

Reaction-Induced Phase Separation in Poly(vinyl acetate)/Polyester Blend

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ABSTRACT: In blends of unsaturated polyester (UP), poly(vinyl acetate) (PVAc), and styrene, a reaction-induced phase separation occurs upon curing that is due to the crosslinking between styrene and the UP molecules. The evolution of the morphology was observed by optical microscopy on a heated stage. Light transmission was used in parallel to precisely detect the onset of phase separation and the formation of microvoids. Using Fourier transform IR spectroscopy in the same conditions, the conversions at phase separation and at microvoiding were evaluated. Phase separation occurs at a very low degree of conversion and microvoiding develops at

around 60% of conversion. The final morphology of the blend was investigated by scanning electron microscopy. The relative influences of the cure temperature, the concentration in PVAc, and the molecular weight of PVAc were investigated. It was confirmed that the early stages of the reaction at high temperature determine the final morphology of the blends. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3877–3888, 2006

Key words: polymer blend; unsaturated polyester; poly(vinyl acetate); phase separation; curing of polymer

INTRODUCTION

Thermoplastic polymers are often used as modifiers in the formulation of thermosetting-based materials. The modifier is added for different reasons, for example, to increase the toughness of the material, to reduce the thermal stresses, or to improve the surface quality of molding surfaces.¹

In this study, specific thermoplastics are added to improve the surface quality of composites based on unsaturated polyester (UP) resins. Curing of UP resins is a free radical chain growth copolymerization between polyester molecules and styrene monomer. This reaction is associated with a volume reduction of about 7%. The polymerization shrinkage induces a series of defects in the final part such as sink marks, surface waviness, cracks, and a loss of dimensional stability. In the presence of specific thermoplastics, referred to as low-profile additives (LPAs), these problems have been partly solved.² LPAs are referred to as compatible or incompatible, depending on whether they are miscible or immiscible, respectively, with the UP resin at room temperature before curing.

The benefit of adding an LPA in the resin formulations is definitely linked to the two-phase structure that

develops upon curing.³ For a compatible LPA, the initial mixture forms one single phase before curing. During curing, the mixture becomes incompatible because of the change in the molecular weight and in the polarity of the polyester molecules. A reaction-induced phase separation occurs and leads to the formation of cocontinuous polyester-enriched and LPA-enriched phases. The literature mostly describes phase separation through a nucleation and growth process.⁴ At the early stages of curing, microgels of polyester form because of the strong tendency toward intramolecular cyclization, which is a characteristic for chain growth polymerization. Soon after, LPA and unreacted styrene separate from these microgels in a matrix that surrounds and isolates the microgels. Upon further curing, microgels contact each other. Gelation takes place and the actual structure stays cocontinuous upon further curing. At the later stages of curing, microvoids develop in the LPA-enriched phase because of further curing shrinkage of the polyester phase. Even though their origin is still controversial,⁵ a strain relief mechanism through cracking from the interface between the phases is often suggested to explain the formation of microvoids.^{6,7} These microvoids are believed to bring the most significant contribution to the mechanism of shrinkage control in the presence of an LPA. In more recent studies, Li and Lee proposed a phase separation mechanism through spinodal decomposition for the low temperature cure of UP–poly(vinyl acetate) (PVAc) systems; they pointed out the importance of the time between the onset of phase separation and gelation to determine the final morphology of the

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samples.⁷ The spinodal decomposition mechanism was recently confirmed by Boyard et al. in a similar system using small-angle laser light scattering.⁸

The literature on these systems is thus quite abundant. However, most of the articles focus on one specific aspect of the cure reaction. For instance, the mechanism of shrinkage control, in particular the formation of microvoids, has been widely investigated.^{7,9-11} In the present study the cure process was examined globally with a particular attention to the early stages of curing, which is often neglected. In addition, cure temperatures close to those used in industrial practice were investigated. The complexity of these systems results from the competition between phase separation and chemical reactions. Therefore, the blends were examined as soon as the cure reaction started in order to understand the development of the morphology, which is a key parameter for controlling polymerization shrinkage. Light transmission and optical microscopy were used to detect the critical changes in the system occurring during curing, for instance, phase separation or the formation of microvoids. These experiments were coupled with Fourier transform IR spectroscopy (FTIR) analysis in order to follow the consumption of reacting species during curing and to evaluate the conversion at critical stages. The final microstructure was examined by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The UP resin was a 1:1 mixture of maleic anhydride and propylene glycol (Norsodyne M0410, Cray-Valley, France) with an average of 10.13 vinylene groups per polyester molecule and an average molecular weight of 1580 g/mol. It was received as a solution containing 35% by weight of styrene. The LPA was PVAc (Dow Automotive) provided as a solution containing 60% by weight of styrene. Three molecular weights were available: 90,000, 125,000, and 180,000 g/mol. Except for the study on the influence of the molecular weight, PVAc with a molecular weight of 90,000 g/mol was used.

In all formulations, the molar ratio of styrene to polyester double bonds was adjusted to 2:1 by adding styrene (Acros Organics). *tert*-Butyl peroxy 2-ethylhexyl carbonate (1.2 wt %, Trigonox 117, Akzo Nobel) was used as a reaction initiator. 1,4-Benzoquinone (300 ppm, Fluka) was used as an inhibitor to control the cure kinetics.

Techniques

Evolution of morphology upon curing revealed by optical microscopy

The evolution of the morphology upon curing was followed by optical microscopy in transmission

mode. A hot plate (Linkam THMS 600 coupled to a Linkam TMS 92 heat controller) was mounted on the microscope to cure the samples. The samples were made of a 20-mg drop of polymer blend placed between two glass slides. The goal was to detect the changes in the morphology of the resin upon curing after phase separation, as well as the appearance of microvoids.

Onset of phase separation detected by light transmission

The decrease in the transmitted light intensity was used to detect the onset of phase separation during isothermal curing. The homemade equipment consisted of three main parts: an He-Ne laser source, a hot chamber to cure the sample, and a photodiode to measure the transmitted light intensity. Additional filters were used to regulate the intensity. The laser was operated at 633 nm. The hot chamber (Linkam THMS 600) was connected to a heat controller (Linkam TMS 92) for isothermal curing. The sample consisted of 20 mg of polymer cast between two glass slides. The photodiode was connected to a computer for direct recording of the intensity as a function of the cure time.

