Low temperature cure of unsaturated polyester resins with thermoplastic additives
I. Dilatometry and morphology study

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Abstract

A dilatometry and morphological study of the effect of the various thermoplastic additives on shrinkage control of unsaturated polyester (UP) resins cured at low temperatures is presented in this article. It was found that shrinkage control is closely related to the morphological changes during curing. There are two major transitions in the relationship of shrinkage and additive concentration that can be explained by the sample morphology. The additive starts to be effective on shrinkage control at the first transition, when a co-continuous phase structure exists in the sample at a certain additive concentration. The shrinkage control effect vanishes at the second transition, when severe particle fusion is observed in the sample because of too high an additive concentration. The effective additive concentration range does not change much for various thermoplastics, but the two transitions occur at different concentrations for each thermoplastic. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Unsaturated polyester resin; Low temperature cure; Phase separation; Shrinkage control

1. Introduction

The cure of unsaturated polyester (UP) resins is accompanied by a high degree of polymerization shrinkage (normally 7–10%). This shrinkage usually causes severe manufacturing problems, which include surface quality flaws such as surface waviness and sink-mark formation, and dimensional control problems such as part warpage and poor reproducibility of molding. An efficient way to eliminate/reduce the shrinkage is to introduce thermoplastics as "low profile" additives (LPAs) in the resin system.

The shrinkage control mechanism of thermoplastics-containing UP resins cured at high temperatures has been studied extensively [1–7]. The presence of thermoplastics helps to create a two-phase structure in the UP resin during curing, which is essential for shrinkage compensation [8–11]. It is generally agreed that thermal expansion during heating and microvoid formation during cooling contribute to the shrinkage control. When the resin is cured at low temperatures, there are far fewer temperature changes (heating or cooling), so the thermal induced shrinkage control often does not exist. In a previous article [12], the volumetric changes of a UP resin containing poly(vinyl acetate) (PVAc) cured at low temperatures were studied. It was found that volume expansion occurred in the late stage of cure for resins containing high molecular weight PVAc. This expansion compensated part of the polymerization shrinkage and reduced the final shrinkage substantially. When the volume expansion occurred, the sample appearance changed quickly from translucent to opaque. The measurements of the internal surface area of the cured samples and the results of the morphological investigation confirmed that the volume expansion and the change of opacity were caused by the formation of microvoids inside the sample.

In this study, we investigate the effect of different thermoplastics, their molecular weight and concentration, and different UP resins on the shrinkage control. The relationship between sample shrinkage and morphological changes is also studied.

2. Experimental

2.1. Materials

The resins used in this study are Q6585 from Ashland

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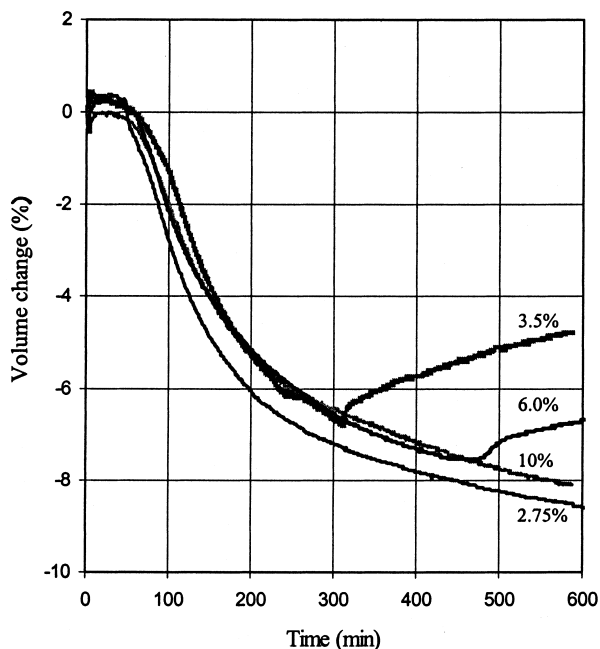
Fig. 1. The volume change vs. time plots of Resin A with different concentrations of PVAc-A curved at 35°C.

Chemical (referred to as Resin A) and Stypol 40-3961 from Cook Composites and Polymers (referred to as Resin B). Resin A is a 1:1 mixture of maleic anhydride and propylene glycol with an average 10.13 vinylene groups per molecule and an average molecular weight of 1580 g mol^{-1}, containing 35% by weight of styrene. Resin-B is a flexible resin constructed by ethylene glycol, propylene glycol, maleic
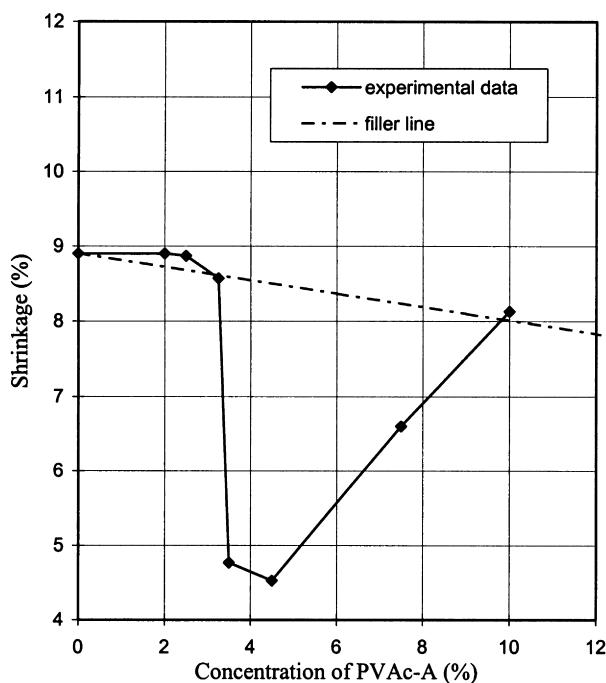
anhydride and isophthalic acid with an average 7.22 carbon–carbon double bonds per molecule and an average molecular weight of 1851 g mol^{-1}. The thermoplastic additives used are two poly(vinyl acetate) based polymers (named PVAc-A and PVAc-C) with different molecular weight ($M_w = 190\,000$ and $90\,000$ g mol^{-1}, respectively) from Union Carbide and a linear polyurethane (PU, LP8505, $M_w \approx 30\,000$) and a saturated polyester (Q8000, $M_w \approx 30\,000$) from Ashland Chemical. Both the UP and the thermoplastics were used as received without further purification.

