, PVAc was essentially compatible with the uncured UP resin, whereas PMMA was incompatible with the resin. For the latter system, although these three components appeared as a homogeneous continuous single phase on thorough mixing, under the observation of an optical microscope, they formed a two-phase dispersion in a continuous medium. In contrast, the PVAc system appeared as a homogeneous continuous single phase on a microscopic scale shortly after mixing. However, on permitting separation to occur, both systems formed two separate layers, each layer being a homogeneous continuous single phase. Clearly, both blends were phase separated from the beginning, but phase separation could not be observed on a macroscopic scale until the mixture had been left to stand. The time taken for phase separation to be observed on a macroscopic scale was shorter for the PMMA system than the

Table I Miscibility of the Static Ternary ST-UP-LPA Systems at 25 and 110°C Prior to Reaction^a

LPA	PVAc				PMMA			
MR	1/1	2/1	3/1	6/1	1/1	2/1	3/1	6/1
$T = 25^{\circ}\text{C}$	1 ^b	1 ^c	2 ^b	2	1	2	2	2
$T = 110^{\circ}\text{C}$	1	1	1	1	1	1	1	1

^a The amount of LPA was 10% by weight and the molar ratio of styrene to polyester C=C bonds was set at MR = 1/1, 2/1, 3/1, and 6/1.

^b 1 denotes one-phase and 2 represents two-phase.

^c A nearly miscible ternary system (see Table II).

Table II Compositions of the Upper and Bottom Layers for ST-UP-PMMA and ST-UP-PVAc Systems at 25°C^a

	Relative Weight (g)	ST	UP (wt %)	LPA	ST/UP C=C (MR)
ST-UP-PMMA System: MR = 2/1					
Upper layer (dispersed phase)	25.4	62.0	13.9	24.1	11.9/1
Bottom layer (continuous phase)	74.6	30.5	64.3	5.2	1.27/1
Total	100	38.5	51.5	10.0	2/1
ST-UP-PMMA System: MR = 3/1					
Upper layer	36.3	66.0	9.1	24.9	19.4/1
Bottom layer	63.7	37.1	61.4	1.5	1.61/1
Total	100	47.6	42.4	10.0	3/1
ST-UP-PMMA System: MR = 6/1					
Upper layer	46.9	69.6	10.0	20.4	18.7/1
Bottom layer	53.1	55.7	43.5	0.8	3.43/1
Total	100	62.2	27.8	10.0	6/1
ST-UP-PVAc System: MR = 2/1					
Upper layer (dispersed phase)	7.95	57.2	10.8	32.0	14.1/1
Bottom layer (continuous phase)	92.05	37.0	54.9	8.1	1.79/1
Total	100	38.6	51.4	10.0	2/1
ST-UP-PVAc System: MR = 3/1					
Upper layer	20.7	61.9	8.9	29.2	18.6/1
Bottom layer	79.3	43.9	51.1	5.0	2.30/1
Total	100	47.6	42.4	10.0	3/1
ST-UP-PVAc System: MR = 6/1					
Upper layer	37.0	75.0	3.4	21.6	58.6/1
Bottom layer	63.0	54.7	42.1	3.2	3.48/1
Total	100	62.2	27.8	10.0	6/1

^a LPA = 10% by weight and MR = 2/1, 3/1, and 6/1 respectively.

PVAc system (1–2 h vs. 5–6 h). The compositions of the two phases are shown in Table II. For the PMMA system, the upper layer was dominated by ST and PMMA (LPA), the amount of UP was less than 15%, and the molar ratio of styrene to polyester

C=C bonds was MR = 11.9/1. The bottom layer was dominated by UP and ST, the amount of PMMA (LPA) was only about 5%, and MR = 1.27/1. In other words, the molar ratio in the upper layer (i.e., dispersed phase) would be greater than that in

Table III Compositions of the Upper and Bottom Layers for ST–UP–PMMA and ST–UP–PVAc Systems at 25°C^a

MR = 2/1	Relative Weight (g)	ST	UP (wt %)	LPA	ST/UP C=C (MR)
ST–UP–PMMA System: LPA = 10%					
Upper layer	25.4	62.0	13.9	24.1	11.9/1
Bottom layer	74.6	30.5	64.3	5.2	1.27/1
Total	100	38.5	51.5	10.0	2/1
ST–UP–PMMA System: LPA = 13.7%					
Upper layer	15.6	50.1	15.1	34.8	8.88/1
Bottom layer	84.4	34.5	55.7	9.8	1.66/1
Total	100	36.9	49.4	13.7	2/1
ST–UP–PMMA System LPA = 20.1%					
Upper layer	19.1	46.0	17.3	37.0	7.07/1
Bottom layer	80.9	31.5	52.4	16.1	1.60/1
Total	100	34.3	45.6	20.1	2/1
ST–UP–PMMA System: LPA = 25.0%					
Upper layer	30.0	40.8	18.3	40.9	5.96/1
Bottom layer	70.0	28.4	53.4	18.2	1.28/1
Total	100	32.1	42.9	25.0	2/1
ST–UP–PVAc System: LPA = 10%					
Upper layer	7.95	57.2	10.8	32.0	14.1/1
Bottom layer	92.05	37.0	54.9	8.1	1.79/1
Total	100	38.6	51.4	10.0	2/1
ST–UP–PVAc System: LPA = 15.3%					
Upper layer	9.2	46.0	15.0	39.0	8.31/1
Bottom layer	90.8	35.2	51.9	12.9	1.82/1
Total	100	36.2	48.5	15.3	2/1
ST–UP–PVAc System: LPA = 20.1%					
Upper layer	4.6	44.1	13.1	42.8	9.00/1
Bottom layer	95.4	33.7	47.3	19.0	1.90/1
Total	100	34.2	45.7	20.1	2/1
ST–UP–PVAc System: LPA = 25.0%					
Upper layer	1.0	26.0	29.2	44.8	2.38/1
Bottom layer	99.0	32.2	43.0	24.8	2.00/1
Total	100	32.1	42.9	25.0	2/1

^a LPA = 10%–25% by weight and MR = 2/1.

the whole mixture, while the trend would be reversed in the bottom layer (i.e., continuous phase). Table I shows that for both systems, a higher molar ratio of styrene to polyester C=C bonds could result in an immiscible two-phase system at 25°C, the compositions of which are also listed in Table II. The dominating components and the variation of molar ratio relative to that of the whole mixture in both layers described above for ST-UP-PMMA system at MR = 2/1 were essentially applied to the PVAc system at MR = 2/1 and both systems at higher molar ratios. However, as the temperature increased to 110°C, both LPAs became compatible with the uncured resin even for the mixture with MR > 2/1.