Cure kinetics via FTIR

FTIR was used to follow the cure kinetics. The main purpose for carrying out this experiment was to evaluate the conversion of styrene and UP at phase separation. Experiments were carried out with a Nicolet Magna IR 560 in the attenuated total reflectance mode. Cure temperatures ranged between 100 and 130°C. A new background was measured for each temperature. Sixteen consecutive scans were taken at each sampling time, and their average was transformed into a frequency-domain spectrum. The sampling interval varied according to the changes in the reaction rate.

Observations of final morphology by SEM

SEM (Philips XL 30) was used to observe the morphology of the polymer blends after curing. The preparation of the samples was as follows: 20 mg of polymer blend was cured in a hermetic aluminum mold. After demolding, the samples were broken into two pieces. The fracture surface was etched in 2-butanone for 5 min in order to dissolve PVAc and unreacted materials. The samples were gold coated before the observations. The influences of the cure temperature, the concentration in PVAc, and the molecular weight of PVAc were investigated.

RESULTS AND DISCUSSION

Evolution of morphology upon curing observed with optical microscopy

The evolution upon curing of a blend containing 14 wt % PVAc is shown in Figure 1. This specific concentration was chosen because it is known to provide good shrinkage control for parts molded in industry. The

micrographs represent the main changes in the morphology from the beginning of curing to the formation of microvoids. The sample was cured isothermally at 120°C on the hot stage.

In Figure 1(a) the sample is composed of one single liquid phase because the polymer mixture is miscible. This state remains during the inhibition step, whereas 1,4-benzoquinone forms a complex of low reactivity on

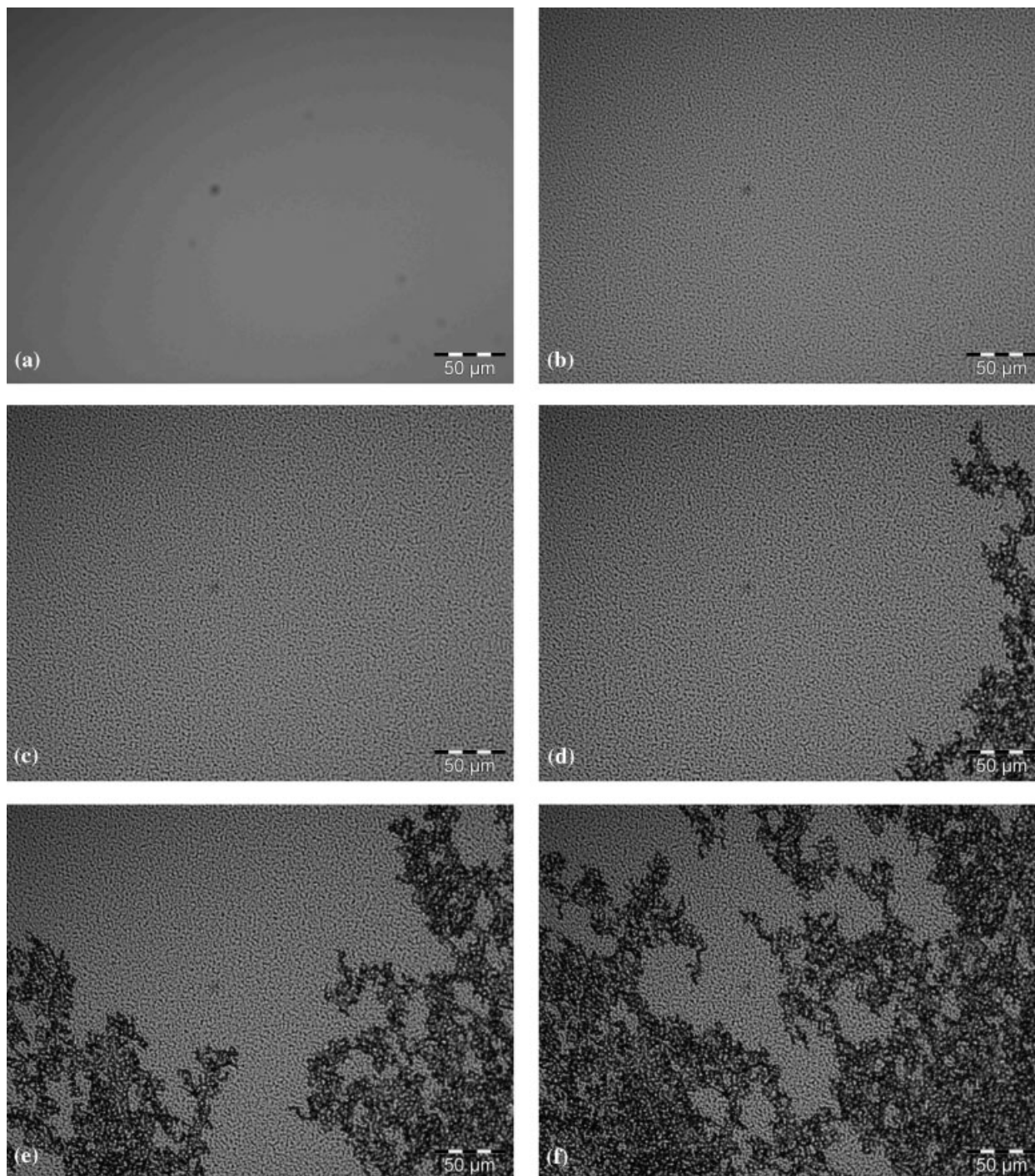


Figure 1 Optical micrographs of the evolution of the morphology upon isothermal curing of a blend containing 14 wt % PVAc at 120°C for (a) 0, (b) 5, (c) 5.5, (d) 10, (e) 10.25, and (f) 10.5 min.

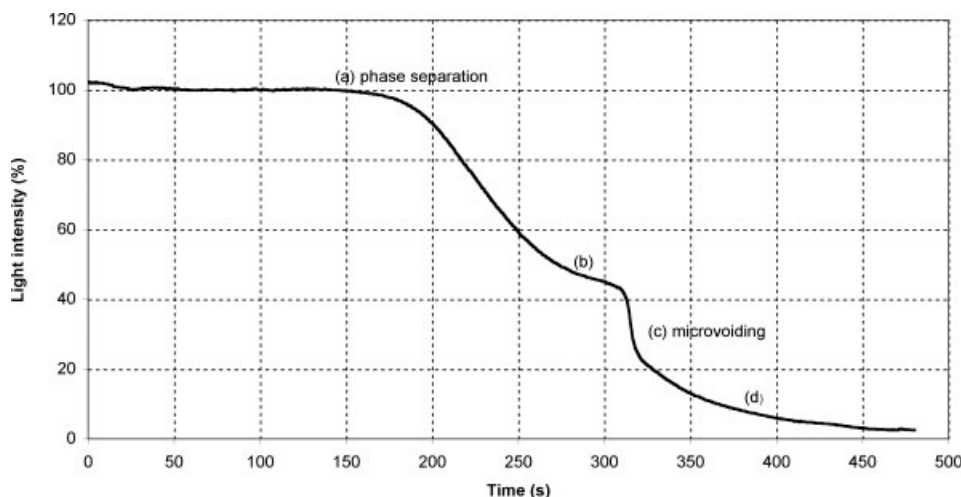


Figure 2 A light intensity profile as a function of time during isothermal curing at 130°C of the blend containing 14 wt % PVAc.