In all formulations, the ratio between the resin double bond and the styrene double bond was adjusted to 2.0 by adding styrene. An amount of 1.5% methyl ethyl ketone peroxide (Aldrich Chemical) and 0.5% cobalt octoate (Pfaltz & Bauer) were used as the low temperature initiator and promoter. All formulations contained 300 ppm benzoquinone to retard the gelation in order to provide enough sample preparation time.

2.2. Instruments and procedures

2.2.1. Dilatometry

The volumetric shrinkage of the sample materials was measured by an in-house made dilatometer. The detailed construction and operation procedures can be found elsewhere [6,12]. The sample weight varied from 5 to 6 g. The measurements were taken under a pressure of 0.69 MPa (100 psi) and 35°C except for some cases.

2.2.2. Scanning electron microscopy

For the morphological measurement, a Philip XL-30 electron scanning microscope was used. The magnification in this study varied from 200 × to 10 000×. Samples cured in the dilatometry test were fractured and gold coated without etching. The fracture surfaces were observed.

3. Results and discussion

3.1. Resin A systems

3.1.1. Resins containing PVAcs

To investigate the detailed relationship between shrinkage control and sample morphology, a series of dilatometry experiments for Resin A with various amount of PVAc-A (0, 2.0, 2.75, 3.125, 3.5, 4.5, 6, 7.5, and 10 wt.%) were carried out. Fig. 1 presents the volume change profiles of several samples cured at 35°C and 0.69 MPa (100 psi). The volume expansion during curing was observed for the two samples with 3.5 and 6% PVAc-A, respectively. Fig. 2 summarizes the final shrinkage results as a function of PVAc-A concentration for this resin. The sample without thermoplastic additive has a final shrinkage of 8.92%. When the concentration level of the PVAc-A was low (i.e. less than 3.125%), the final shrinkage decreased slightly and the PVAc-A simply acted as a filler without any "low
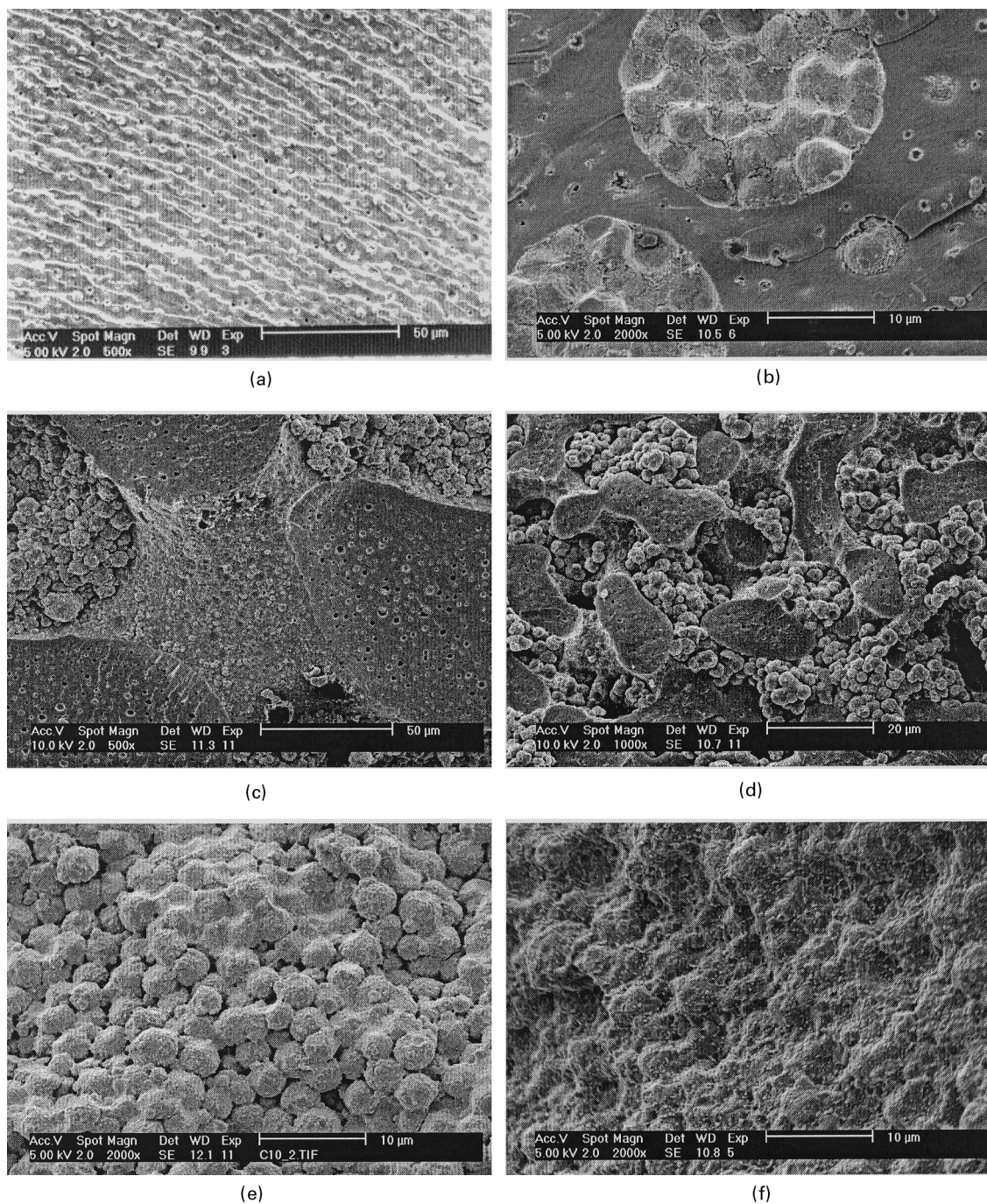

Fig. 2. The final shrinkage vs. the PVAc-A concentration for Resin A curved at 35°C.