For the ST-UP-LPA system with MR = 2/1 at 25°C, Table III shows the effect of LPA content on phase characteristics. For the PMMA-containing sample, increasing the amount of LPA from 10 to 13.7% could lead to a depression of the phase separation since the weight percent of the dispersed phase decreases. However, further increasing the amount of LPA could enhance the phase separation. In contrast, for the PVAc-containing sample, as the LPA content increases, the phase separation could be generally depressed. For both systems, as the amount of LPA increases, the percent of LPA content in either the continuous phase or the dispersed phase also increases. Moreover, the molar ratio in the dispersed phase generally decreases, whereas the molar ratio in the continuous phase would be closer to that in the whole mixture (i.e., MR = 2/1) when

the phase separation phenomenon is less pronounced. It is seen from Table III that at the same level of LPA content, the percent of LPA in both the continuous phase and the dispersed phase, as well as the molar ratio in the continuous phase, exhibits a higher value for the PVAc-containing sample than for the PMMA-containing sample.

Reaction Kinetics

Differential Scanning Calorimetry

Figure 2 shows the effects of LPA on DSC reaction rate profiles for UP resins at MR = 2/1. Adding LPA could delay the induction time, t_2 , and the time to reach the maximum reaction rate, t_m . A small shoulder prior to the onset of the gel effect¹⁹ was observed, which appeared at 8–10 min and 10–12 min for the PVAc-containing and PMMA-containing samples, respectively. Also, with LPA, a lower maximum reaction rate resulted. Judging from the height of the shoulder in the early portion of the DSC rate profile, among the three samples, the initial reaction rate of the PVAc-containing sample would be the highest, followed by the PMMA-containing and the neat resin samples (no shoulder).

The small shoulder in Figure 2 indicates the occurrence of noticeable phase separation.²⁰ Therefore, the relative time scales for reaction and noticeable phase separation to occur were 5 min (i.e., t_2) and 8–10 min for the PVAc system and 6 min and 10–

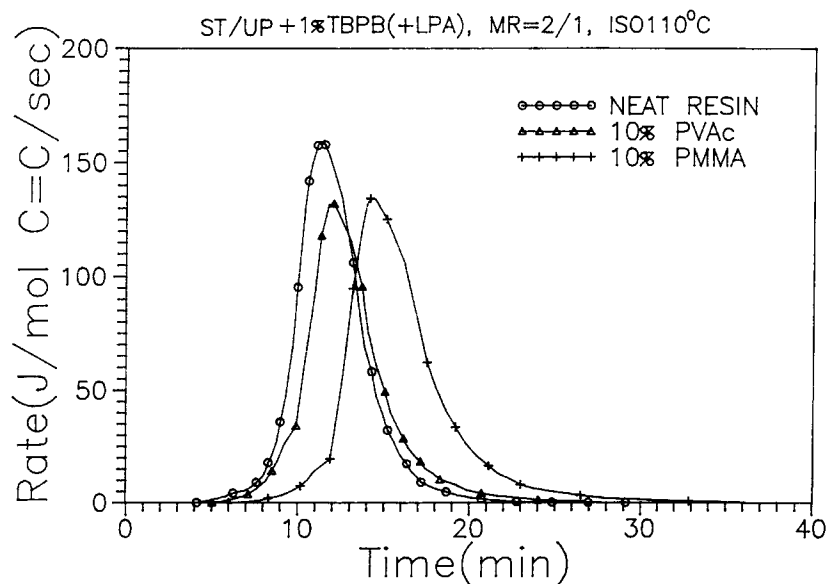


Figure 2 DSC reaction rate profiles for UP resins at MR = 2/1 containing no LPA, 10% PVAc, and 10% PMMA cured isothermally at 110°C.

12 min for the PMMA system. Apparently, reaction could enhance phase separation since the unreacted styrene-UP-LPA system at 110°C formed a homogeneous continuous single phase. Also, the earlier onset of the reaction (i.e., the PVAc-containing sample) would lead to a faster noticeable phase separation to occur, where the monomer conversion, α , was less than 5–7% for both systems (see Figs. 7 and 8). It should be noted that the true onset of phase separation would occur at the very early stage of reaction ($\alpha < 1\%$) and could be detected by light-scattering experiments and morphological studies.²⁰

For the three samples at MR = 2/1, the final conversion of the PMMA-containing sample measured by DSC is the highest, followed by the neat resin, with a slightly lower value, and the PVAc-containing samples. However, their differences are within 5%. The detailed DSC results are summarized in Table IV. It should be pointed out that although the amount of LPA contained in the sample was ex-

cluded in the calculation of total heat of reaction, ΔH_S or ΔH_{iso} value still revealed a 10% decrease for the PVAc-containing sample when compared with that for the neat resin at MR = 2/1. It was not the case for the PMMA-containing sample, where the total heat of reaction was pretty much close to that for the neat resin.

The effects of varying styrene content on DSC reaction rate profiles for UP resins with different LPAs are shown in Figures 3–5. The addition of LPA decreased the maximum reaction rate at all the molar ratios, which showed the same trend as that at MR = 2/1. Except for MR = 3/1 and 6/1, the LPA-containing samples generally possessed longer time to reach the maximum reaction rate than the neat resin. As the molar ratio increased to MR = 3/1 and 6/1 shown in Figures 4 and 5, a kinetic-controlled plateau in the initial portion of the DSC rate profile was observed for the sample with or without LPA, which resembled the phenomena re-

Table IV Summary of Kinetic Information by DSC and FTIR for UP Resins at MR = 2/1 with and without 10% LPA (PVAc or PMMA) for Isothermal Reactions at 110°C^a