chains activated by the decomposition of the initiator. A visible two-phase microstructure develops after the reaction-induced phase separation. A polyester-enriched phase and a PVAc-enriched phase are shown in Figure 1(b). The two phases seem to be cocontinuous, but the magnification is too low to state the exact microstructure. The morphology evolves for a rather short time, but the global morphology remains unchanged. In Figure 1(c), which most probably corresponds to gelation, the morphology stops evolving. Further curing does not change the morphology; but, because of the ongoing reaction and further shrinkage, microvoids are initiated [Fig. 1(d)] and then propagate in the whole sample [Fig. 1(d–f)].

This sequence of micrographs is characteristic of reaction-induced phase separation.^{7,12} Morphology develops only between phase separation and gelation. Gelation then locks the structure and impedes any fur-

ther development even if chemical reactions are still going on. In a previous study, the gel time was measured on the same system as a function of the cure temperature.¹³ An expected decrease in gel time was observed for increasing temperature, which means that the time available for the development of the microstructure is rather short at elevated temperature. Any attempts to determine a precise value of the gel conversion remains challenging in this system because of the difficulty in providing a direct comparison between different analytical techniques, which require a different sample volume or packaging. However, on the basis of data reported in the literature and our own investigation, a gel conversion value between 5 and 15% seems reasonable.^{7,14} This low value is characteristic of a free radical chain growth copolymerization, because of the high degree of polymerization of the formed chains. In contrast to step growth polymeriza-

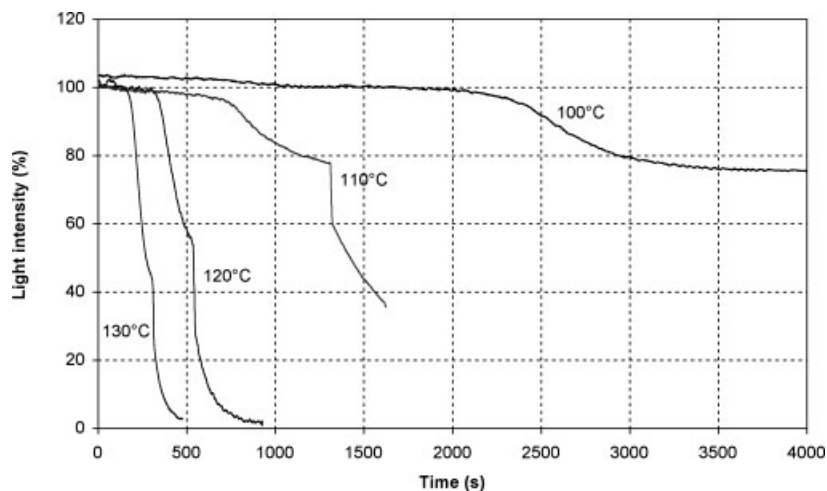


Figure 3 A light intensity profile as a function of time during curing of the blend containing 14 wt % PVAc at four isothermal temperatures: 100, 110, 120, and 130°C.

TABLE I
Time for Phase Separation and Microvoiding as
Function of Cure Temperature

Cure temp. (°C)	Phase separation (min)	Microvoiding (min)
100	29	—
110	10.8	23
120	5.3	10
130	1.8	5.5

tion, in this system gel conversion may also vary with the cure temperature because it depends on the kinetics of initiation, propagation, and termination, which have different dependences on the temperature.¹ The low gel conversion implies that most of the chemical reaction occurs in a gel to solid state. Considering the volume shrinkage of polyester upon curing, this leads to a high level of internal stresses in the system and, as a consequence, to the formation of microvoids. This is not encountered in other systems, which are also subjected to a significant polymerization shrinkage and which exhibit the same type of morphology, such as epoxy-based blends.^{15,16} In these later systems, gel conversion is clearly higher and shrinkage after gelation is not large enough to induce microvoids.

Onset of phase separation by light transmission

With optical microscopy it was possible to follow the development of the two-phase structure after phase separation. However, the onset of phase separation could not be detected precisely. Light transmission was used to obtain this information.

Figure 2 shows the changes of the transmitted laser intensity during isothermal curing of the blend con-

taining 14 wt % PVAc at 130°C. Initially, the blend is fully miscible and transparent so that the intensity is maximal. It was normalized to 100%. Phase separation [Fig. 2(a)] is characterized by a decrease in the intensity due to scattering of the light by the two-phase structure shown in Figure 1(b). It was shown by light scattering experiments that this structure right after phase separation is cocontinuous for this system.⁸ For this particular concentration and cure temperature, the reaction-induced phase separation occurs through spinodal decomposition. The intensity further decreases after phase separation during the development of the phases for reaching a plateau [Fig. 2(b)]. This plateau might approximately correspond to gelation, which impedes any further changes of the morphology. Transmitted light thus remains constant. Then, the profile exhibits a sudden decrease in intensity [Fig. 2(c)]. This step corresponds to the formation of microvoids. After a rapid propagation in the sample, the microvoids develop more slowly upon further curing. The slope is thus gentler by the end of curing. Finally, a value close to zero is reached. The decrease in the intensity during microvoiding proves that the dimensions of the microvoids are very small because they are able to diffract the laser (633 nm). Large voids would lead to an increase in the intensity. This confirms previous observations,¹³ where transmission electron microscopy pictures of the same blends showed that the microvoids are indeed in the range of 700 nm and occur in the form of rounded cavities (not cracks or interfacial decohesion) in the PVAc-enriched zones, as expected at a temperature so high above the glass-transition temperature of PVAc.