Fig. 3. The SEM micrographs of Resin A with various amount of PVAc-A curved at 35°C: (a) 2.75%; (b) 3.125%; (c) 3.5% (first transition); (d) 4.5%; (e) 7.5%; (f) 10% (second transition).

profile" (i.e. shrinkage control) effect. At 3.5% PVAc-A, there was a large drop of final shrinkage, and the shrinkage decreased to 4.77%. The sample with 4.5% PVAc-A also achieved good shrinkage control (4.53%). However, when the PVAc-A concentration was further increased, the efficiency of shrinkage control decreased. At 10% PVAc level, the "low profile" effect totally disappeared.

Fig. 2 clearly demonstrates that there are an upper and a lower concentration limit for the thermoplastic to be effective for shrinkage control. The optimum thermoplastic concentration for the shrinkage compensation lies in the early part of this range. The appearance of the cured samples within this range is also quite different from those outside the range. The former is stark white (opaque), whereas the appearance of the latter is translucent.

The scanning electron microscopy (SEM) micrographs of the cured samples are shown in Fig. 3(a)–(f). With an increase of the PVAc-A concentration, the fracture surface
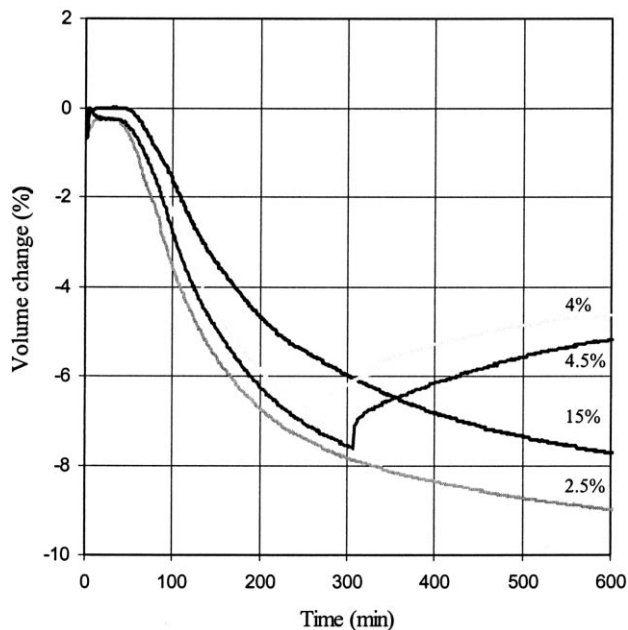
Fig. 4. The volume change vs. time plot of Resin A with different concentrations of the PVAc-C curved at 35°C.

morphology of the samples went through a series of transitions. The surface morphology of the sample without PVAc-A was found to be plain and flake-like. At low PVAc-A concentrations, such as 2.75%, a two-phase structure was found, as presented in Fig. 3(a). The dispersed phase consists of small droplets with diameters ranging from 2 to 4 μm. Inside the droplets, small particles with diameter
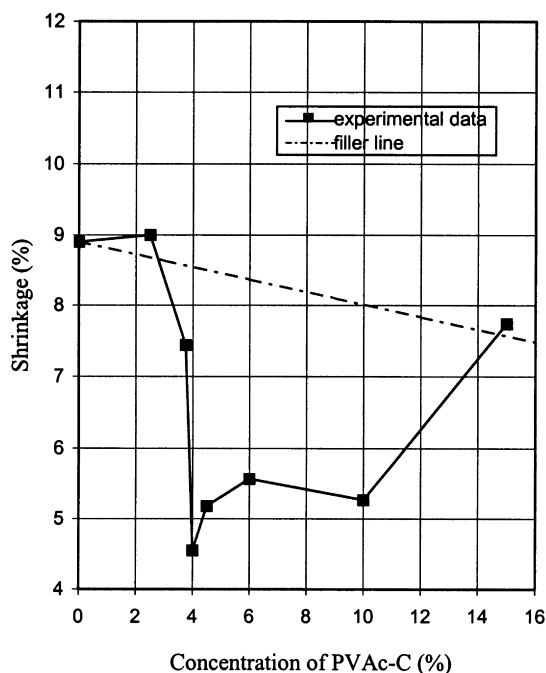

Fig. 5. The final shrinkage vs. the PVAc-concentration for Resin A curved at 35°C.

less than 1 μm were found tightly packed and coagulated. The droplets are LPA-rich, while the flake-like region is UP-rich.

Raising the PVAc-A concentration to 3.125% did not change the two-phase structure. However, a remarkable change of the droplet size and the size distribution was observed (Fig. 3(b)). The droplet diameter varied from 1 to 25 μm. Inside the large droplet, particles with diameter around 5 μm were clearly identified. These particles were constructed by smaller particles with size less than 1 μm, while being observed at a higher magnification. According to the work of Hsu et al. [11], the size of the primary polymers (microgels) formed in the cross-linking reaction between the UP pre-polymers and the styrene monomers is around 10 nm. Here, the size of the smallest particles is on the level of several hundred nanometers. Further increasing the PVAc-A concentration to 3.5%, a major structure change occurred. The LPA-rich phase (particulate) and the UP-rich phase (flake-like) became co-continuous, as presented in Fig. 3(c). Inside the flake-like region, small droplets were dispersed in the flake-like matrix, and the structure is virtually the same as that with 2.75% PVAc-A. The particulate area consists of loosely packed spherical particles with a wide range of size (diameters varied from 1 to 8 μm). The traces of microcrack can be clearly seen when the magnification is increased to 10 000×.