LPA	t_z^b	t_m^b	ΔH_S^c	ΔH_{iso}^c	ΔH_{res}^c	α_m^d	α_{iso}^d	α_S^e	α_E^e	α_{TOT}^e
MR = 2/1										
None	4.14	11.17	15.78	12.16	0.84	28.49	77.1	84.9	68.1	79.3
PVAc	5.09	11.73	14.62	10.80	0.94	27.66	73.9	80.1	74.1	78.1
PMMA	6.00	14.12	15.52	12.00	1.07	26.18	77.3	84.4	71.0	79.9
MR = 1/1										
None	4.10	12.22	15.15	9.45	1.02	31.64	62.4	80.3	58.2	69.1
PVAc	2.31	14.27	14.11	10.12	1.48	29.85	71.7	77.1	68.0	72.6
PMMA	3.93	18.30	13.57	8.09	1.30	29.30	59.6	76.8	56.2	66.5
MR = 3/1										
None	1.68	10.96	15.30	13.22	0.92	30.52	86.4	86.0	69.2	81.3
PVAc	1.22	8.80	15.21	13.31	0.83	30.78	87.5	87.2	72.4	83.5
PMMA	1.56	10.72	15.39	13.10	0.94	29.63	85.1	86.2	71.2	82.5
MR = 6/1										
None	1.30	8.00	15.85	14.54	0.37	26.83	91.7	89.5	72.3	87.0
PVAc	1.59	8.71	16.06	14.59	0.38	11.72	90.8	92.0	76.8	89.8
PMMA	1.40	7.89	16.44	14.89	0.45	17.74	90.6	92.3	77.7	90.2

^a The data at MR = 1/1, 3/1, and 6/1 are also listed.

^b t_z is the induction time (min), and t_m is the time to maximum rate (min).

^c The unit of ΔH_S , ΔH_{iso} , and ΔH_{res} is kcal/mole C=C, where ΔH_S is the heat release at 2.5°C/min scanning rate from room temperature to 210°C, ΔH_{iso} is heat release for isothermally cured sample, ΔH_{res} is the heat release by rescanning the isothermally cured sample at 2.5°C/min from room temp. to 210°C.

^d α_m (%) is the conversion at the time to maximum rate, α_{iso} (%) is the overall conversion based on the ΔH_S for each sample as 100% conversion, i.e., $\alpha_{iso} = \Delta H_{iso}/\Delta H_S$.

^e α_S is styrene conversion, α_E is polyester vinylene conversion, and α_{TOT} is total conversion of C=C bonds measured by FTIR (all in %).

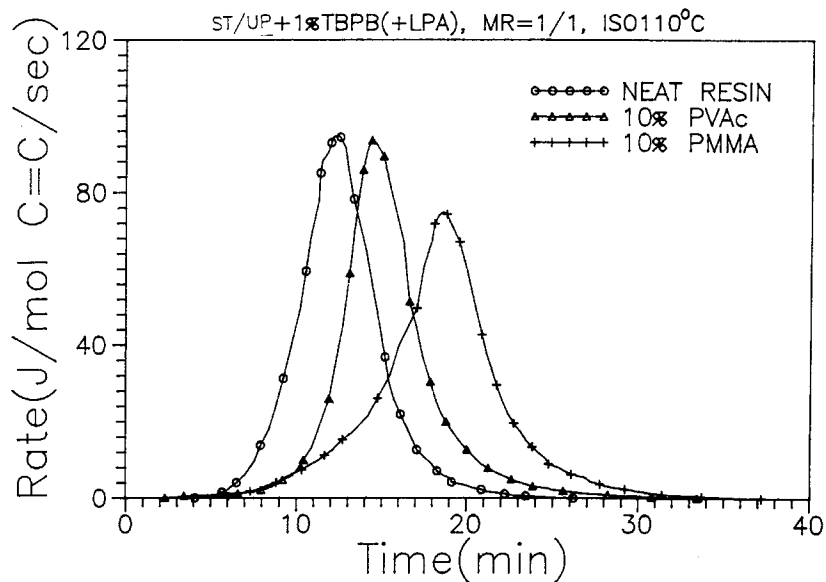


Figure 3 DSC reaction rate profiles for UP resins at MR = 1/1 containing no LPA, 10% PVAc, and 10% PMMA cured isothermally at 110°C.

ported for the neat UP resin cured under pressure.²¹ In the plateau region, the reaction rate was the highest for the PVAc-containing sample, followed by the PMMA-containing and the neat resin samples at MR = 3/1, while the order of reaction rate for the three samples at MR = 6/1 was reversed. At MR = 6/1, a shoulder after the peak of the rate

profile was also observed, which was more conspicuous for the LPA-containing samples than the neat resin.

DSC results displayed in Table IV show that at higher molar ratios, such as MR = 3/1 and 6/1, ΔH_s or ΔH_{iso} value for the PVAc-containing sample turned out to be essentially the same as the neat

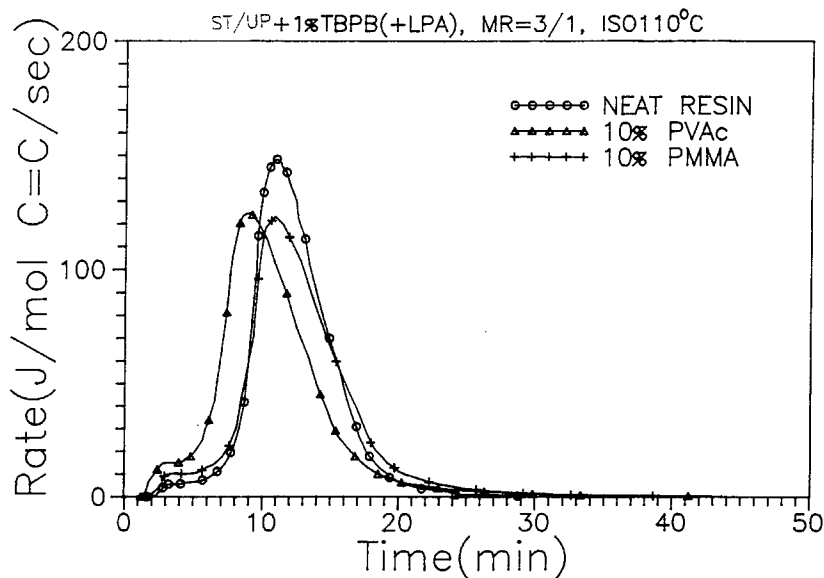


Figure 4 DSC reaction rate profiles for UP resins at MR = 3/1 containing no LPA, 10% PVAc, and 10% PMMA cured isothermally at 110°C.