Figure 3 gives examples of the light intensity curves as a function of time for the other cure temperatures. For 100°C, as observed by optical microscopy, no

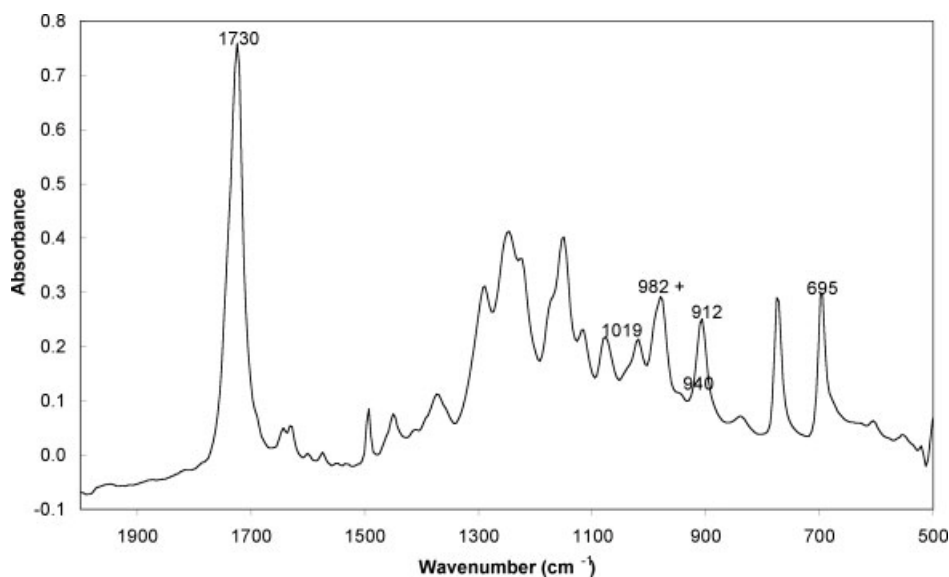


Figure 4 The FTIR spectrum for a blend containing 14 wt % PVAc before curing.

TABLE II
Identification of Main Peaks of Spectrum in Figure 4

Wavenumber (cm^{-1})	Identification
695	C–H out of plane bending in styrene
912	C–H out of plane bending in $\text{CH}_2=\text{CHR}$ for styrene
940	OH out of plane bending in polyester terminal groups + PVAc
982	C–H out of plane bending in $\text{CHR}=\text{CHR}$ for polyester
992	C–H out of plane bending in $\text{CH}_2=\text{CHR}$ for styrene
1019	C–H in-plane bending in benzene ring for styrene + C–O–C stretching in PVAc
1730	C=O stretching

microvoid could be detected under isothermal conditions. The intensity decreases after phase separation and then stabilizes to a constant value. For the other temperatures, the curves are similar to that presented in Figure 2.

From these curves, two times were selected: the onset of phase separation and the time that was necessary for the formation of microvoids. The values as a function of the cure temperature are reported in Table I. As expected, an increase in temperature accelerates all phenomena. The times indicated in Table I are used in the next section, in which FTIR experiments are presented.

Cure kinetics via FTIR

Figure 4 shows the FTIR spectrum for the blend containing 14 wt % PVAc before curing at room temperature. The identification of the main peaks corresponding either to styrene or to the UP resin is indicated in Table II.¹⁷

The peaks at 912 and 982 cm^{-1} were used to follow the consumption of styrene and polyester double bonds, respectively. Because the peak at 982 cm^{-1} overlaps the peak at 992 cm^{-1} assigned to styrene, a subtraction method was used to separate the overlapping peaks. Styrene loss due to evaporation could be estimated with the peak at 695 cm^{-1} . For the calcula-

tion of the conversion, the peak at 1730 cm^{-1} was used as a reference. It is contributed by both UP and PVAc. The conversion (α) of the different species can be calculated as^{18,19}

$$\alpha = 1 - \bar{A}^t / \bar{A}^0 \quad (1)$$

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 , respectively. These areas are respectively normalized by A^0_{1730} and A^t_{1730} .

The total conversion of styrene (α_{St}), which includes the reaction conversion and evaporation loss, can be calculated as

$$\alpha_s = \alpha'_s - \alpha''_s \quad (2)$$

where α'_{St} corresponds to the conversion evaluated with the peak at 912 cm^{-1} and α''_{St} corresponds to styrene loss evaluated with the peak at 695 cm^{-1} .

Figure 5 provides an example of the changes of the spectra as a function of the time during isothermal curing at 110°C. The evolution of the peaks at 912 and 982 cm^{-1} that are used to calculate the conversion of styrene and polyester, respectively, are illustrated in Figures 6 and 7.

The conversion curves at different isothermal temperatures are represented in Figure 8. Even if the sty-

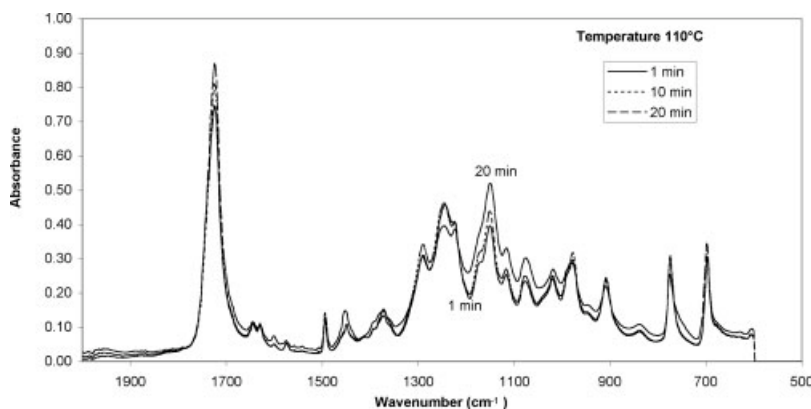


Figure 5 The evolution of the whole FTIR spectrum upon curing at 110°C.

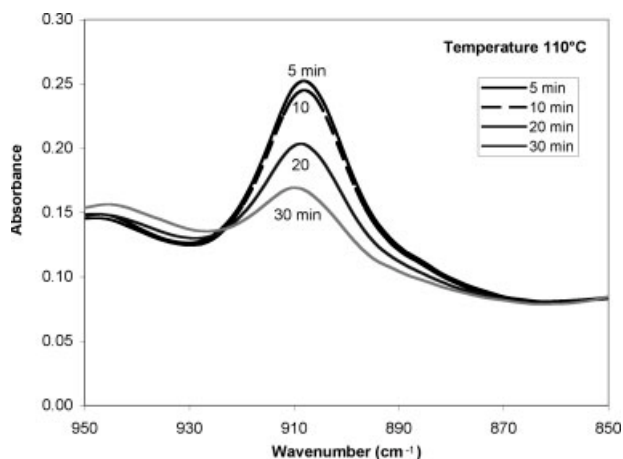


Figure 6 The evolution of the peak at 912 cm^{-1} corresponding to the consumption of styrene during isothermal curing at 110°C .

rene loss was negligible, it was taken into account in the calculation. As expected, the conversion increases as a function of the temperature. Differences can be noted between the conversion of styrene and that of UP double bonds at high conversion. At low temperature (100°C) the conversion of styrene is lower than that of UP. At high temperatures (120°C) the trend is reversed. Styrene conversion was found to be higher at the later stages of curing according to Huang and Su.¹⁷ Conversion is not complete after curing in particular for a low temperature. Residual styrene thus remains in the system after curing. This could explain some problems encountered during manufacturing or handling of parts based on this material, such as blisters during painting or degassing during service.