At the level of 4.5% PVAc-A, a similar two-phase structure was again observed, as described in Fig. 3(d). The difference is that the flake-like region became the dispersed phase, while the particulate region formed the continuous matrix. The structure of the sample with 6% PVAc-A is similar to that with 4.5% PVAc-A except that the size of the flake-like area is even smaller, and the size of the particles is more uniform.

When the PVAc-A concentration reached 7.5%, the morphology turned to be a uniform, particulate phase (Fig. 3(e)) with the size of spherical particles around 5 μm. Some particles observed were fused together, which indicates that the microcracks did not occur in those areas. Accordingly, the shrinkage control efficiency decreased. The surface morphology of the sample with 10% PVAc-A was single-phase, homogeneous and particulate-like (Fig. 3(f)). The fusion among the particles was very severe and the shrinkage control efficiency totally disappeared.

The dilatometry studies of the resins with a lower molecular weight PVAc (PVAc-C) were also carried out. The volume change profiles are presented in Fig. 4 and the final shrinkage results are summarized in Fig. 5. The two major transitions were also found for this resin-thermoplastic system. The decrease of the PVAc molecular weight shifted the effective thermoplastic concentration to a higher level and the effective shrinkage control region became broader. The resin with PVAc-C started to exhibit volume expansion at a concentration of 4%, and the shrinkage control effect remained at 10% PVAc-C. When the PVAc-C content reached 15%, the shrinkage control effect vanished
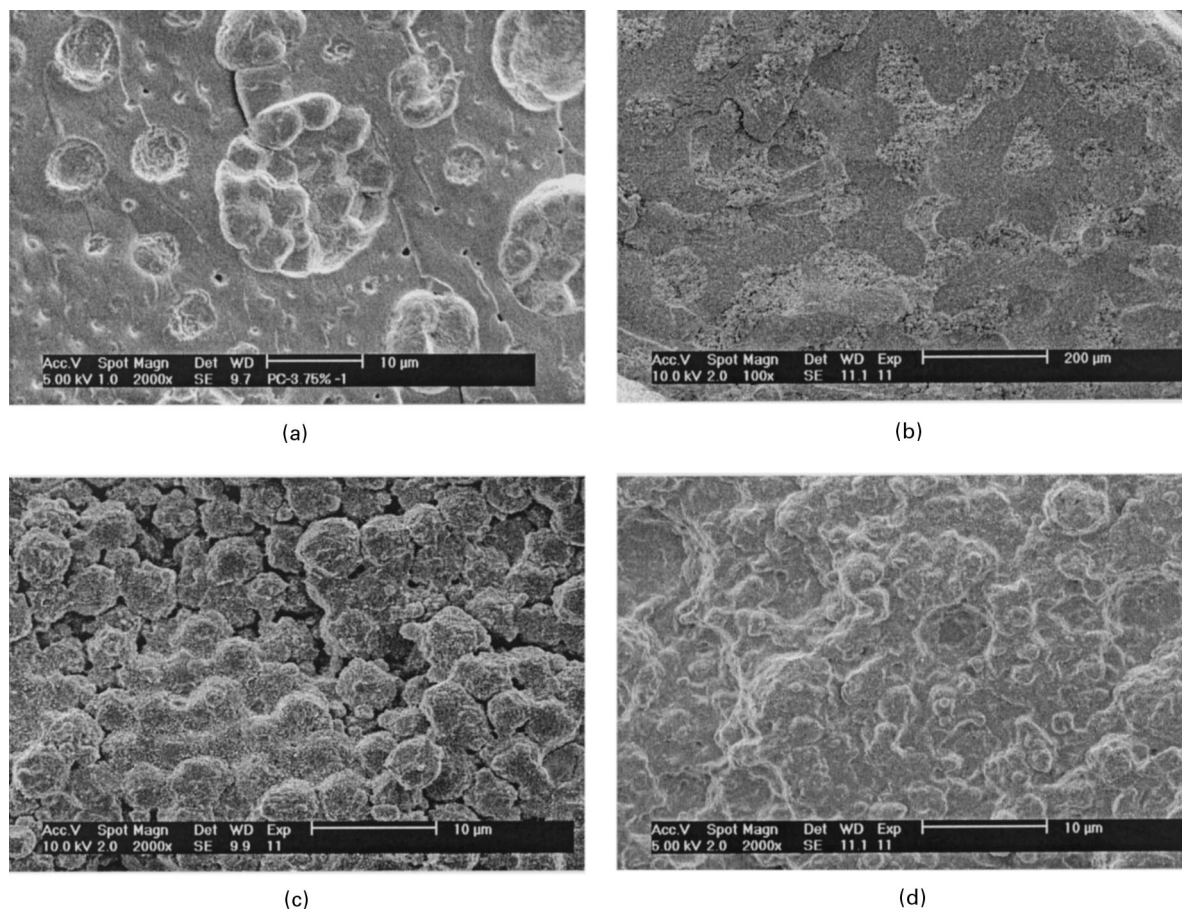
(a)

(b)

(c)

(d)