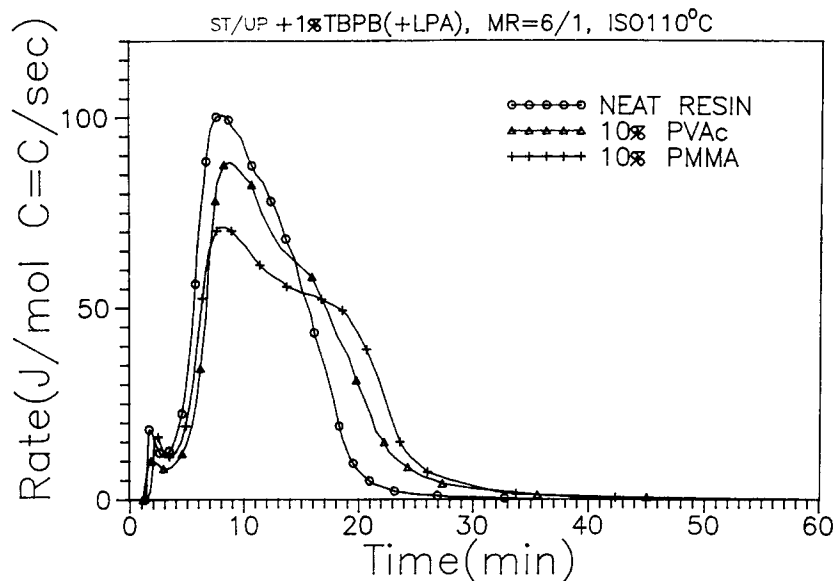


Figure 5 DSC reaction rate profiles for UP resins at MR = 6/1 containing no LPA, 10% PVAc, and 10% PMMA cured isothermally at 110°C.

resin, unlike that at MR = 2/1. Generally speaking, the higher the molar ratio, the higher the final conversion for all the three samples (see α_{iso} in Table IV).

In the calculation of overall conversion, it was based on the ΔH_S for each sample as 100% conversion. This is because the heats of polymerization associated with styrene and polyester C=C bonds are slightly different,²² where ΔH_S listed in Table IV varies with the mole ratio of styrene to polyester C=C bonds, and hence the use of ΔH_S for each sample would be appropriate in conversion calculations based on the thermal method¹⁶ in order to reflect the correct α_{iso} value. The use of a ΔH_S value that is blend specific, which disregards the variation of ΔH_S with the mole ratio of styrene and polyester C=C bonds, would not be suggested.

Fourier Transform Infrared Spectroscopy

The effects of LPA on the detailed reaction kinetics in the cure of UP resins at MR = 2/1 by FTIR measurements are shown in Figures 6–8. For comparison, the DSC rate profile and total conversion profiles (based on ΔH_S) are also plotted. For the three samples, the final conversions measured by both FTIR and DSC showed good agreement (within 5% difference), where the reproducibility of the cure quantitative results in terms of final conversions was very good (within 1–2% errors for 3–5 measurements of each sample) for the FTIR and DSC measure-

ments. However, the initial overall conversion profiles measured by the two instruments could not match well, and the reaction carried out in FTIR started earlier than in DSC. It was presumably due to the better heat transfer effect in the liquid sampling cell (i.e., TFC) of the FTIR than in the DSC aluminum sample pan since the amount of sample solution placed in the TFC was much less than that in the DSC pan (0.8 vs. 6–10 mg). Despite the deviation in the reaction starting time (i.e., induction time) caused by the two instruments, the overall conversion history in the cure of the resin should be essentially the same. This is because samples in both the instruments experienced the same thermal history (i.e., 110°C isothermally) for almost the entire reaction course, and the monomer conversion would be negligibly low during the very beginning period when the reaction temperature throughout the sample mass reached 110°C. Besides, although the thickness of the films used in the on-line FTIR kinetic studies was around 5–10 μm , their ability to develop and sustain the microstructures as seen in the corresponding SEM micrographs for samples partially cured in DSC (about 50 times larger in sample thickness) was essentially unaffected.²⁰ Therefore, on the basis of the same overall conversion for FTIR and DSC, instead of the same cure time, one may construct the interrelationships between the variation of styrene and polyester C=C bond conversions measured by FTIR and the variation in the DSC rate profile throughout the reaction.

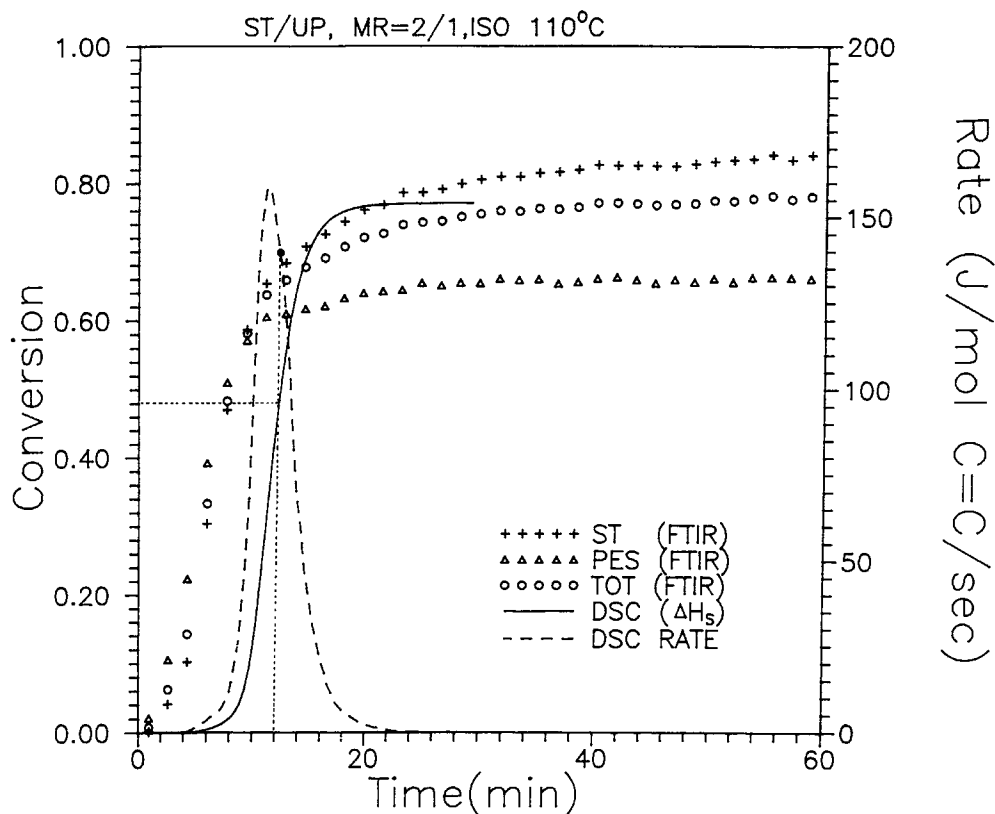


Figure 6 Conversion profiles of styrene, polyester C=C bonds, and overall C=C bonds measured by FTIR for neat UP resins cured at 110°C, with MR = 2/1. The DSC reaction rate and overall conversion profiles based on ΔH_s are also plotted for comparison. The filled circle designated in the DSC rate profile denotes the transition point for $\alpha_S > \alpha_E$ (see text).