Conversion values obtained with FTIR were compared with light transmission data presented in Table I in order to estimate the conversion of styrene and that

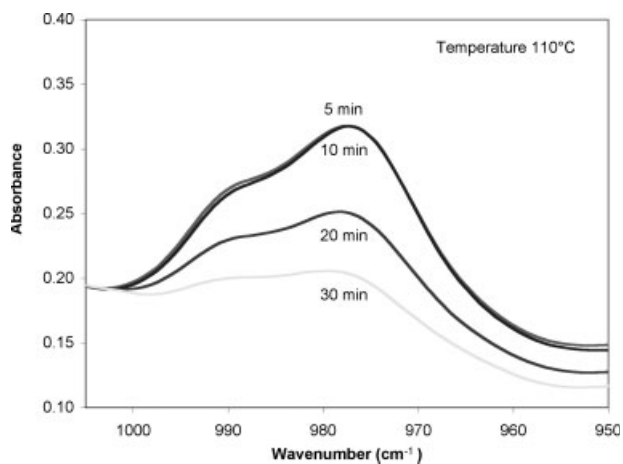


Figure 7 The evolution of the peak at 982 cm^{-1} corresponding to the consumption of UP double bonds during isothermal curing at 110°C . This peak overlaps with the peak at 992 cm^{-1} .

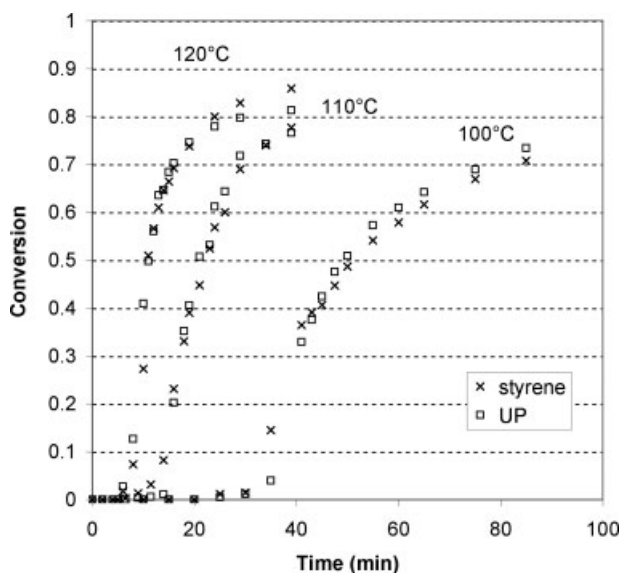


Figure 8 Conversion profiles during curing of the blend containing 14 wt % PVAc at different cure temperatures.

of polyester at phase separation. The values are summarized in Table III as a function of the cure temperature. The conversion at phase separation was very low. Thus, as soon as double bonds are consumed by the crosslinking reaction between styrene and UP chains, the system becomes unstable and phase separates. A small change of the chemistry of the system that modifies the molecular weight or the polarity of the UP molecules is thus sufficient to make the system immiscible. Conversion at phase separation was almost constant, even though a slight increase could be noted with the cure temperature. An increase in conversion at phase separation is characteristic for blends exhibiting an upper critical solution temperature.¹

From the curves presented in Figure 8 and the time for microvoiding reported in Table I, it was also possible to evaluate the conversion at microvoiding at about 60%.

Morphology after curing examined with SEM

Influence of concentration in PVAc

The influence of the concentration in PVAc on the morphology was examined after isothermal curing at 100°C . Figure 9 shows the most relevant cliches of the

TABLE III
Conversion of Styrene and Polyester at Phase Separation

Temp. ($^\circ\text{C}$)	Conversion at phase separation	
	Styrene (%)	UP (%)
100	1	0.5
110	1	0.5
120	1	1
130	1.5	1.5