Fig. 6. The SEM micrographs of Resin A with various amount of PVAc-C cured at 35°C: (a) 3.75%; (b) 4.0% (first transition); (c) 10%; (d) 15% (second transition).
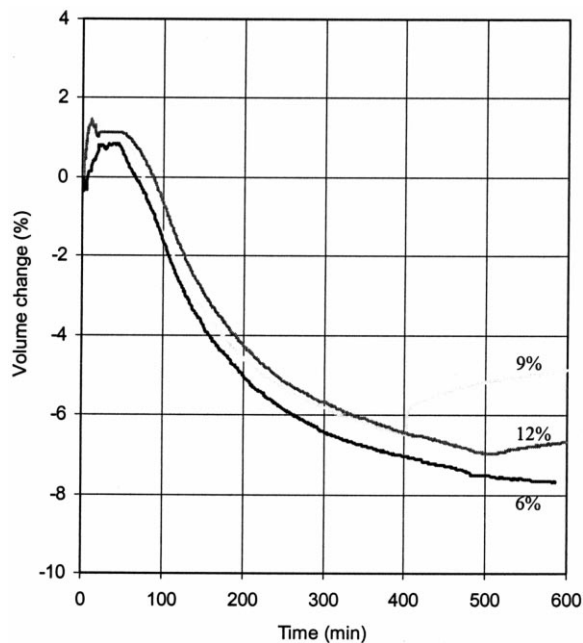

Fig. 7. The volume change vs. time plots of Resin A with different concentrations of saturated polyester cured at 35°C.

with a 7.7% final shrinkage, which matches the calculated value if PVAc-C is treated as a filler. The above results indicate that a higher molecular weight PVAc works more effectively at a lower concentration for the shrinkage control, while a lower molecular weight PVAc needs a higher concentration to be effective.

The morphological change of the fracture surface of the PVAc-C containing samples is virtually the same as that of the PVAc-A containing samples, as shown in Fig. 6(a)–(d). The transition from a dispersed two-phase structure to a co-continuous two-phase structure took place at 4% PVAc-C. A single-particulate phase structure formed at 10% PVAc-C. At 15% PVAc-C, a strong fusion among the particles was observed.

The above results reveal that increasing the thermoplastic concentration in the UP resin systems would cause changes of the sample morphology from flake-like to partially flake-like and partially particulate, and then to complete particulate structure. Comparing to the volume shrinkage results, there are two major transitions in the morphological change. The first transition is when the particulate structure turns from a dispersed phase to a co-continuous phase, which occurs at 3.5% level for PVAc-A and 4% level for PVAc-C. The second transition is the fusion of the well-defined
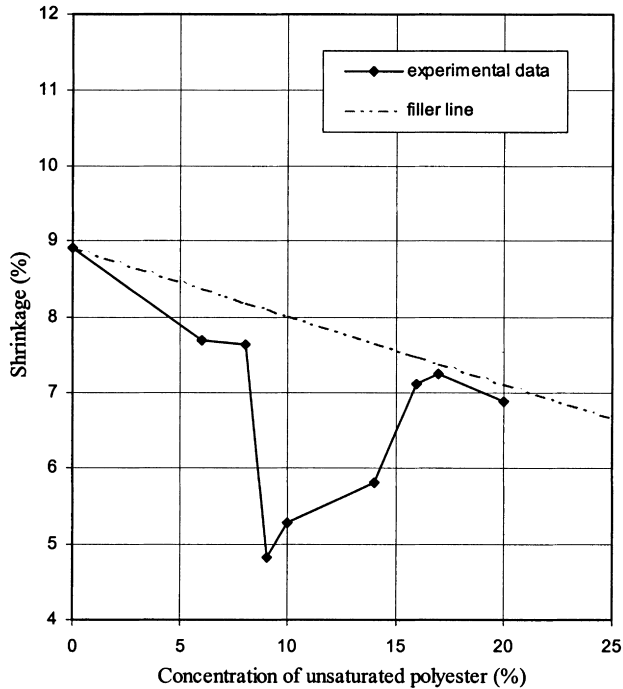
Fig. 8. The final shrinkage vs. the saturated polyester concentration for Resin A cured at 35°C.

particles at high PVAc concentrations (i.e. 10% level for PVAc-A and 15% level for PVAc-C). These two transitions match very well with the final shrinkage of the sample. In other words, the sudden exhibition of the "low profile" effect occurs at the first transition, which may be attributed to the occurrence of a structure change. A continuous (or co-continuous) particulate structure allows the formed micro-voids to cover the entire sample, which effectively reduce the sample shrinkage. The loss of the shrinkage control effect takes place at the second transition, which is due to the fusion of particles at high thermoplastic concentrations. A severe fusion of particles reduces the possibility of micro-void formation at the particle interface. Further investigations were conducted to verify these observations in resins containing other thermoplastics.