As shown in Figure 6 for the neat resin system, prior to 48% overall conversion, the conversion of polyester C=C bonds, α_E , always exceeded that of styrene, α_S . From then on, the trend was reversed. This transition point corresponded to a time at 12.0 min in the DSC overall conversion curve where the DSC rate profile just descended from the peak ($t_m = 11.2$ min and $\alpha_m = 28.5\%$). Similar observations have been reported in our previous works.^{21,23}

On the other hand, the characteristics of the conversion variation for α_S and α_E in the cure of UP resin with 10% LPA as shown in Figures 7 and 8 were essentially unaltered except that the transition point of $\alpha_S > \alpha_E$ was delayed markedly. With the addition of PVAc (more compatible with the UP resin), the overall conversion in the transition point was higher, and the transition point was closer to the end of the reaction when compared with that of the addition of PMMA (less compatible with the UP resin).

The relative conversion profiles of styrene and polyester C=C bonds at MR = 2/1 as shown in Figure 9 shows that with the addition of LPA, the curve moves to the right, indicating that the conversion of polyester C=C bonds became more favorable than that of styrene by adding LPA. For the final conversion, the LPA-containing samples revealed a higher α_E by 5–10% than the neat resin sample, while α_S seemed to be less affected than α_E . Also, the conversion of polyester C=C bonds in the PVAc-containing (more compatible with UP) sample was enhanced about 5% more than the PMMA-containing (less compatible with UP) sample.

For MR = 1/1, 3/1, and 6/1, the detailed reaction kinetics with and without LPA were also measured by FTIR at 110°C.¹⁵ The addition of LPA generally affected α_E and α_S in a similar manner to that at MR = 2/1. At higher molar ratios, such as MR = 3/1 and 6/1, although the initial kinetic-controlled

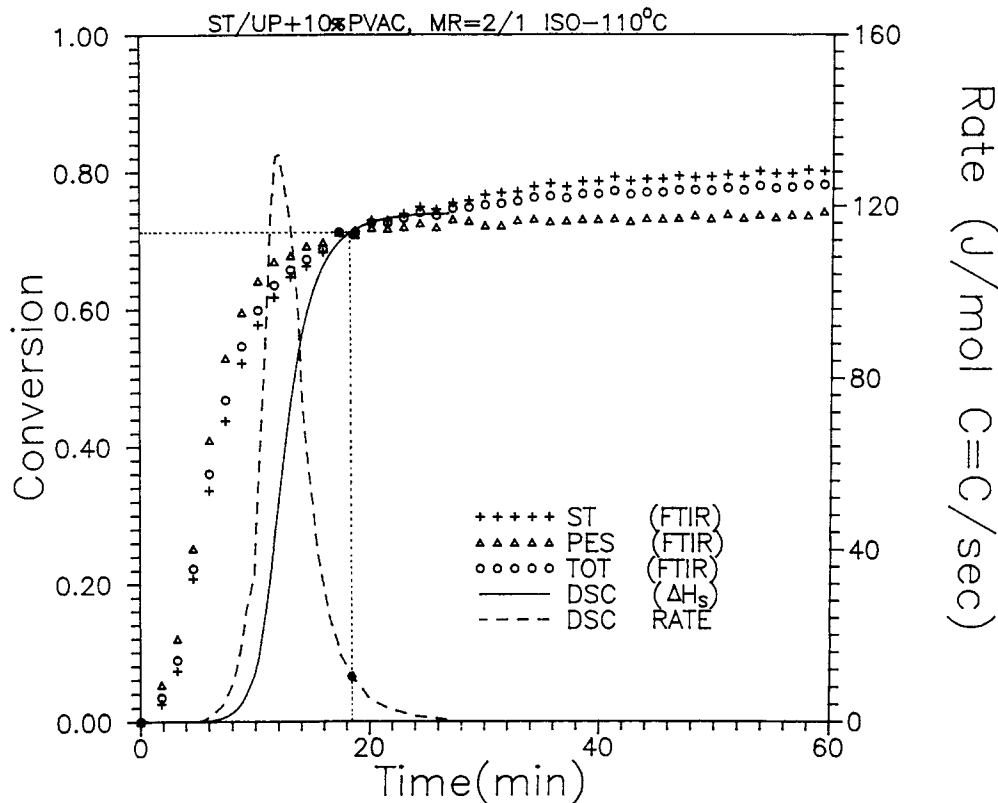


Figure 7 Conversion profiles of styrene, polyester C=C bonds, and overall C=C bonds measured by FTIR for UP resins containing 10% PVAc cured at 110°C, with MR = 2/1. The DSC reaction rate and overall conversion profiles based on ΔH_S are also plotted for comparison. The filled circle designated in the DSC rate profile denotes the transition point for $\alpha_S > \alpha_E$ (see text).

plateau as shown in Figures 4 and 5 could be a result of styrene homopolymerization due to high styrene content in the mixture, the higher conversion of polyester C=C bonds than that of styrene in that region (not shown) would not suggest this speculation. Besides, since the reaction rate for the copolymerization of styrene with polyester C=C bonds would be greater than that of self-bonding of styrene,^{22,24} during the copolymerization of styrene and polyester C=C bonds at MR = 3/1 and 6/1, independent styrene homopolymerization which does not pertain to the styrene-polyester network would be unfavorable especially at the initial stage of reaction, where the concentration of polyester C=C bonds remains at a high level. As shown in Table IV, for the three samples, the deviation of the two final conversions measured by FTIR (i.e., α_{TOT}) and DSC (α_{iso}) was within 7% at all molar ratios. The conversions of styrene (α_S) and polyester C=C bonds (α_E) increased with increasing molar ratios.