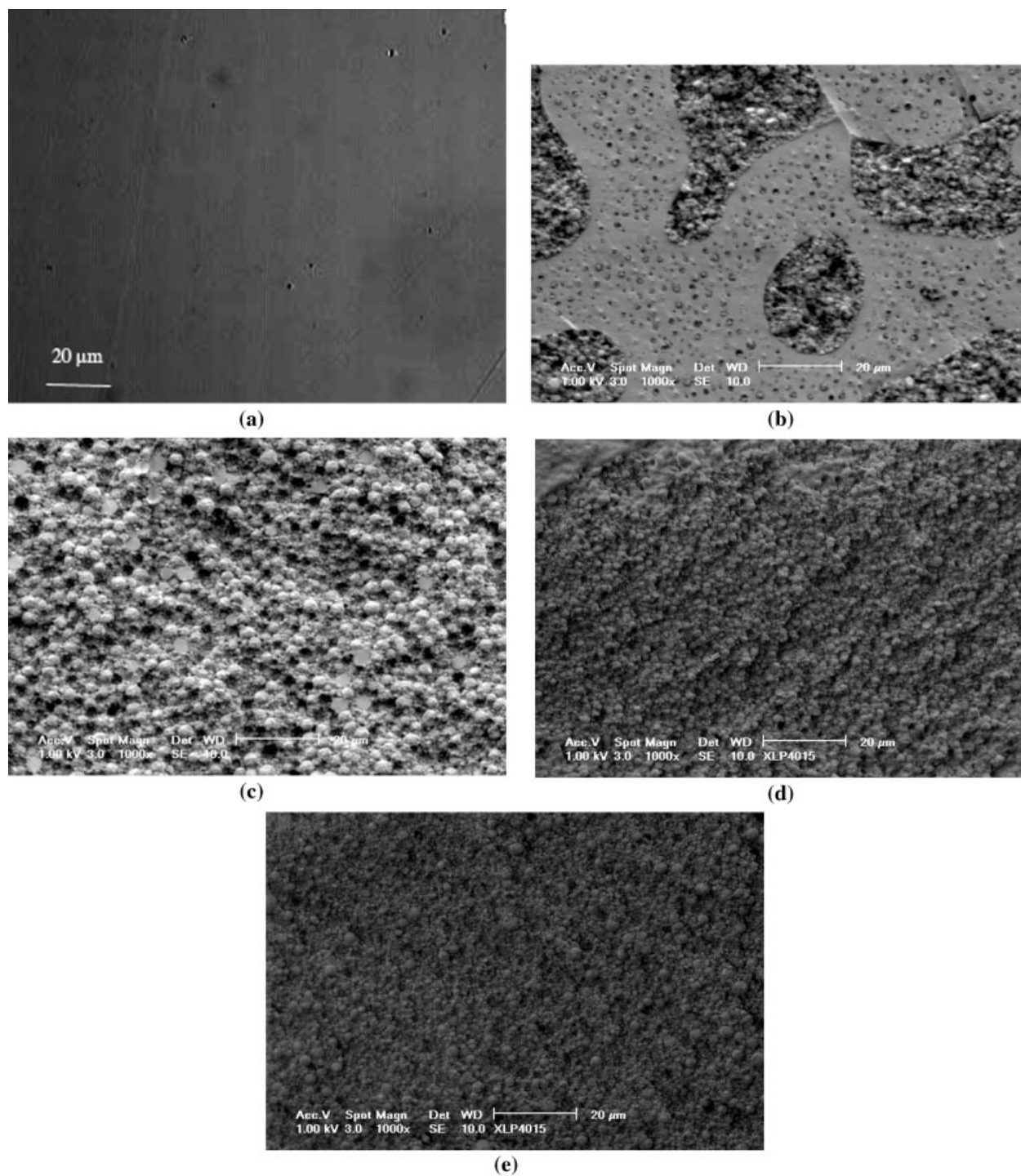


Figure 9 SEM micrographs showing the characteristic morphologies after 90-min curing at 100°C as a function of the concentration in PVAc: (a) 0, (b) 5, (c) 6, (d) 11, and (e) 14 wt %. All samples were etched in 2-butanone, except (a).

surfaces after etching the surface with 2-butanone, except for Figure 9(a). The structures in all figures thus represent the polyester phase.

For the neat polyester resin, which was polished in the micrograph [Fig. 9(a)], the morphology of the sample is composed of one single phase and is therefore featureless. It referred to as flakelike when the surface is a fracture surface, because cracks then appear as in

glassy materials.²⁰ The addition of PVAc induces a two-phase structure. At low concentration in PVAc [Fig. 9(b)], the PVAc-enriched phase forms domains of about 20 μm in diameter dispersed in the continuous polyester phase. The PVAc-enriched phase is composed of a globular structure. Small inclusions of PVAc are visible in the continuous polyester phase. Increasing the concentration over 5 wt % led to a transition in

the morphology. The samples shown in Figure 9(c–e) are all entirely composed of fine polyester globules of a few microns in size that seem to be connected to each other. They correspond to polyester microgels. This connected globule structure implies a two-phase morphology of interconnected domains of a polyester-rich phase regularly dispersed in a matrix enriched in PVAc. This morphology is referred to as cocontinuous by most of the authors in this field,¹⁴ even though this

term might not be fully appropriate because the cocontinuity might be lost. Increasing the concentration of PVAc leads to a decrease in the size of the polyester globules, probably because of better insulation of the polyester globules by the PVAc-enriched phase after phase separation.

For the particular concentration of 14 wt % PVAc, which was investigated thus far, this interconnected globule morphology implies a step of coarsening and