3.1.2. Resins containing saturated polyester and polyurethane

Other than PVAc, we also studied two well known LPAs, a saturated polyester and a linear PU. The dilatometry experiments of the same resin with different amount of saturated polyester were also carried out at 35°C and 0.69 MPa (100 psi). Fig. 7 gives the volume change profiles,
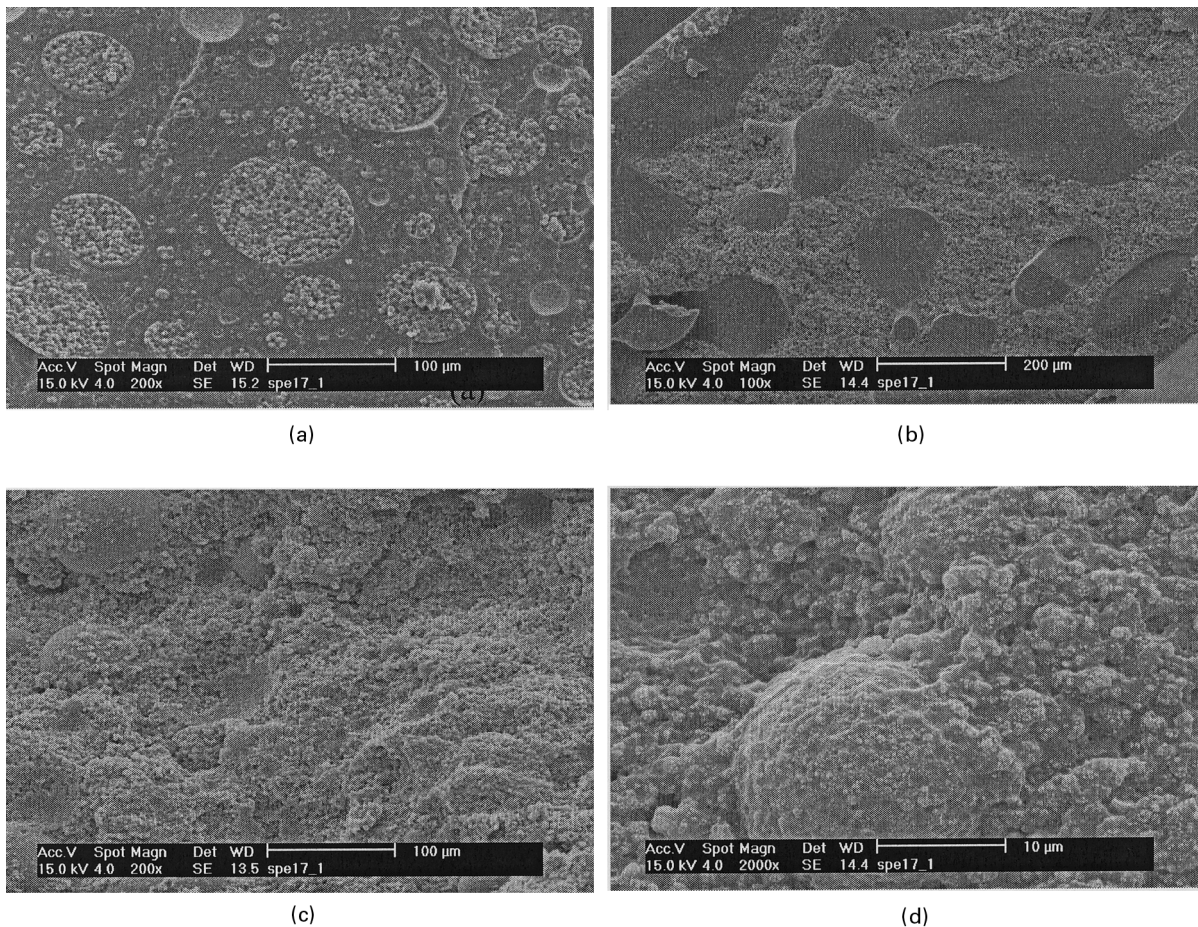

(a)

(b)

(c)

(d)

Fig. 9. The SEM micrographs of Resin A with various amounts of saturated polyester cured at 35°C: (a) 8%; (b) 9% (first transition); (c) 17% (second transition); (d) 20%.
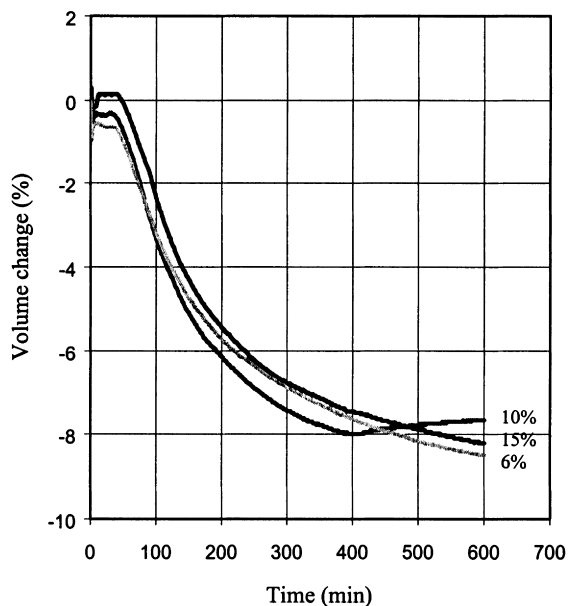
Fig. 10. The volume change vs. the time plots of samples with different concentrations of PU curved at 35°C.

which show the same pattern as those containing PVAcs. Fig. 8 illustrates the final shrinkage-thermoplastic concentration relationship of this system. The trend of the final shrinkage versus saturated polyester concentration is very similar to that of PVAc, except that the effective concentration range of saturated polyester is at a much higher level. The morphological change of the fracture surface of the saturated polyester containing samples is also very similar to that of the PVAc-containing samples (Fig. 9(a)–(d)).

Fig. 10 summarizes the percent volume change as a function of time of the resin with PU as thermoplastic additive.
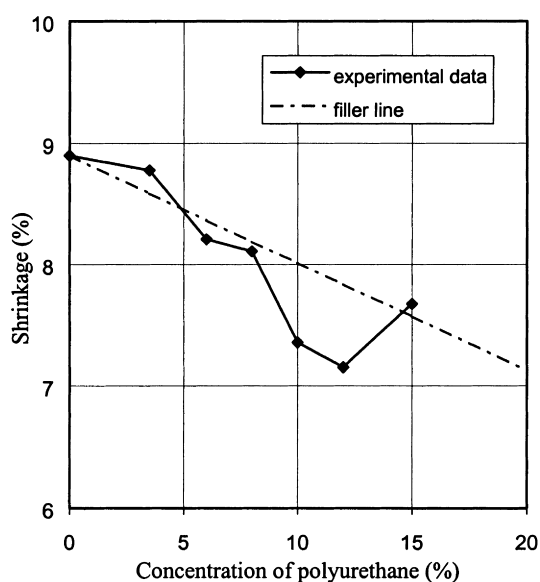

Fig. 11. The final shrinkage vs. the PU concentration for Resin A cured at 35°C.