DISCUSSION

Effects of Microgel Structure on the Reaction Kinetics

Segregating Effect of LPA on Microgel Formation

The microgel formation is the main feature in the cure of UP resins,²⁵ where the styrene-unsaturated polyester copolymerization is involved. For the neat UP resin reaction system, the formation of microgel particles at the very early stage of reaction has seldom been verified experimentally. This is due to the fact that the incipient microgel particle (i.e., intramolecularly crosslinked macromolecule, ICM)²⁶ tends to dissolve in styrene contained in the UP resins and the separation procedure prior to SEM observation becomes somewhat difficult. In our laboratory, the microgel particles at very low conversion for the neat UP resin reaction system, cured at 100°C and initiated by 1% TBPB in the DSC sample

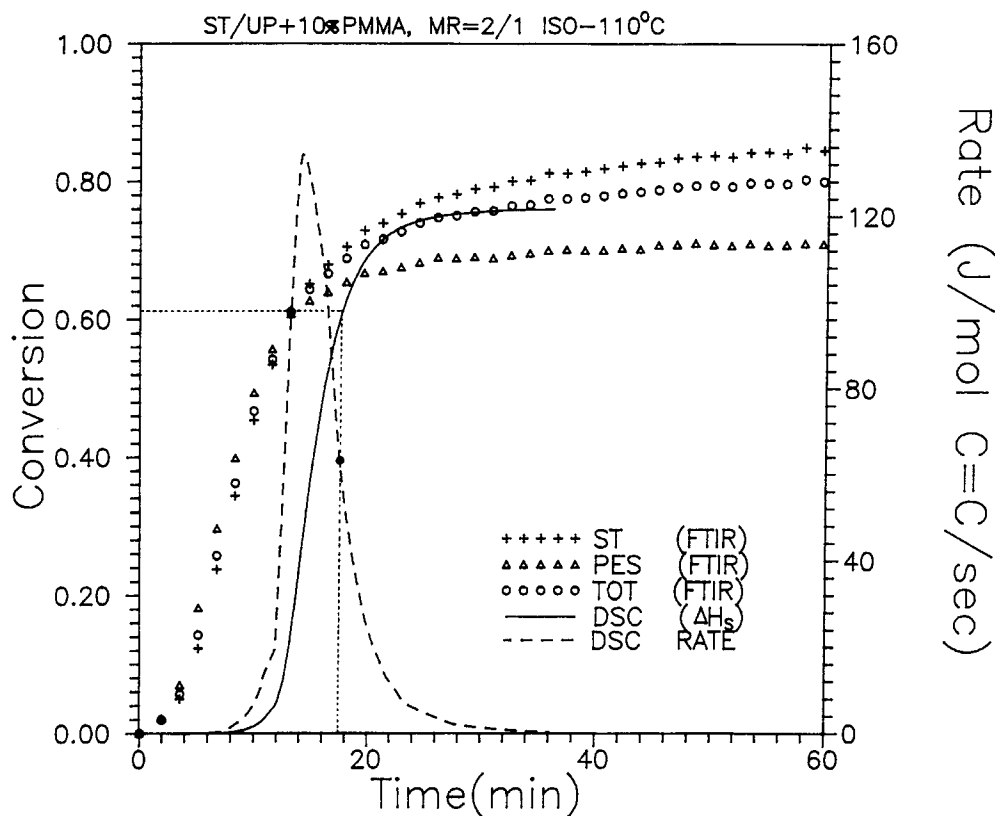


Figure 8 Conversion profiles of styrene, polyester C=C bonds, and overall C=C bonds measured by FTIR for UP resins containing 10% PMMA cured at 110°C, with MR = 2/1. The DSC reaction rate and overall conversion profiles based on ΔH_S are also plotted for comparison. The filled circle designated in the DSC rate profile denotes the transition point for $\alpha_S > \alpha_E$ (see text).

pan, with MR = 1/1, 3/1, and 6/1 have been observed by using SEM, as shown in Figures 10(a), (b), and (c). It is seen that the higher the molar ratio, the more swollen and loose the microgel. The size of the incipient microgel particle increases with increasing molar ratio (4–5, 7–8, and 10 μm for MR = 1/1, 3/1, and 6/1, respectively).

As pointed out in our previous study,²³ basically, the formation of microgel particles would continue from the beginning of the reaction until the microgels meet and closely overlap with one another throughout the system. After the peak of the DSC rate profile, the rate of microgel formation would then slow down considerably due to the diffusion-controlled propagation reactions for polyester C=C bonds. Sometime later, when the existing microgels are highly overlapped via crosslinking and a compact global network structure is formed, no new microgel particles would be generated. For the isothermal UP curing reactions at high temperatures, such as

110°C, prior to the peak of the DSC rate profile, the intramicrogel crosslinking reaction would proceed more favorably than the intermicrogel crosslinking reaction. After the peak, the trend would be reversed.

Adding LPA in the neat UP resin reaction system could enhance the microgels to be clearly identified throughout the reaction.²⁰ As shown schematically in Figure 11 for UP resins at MR = 2/1 with 10% LPA (PVAc or PMMA), the LPA material is shown to surround the microgel particles and thus exhibit segregating effects on them.

Diffusion Barrier and Segregating Effects of LPA on Intramicrogel Crosslinking Reactions

For the UP resins with LPA, the LPA would affect the intramicrogel crosslinking reactions in two opposing directions by diffusion barrier effect and segregating effect on microgel particles. On one hand, the thin layer of LPA covering the surface of mi-