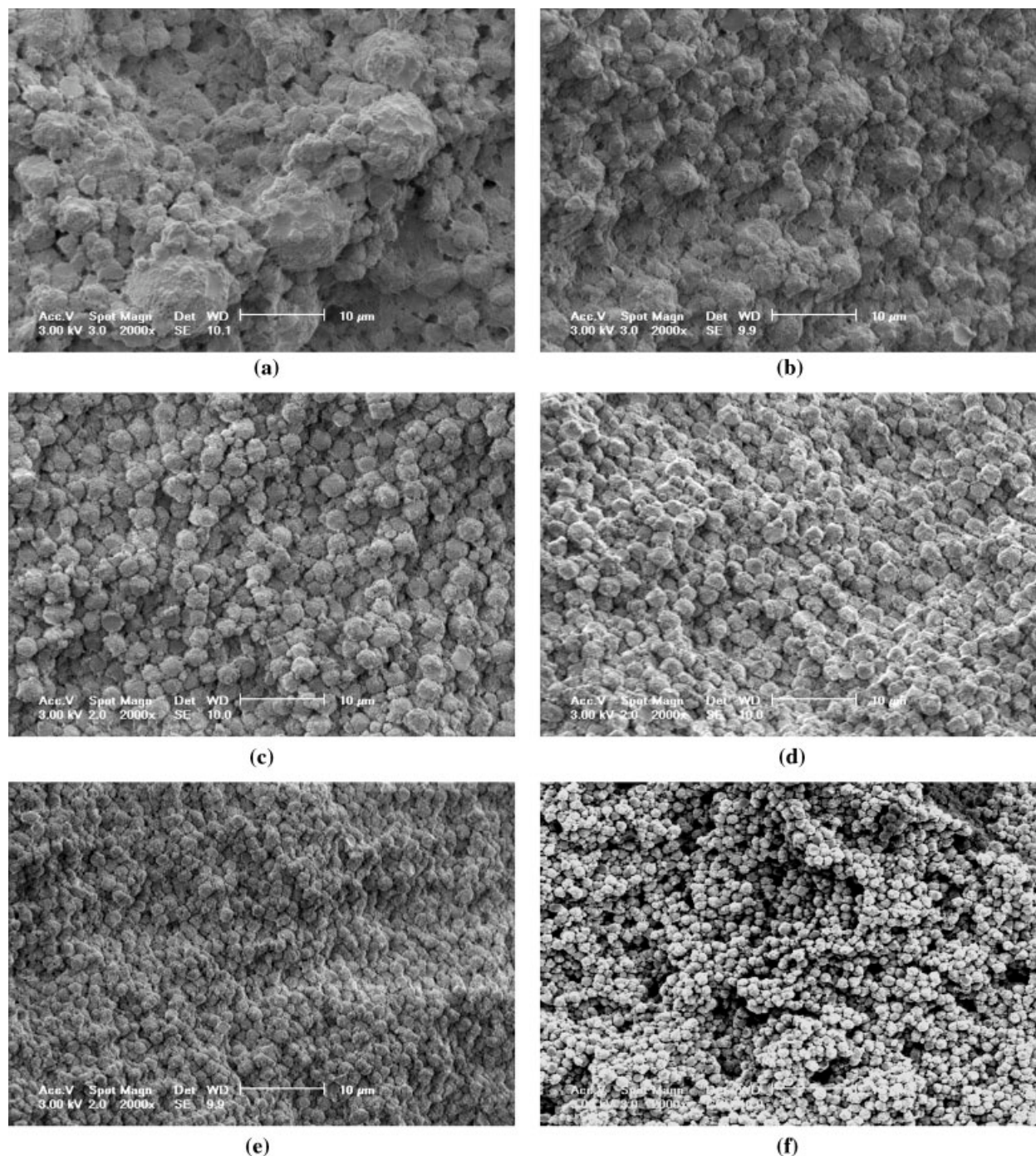


Figure 10 SEM micrographs of the morphology of the blend containing 14 wt % PVAc cured isothermally at (a) 70, (b) 90, (c) 110, (d) 130, (e) 150, and (f) 170°C. Cure times varied as a function of temperature to attain a high degree of conversion.

growth of the structure between phase separation and gelation. The structure that was shown to be cocontinuous after phase separation would tend to form spherical domains of polyester because of differences in the interfacial tension between the phases, as reported in epoxy-based systems,¹² and because of intramolecular cyclization of the polyester molecules.

Influence of temperature

The influence of temperature is illustrated by the series of micrographs presented in Figure 10. These images all correspond to a PVAc concentration of 14 wt %. For this concentration, the global morphology is again composed of interconnected globules of polyester for all temperatures. However, a severe decrease in the size of the microgels can be observed as the temperature increases. This is in agreement with observations made in other studies based on PVAc as an LPA.^{21,22} The diameter of the larger microgels is about 15 μm at 70°C. It is even likely that larger independent microgels detached from the surface during sample preparation. At 170°C, microgels with a diameter smaller than 1 μm can be detected. For other PVAc concentrations between 6 and 15 wt %, the same conclusion could be drawn. The interconnected globule morphology remained with a decrease in the size of the globules as the temperature increased.

As shown by our light transmission experiments, all processes are accelerated at elevated temperature. In particular, gelation occurs earlier, as shown by Bulliard et al.¹³ Furthermore, it was shown by FTIR that conversion of styrene and polyester at phase separation is slightly higher at elevated temperatures. The time available for the development of the morphology between phase separation and gelation is thus limited, leading to a finer morphology at elevated temperatures. At low temperatures, the time for the develop-

ment of the structure is longer, leading to a coarsened morphology. Globules are free to grow in size, as shown in Figure 10(a), and potentially coalesce.

The temperature showed an even stronger influence on the morphology at low concentrations in PVAc, that is, at a concentration lower than the transition noted at 6 wt %. Figure 11 shows different magnifications of the morphology of a blend containing 5 wt % PVAc cured at 120°C. Compare these micrographs to Figure 9(b). At low temperatures (i.e., up to 100°C) the morphology was composed of two easily distinguishable phases. At temperatures higher than 100°C the polyester phase is still continuous but small PVAc domains are homogeneously dispersed in the polyester phase.

An explanation for this particular morphology is as follows. At low temperatures, the reaction starts with the formation of microgels of polyester. They contact each other to form a continuous polyester phase. PVAc originally distributed homogeneously in the solution separates from the forming polyester phase. Concentration gradients are created in the blend. Because gelation occurs later at low temperatures, areas with a higher concentration in PVAc form. In these areas, the concentration in PVAc ultimately reaches the concentration for which the morphology is composed of interconnected globules of polyester, for the given temperature. The main difference at higher temperatures is the earlier onset of gelation. The development of the morphology stops earlier and large areas rich in PVAc cannot coalesce. PVAc stays homogeneously distributed in the sample. Furthermore, the concentration in PVAc is too low to permit any discontinuities in the polyester phase.

Influence of molecular weight of PVAc

The next series of micrographs in Figure 12 represents the observed morphology for PVAc with three molecu-

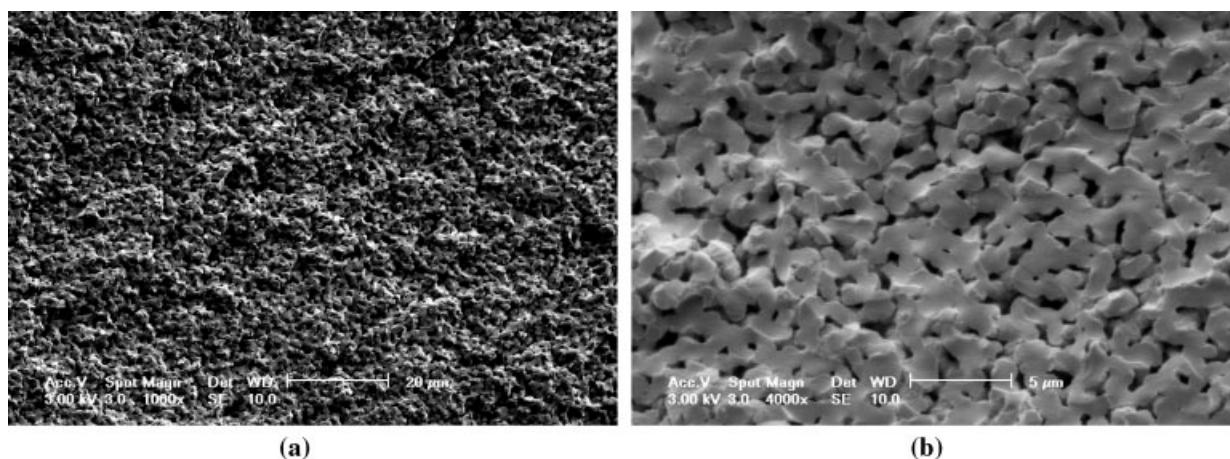


Figure 11 SEM micrographs of the morphology of the blend containing 5 wt % PVAc after 30-min isothermal curing at 120°C at original magnifications of (a) $\times 1000$ and (b) $\times 4000$. Compare this figure to Figure 9(b).