At low PU concentrations, such as 3.5 and 6%, the PU-containing samples did not show any shrinkage control. The cured resins were translucent. At a level of 10% PU, a small volume expansion took place at about 418 min. The expansion caused 0.34% volume increase, and the specimen turned stark white. Further increasing the PU concentration to 15%, no expansion was observed. However, after the sample was stored at room temperature overnight, it turned stark white. Similar phenomenon was also observed for the resin with 10% PVAc-A in the previous experiment. These results suggest that the sample may be able to expand volumetrically and turn opaque after a longer time period at a lower temperature. The final shrinkage at 10 h (i.e. at the end of the dilatometry measurement) as a function of the PU concentration is presented in Fig. 11. The two transitions can be clearly identified at 9 and 15%. The morphology of the fracture surface of PU series was also observed by using SEM, and the trend is virtually the same as the other thermoplastics.

The above results indicate that the UP-styrene systems with different thermoplastics, including the PVAc, saturated polyester and linear PU, all show a certain degree of shrinkage control when cured at low temperatures. The effective concentration range of shrinkage control varies, depending on the thermoplastic type and its molecular weight. In general, the low molecular weight thermoplastics require a high concentration to be effective, while the high molecular weight thermoplastics would not function at high concentrations. The experimental results show that PVAcs work better in the low concentration range. PU does not work very well at low temperature cure.

The above study also demonstrates that all four resin-thermoplastic systems exhibit two transitions, in both volumetric and morphological changes, when the thermoplastic concentration varies. The two transition points are summarized in Table 1. The first transition occurs when a critical thermoplastic content is reached and the flake-like UP-rich phase and the particulate-like LPA-rich phase become co-continuous. This transition results in sudden volume expansion and significant shrinkage compensation. After the first transition, the particulate structure gradually dominates the sample morphology. With higher thermoplastic concentrations, the microscale phase separation in the particulate phase is enhanced. The size of the particle turns to be more uniform, as demonstrated in the SEM photos. The UP-rich regions finally vanish when the thermoplastic concentration is sufficiently high. However, further increase of the thermoplastic level starts to cause fusion among the particles and the microcrack is no long possible in those areas. The second transition is less clear than the first one. When the thermoplastic content continues to increase, the fusion among the particles gradually undermines the shrinkage control efficiency and eventually results in the disappearance of the shrinkage control effect. The thermoplastics are found to be effective only in the range between the two transitions.

Table 1
Summary of the effective concentration range of different resin-thermoplastic pairs

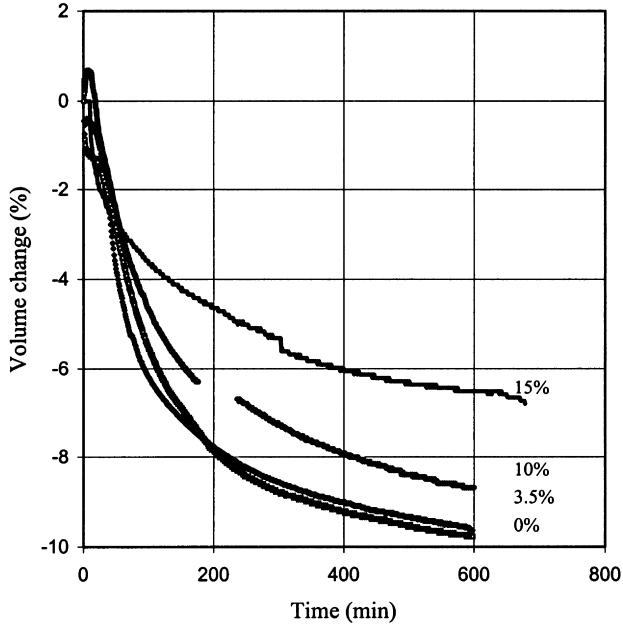| Resin A/thermoplastics	First transition point (%)	Second transition point (%)
PVAc-A high M.W. PVAc	3.5	10
PVAc-C low M.W. PVAc	4.0	15
Saturated polyester	9	17
PU	8	15

Fig. 12. The volume change profiles of Resin B with different amounts of PVAc-A cured at 35°C.
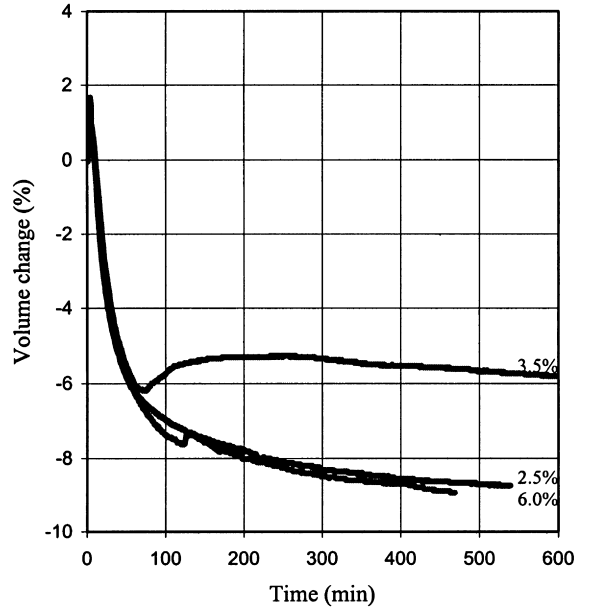