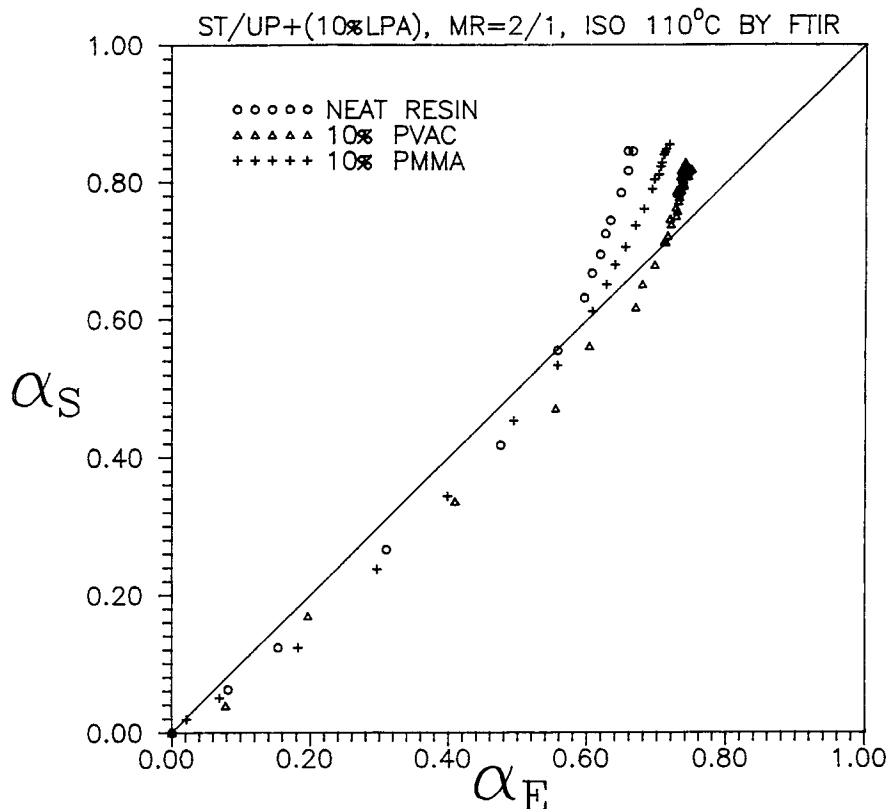


Figure 9 Relative conversion profiles of styrene vs. polyester C=C bonds for UP resins at MR = 2/1 containing no LPA, 10% PVAc, and 10% PMMA cured at 110°C.

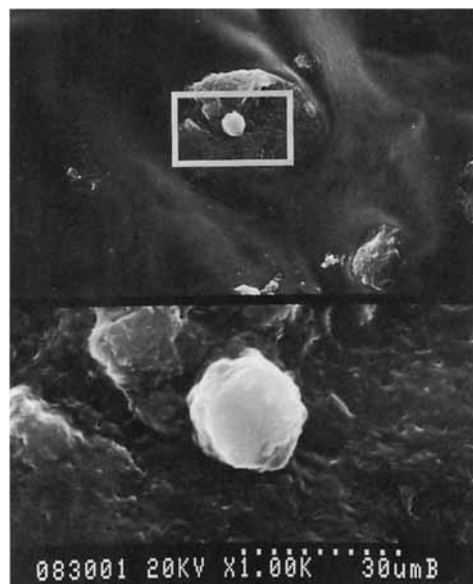
crogel particles could reduce the diffusion rate of styrene into the microgels and would tend to diminish the intramicrogel crosslinking reaction rate. On the other hand, the less merging of microgel particles due to the segregating effect of LPA could facilitate the intramicrogel crosslinking reactions as compared with those of the neat UP system, where the microgels tend to be overlapped with each other faster via crosslinking and hence the intermicrogel crosslinking reactions would be getting competitive with the intramicrogel crosslinking reactions at an earlier time.

Depending on the relative importance of the two effects caused by LPA, the reaction rate for the LPA-containing sample at the very early stage of reaction could be lower (e.g., MR = 1/1 and 2/1 in Figs. 2 and 3) or higher (e.g., MR = 2/1 for the shoulder region in Fig. 3) than that of neat resin sample. Since the number of microgel particles generated around the shoulder ($\alpha = 5\text{--}7\%$)²⁰ is greater for the PVAc-containing sample than for the PMMA-containing sample, the initial reaction rate, as evidenced by the height of the shoulder, follows the same trend.

Swelling and Segregating Effects of Styrene on Intramicrogel Crosslinking Reactions

The higher initial molar ratio of styrene to polyester C=C bonds would further enhance the intramicrogel crosslinking reactions, and a kinetic-controlled plateau could then appear in the initial portion of DSC rate profile at MR = 3/1 and 6/1 (see Figs. 4 and 5). This is because of both the swelling and the segregating effects of styrene on microgels. The former would lead to the looseness of microgel particles, while the latter could result in the slow overlapping of microgel particles via crosslinking since the self-bonding of styrene monomers would be much less favorable than copolymerization of styrene and polyester C=C bonds as mentioned earlier. Both the styrene effects would influence the relative importance of LPA effects on intramicrogel crosslinking reactions.

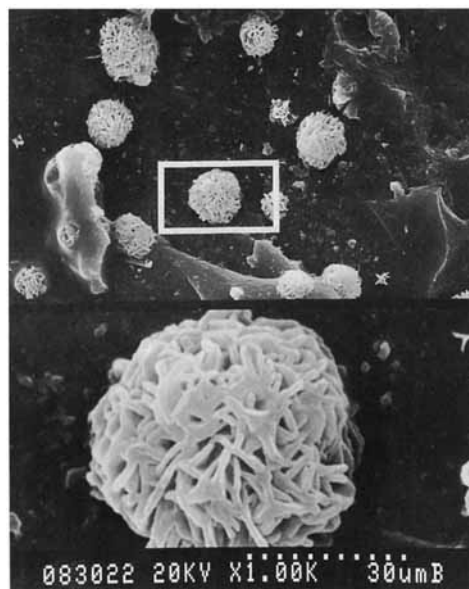
At MR = 3/1, the adverse diffusion barrier effect of LPA on microgel particles may be mitigated by the swelling effect of styrene, and hence the reaction rate in the initial plateau region would be predom-



(a)



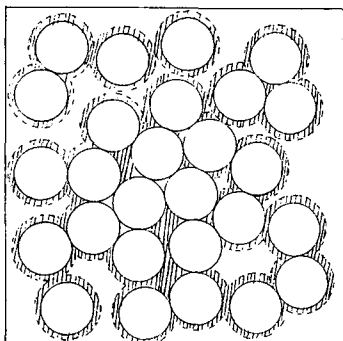
(b)



(c)

Figure 10 SEM micrographs of the fractured surface for the neat UP resin with various molar ratios cured at 100°C and initiated by 1% TBPB at very low conversions. (a) MR = 1/1, $\alpha = 2.0\%$; (b) MR = 3/1, $\alpha = 0.9\%$; and (c) MR = 6/1, $\alpha = 1.4\%$. The upper picture is obtained at 1000 \times and the lower one for the upper designated region at 5000 \times . (b) is obtained at 1000 \times .