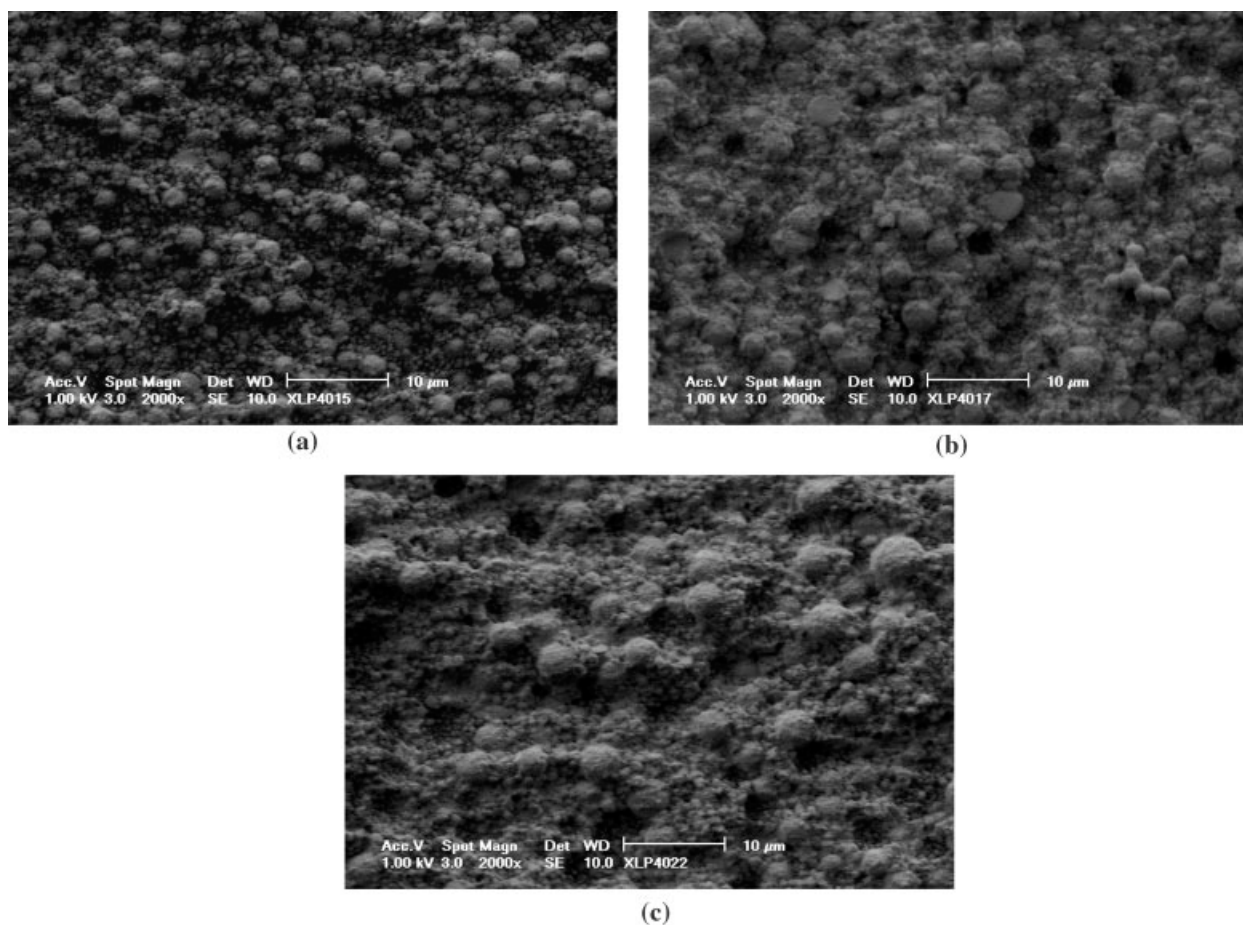


Figure 12 SEM micrographs of the morphology of the blend containing 14 wt % PVAc after isothermal curing at 100°C: $M_{w(\text{PVAc})}$ = (a) 90,000, (b) 125,000, and (c) 180,000 g/mol.

lar weights: 90,000, 125,000, and 180,000 g/mol. The samples were all cured at 100°C and contained 14 wt % PVAc. For all molecular weights, the morphology is again composed of interconnected globules of polyester. The main consequence of an increase in the molecular weight is an increase in the diameter of the polyester globules. Different reasons can explain this dependence. First, a change in the molecular weight can shift the miscibility gap of the blend in the phase diagram to other concentrations. This may in turn modify the conversion at which phase separation occurs. Second, blends usually become less miscible as the molecular weight of the additive increases. Phase separation thus occurs at a lower degree of conversion in the presence of an additive with a high molecular weight.¹ The time between phase separation and gelation is therefore longer, leading to larger globules.

In conclusion, it is possible to modify the morphology of the blends by acting on several parameters. The concentration is definitely the most influential parameter, followed by temperature and molecular weight. For this reactive system, these parameters can all affect the phase diagram by shifting the equilibrium line to either lower or higher conversion values.

CONCLUSION

The different stages associated with curing of a UP resin mixed with PVAc were summarized. In the initial state, after mixing of the components, the blend was miscible. During curing, the free radical chain growth copolymerization between styrene and UP induced a phase separation at a very low degree of conversion of around 1%. The resulting cocontinuous structure coarsened and grew to lead to interconnected globules of polyester in a matrix rich in PVAc. Gelation, which also occurred early in this system (5–15% according to the literature), locked the structure and this interconnected globule morphology remained for the rest of curing. After gelation, the ongoing chemical reaction induced internal stresses that could be released through the formation of microvoids in the PVAc-enriched phase. These occurred at a conversion of about 60% during isothermal cure for temperatures above 100°C. The final conversion was not complete after isothermal curing, especially at low temperatures, and this could have led to styrene release in the part. PVAc concentration and molecular weight exerted an influence on the final morphology by their action on

the phase separation mechanism and on the phase growth.

All phenomena were accelerated by an increase of the temperature blocking the phase separation process earlier and in turn, leading to a finer microstructure. The early stages of curing were thus crucial for the final morphology of the blends. In order to gain a better understanding of the morphology that developed right after phase separation, an extensive study by dynamic light scattering would be necessary. Indeed, a transition from a phase separation through spinodal decomposition to a nucleation and growth mechanism was expected in this system by changing the concentration or the cure temperature, for example. However, these results provided some insight into an improvement of the low profile effect, which was shown to be improved if the microstructure was separated early and the gelation delayed¹³: a high temperature was not desirable, because it tends to increase the reaction kinetics after phase separation, but high molecular weight might present some interest. In addition, the PVAc concentration for a given cure temperature should be adjusted to slow down the reaction kinetics, while preserving a homogenous microstructure.

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