A>.10%PVAc



B>.10%PMMA

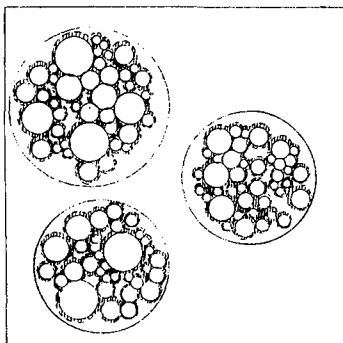


Figure 11 Schematic diagram of the fractured surface for the 10% LPA-containing sample with MR = 2/1 cured isothermally at 110°C. (a) 10% PVAc and (b) 10% PMMA. The LPA materials (shaded area) are shown to surround the microgel particles and thus exhibit segregating effects on them.

inated by the favorable segregating effect of LPA, leading to the order of reaction rate: neat UP resin < that with 10% PMMA < that with 10% PVAc (see Fig. 4). At even higher styrene content, such as MR = 6/1, the favorable segregating effect of LPA on microgel particles may be overshadowed by the segregating effect of styrene, and the adverse diffusion effect of LPA would be dominant, leading to a reverse trend of reaction rate in the plateau region when compared with MR = 3/1 (see Fig. 5).

Diffusion Hindrance Effects of LPA on Intermicrogel Crosslinking Reactions

For the UP resins with LPA, the LPA segregating adjacent microgel particles would generally lead to a decline in the rate of intermicrogel crosslinking reactions since the diffusion of styrene monomers in the LPA medium could be depressed during the crosslinking reactions. As mentioned earlier, after the peak of the DSC rate profile, the intermicrogel crosslinking reaction predominates over the in-

tramicrogel crosslinking one. Thus, the LPA-containing sample would exhibit a lower overall reaction rate than the neat UP resin sample at the maximum reaction rate due to a lower intermicrogel crosslinking reaction rate (see Figs. 2-5).

Effects of Globule Microstructures on Relative Conversions of α_S and α_E and Final Conversions

The microgel formation and the subsequent intramicrogel crosslinking reaction could cause a fast consumption of polyester C=C bonds.²⁵ Due to the enhancement of intramicrogel crosslinking reactions caused by the segregating effect of LPA on microgel particles, the relative conversion of polyester C=C bonds to styrene is higher for the LPA-containing sample than for the neat UP resin sample (see Fig. 9). Since the microgel particles generated are larger in number for the PVAc-containing sample than for the PMMA-containing sample,²⁰ α_E also shows a higher value under the same level of α_S throughout the reaction.

For the PVAc-containing sample, the segregating effect of LPA on microgel particles would also enhance the final conversion of polyester C=C bonds, α_E , as compared with that of the neat resin sample (see Table IV). Since styrene monomer could also exert a segregating effect on the generated microgel particles, the extent of α_E increase for the PVAc-containing sample in reference to the neat resin sample decreased with increasing initial molar ratios of styrene to polyester C=C bonds (see Table IV).

On the other hand, for the PVAc-containing sample, the characteristics of a globule microstructure during the cure would result in either a decrease (MR = 1/1 and 2/1) or an increase (MR = 3/1 and 6/1) in the final conversion of styrene, α_S , as compared with that of the neat resin sample. The effects of LPA on overall final conversions would then rely on the relative increase and/or decrease of α_E and α_S (see Table IV).

For the PMMA-containing sample, at MR = 2/1 and 3/1, since the microstructure with distinguishable microgel particles constitutes only part of the overall morphology²⁰ (also see Fig. 11), α_E and α_S shown in Table IV generally lie between those of the neat UP resin and the PVAc-containing samples. At a lower molar ratio, such as MR = 1/1, the continuous phase for the PMMA-containing sample would possess a molar ratio of MR < 1/1 due to the phase separation, and hence the microstructure could be in lack of styrene swelling effect considerably. This would then lead to a reduction of polyester C=C bond conversion in the continuous phase and, in turn, could counterbalance the increase of polyester C=C bond conversion in the

PMMA-dispersed phase due to the favorable segregating effect of LPA on microgel particles. Consequently, ΔH_{iso} and α_{iso} show lower values than those for the neat resin sample, so do the α_S and α_E (see Table IV). At a higher molar ratio, such as MR = 6/1, since the globule microstructure predominates throughout the PMMA-containing sample,²⁰ ΔH_{iso} , α_{iso} , α_S , and α_E turn out to be pretty much the same as those of the PVAc-containing sample with a similar overall globule microstructure.

CONCLUSIONS

The effects of LPA on the curing kinetics for the UP resins at various molar ratios of styrene to polyester C=C bonds have been investigated at 110°C. The LPA materials would surround the microgel particles generated during the reaction, and could thus exhibit segregating effects on them.

In the cure of UP resins, the overall reaction rate is a summation of the intramicrogel crosslinking reaction rate and the intermicrogel crosslinking reaction rate. For the LPA-containing samples, the intramicrogel crosslinking reaction rate would be reduced by the diffusion barrier effect of LPA, but could be enhanced by the segregating effect of LPA on microgel particles. As the molar ratio increases, both the swelling and the segregating effects of styrene would come into play in facilitating the intramicrogel crosslinking reactions, and a shoulder or a kinetic-controlled plateau region in the DSC rate profile could appear at the early stage of reaction. After the peak of DSC rate profile, the intermicrogel crosslinking reaction would predominate over the intramicrogel crosslinking one. For the LPA-containing sample, the diffusion hindrance effect of LPA would generally lead to a decline in the rate of intermicrogel crosslinking reactions.

For the LPA-containing sample, the relative conversion of polyester C=C bonds (α_E) to styrene (α_S) is higher than that for the neat UP resin during the reaction because a large number of highly independent microgel particles could be generated, which would cause a fast consumption of polyester C=C bonds. Since the microgel particles generated are larger in number for the PVAc-containing sample than for the PMMA-containing sample, α_E also shows a higher value under the same level of α_S throughout the reaction.

The LPA-induced globule microstructure during the cure could enhance the final conversion of α_E , but would result in an increase or a decrease of the final conversion of α_S , depending on the initial molar ratio of styrene to polyester C=C bonds.

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