Fig. 14. The volume change profiles of Resin B with different amounts of PVAc-A cured at 55°C.
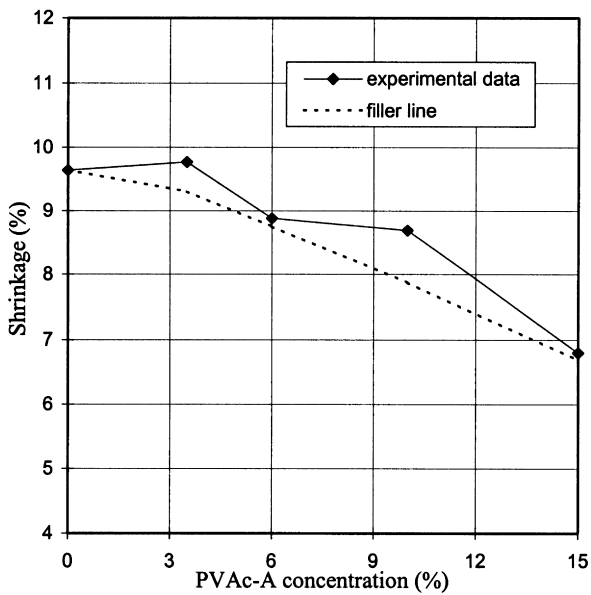

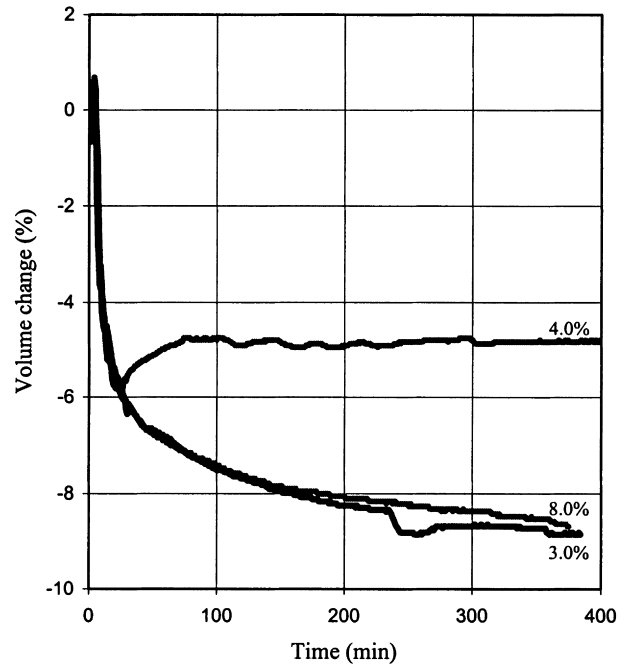Fig. 13. The final shrinkage vs. the PVAc-A concentration of Resin-B cured at 35°C.

Fig. 15. The volume change profiles of Resin B with different amounts of PVAc-A cured at 80°C.
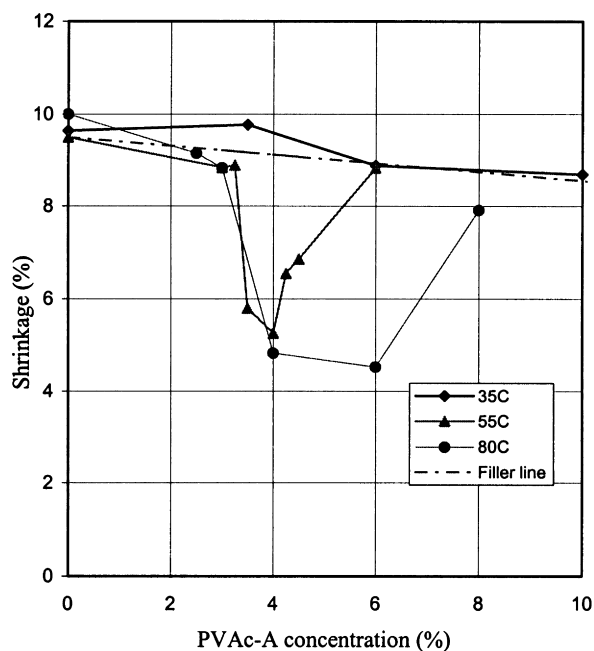
Fig. 16. The final shrinkage vs. the PVAc-A concentration for Resin-B cured at 35, 55 and 80°C, respectively.

3.2. Resin B systems

The UP resins are synthesized by using unsaturated and saturated diacids (or anhydride) and difunctional alcohols. The unsaturated carbon–carbon double bonds on the main chain come from the unsaturated diacids or anhydrides. By adjusting the content of unsaturated diacids, the degree of unsaturation, the reactivity of the resin, and the compatibility of the resin with styrene can be varied. The

pairing of the UP resin and the thermoplastics has been reported to be important for the optimum shrinkage control [2]. Generally, the LPA works well in the PG-MA type UP resins, whereas for the UP resins containing orthophthalic acid or isothphalic acid units, thermoplastics are less effective.

A series of dilatometry tests were conducted with various PVAc-A concentration at 35°C to investigate the shrinkage control behavior of PVAc-A with Resin B. Fig. 12 presents the volume change profile versus time during the curing process. At 35°C, the final shrinkage of Resin B without PVAc-A was found to be 9.64%. All the samples (with various amount of PVAc-A) exhibited different degrees of shrinkage, but followed the same shrinkage profile pattern. The volume expansion phenomenon, which was observed in Resin A/PVAc-A systems in the previous section, was not found in Resin B systems at the same cure temperature.

The final shrinkage data from the above tests were plotted versus PVAc-A concentration as shown in Fig. 13. The dashed line again represents the results if PVAc-A simply works as a filler with no shrinkage control effect. As revealed in Fig. 13, in the range of 0 to 15% PVAc-A, the experimental data follow closely the filler line, suggesting that the PVAc-A is totally ineffective under this curing condition. All cured samples appeared to be translucent, indicating that there is no microvoid inside the sample.

Similar experiments were carried out at a higher temperature, i.e. 55°C. Fig. 14 demonstrates the volume change profiles of samples with 2.5, 3.5 and 6% PVAc-A cured at this temperature, respectively. In the first 60 min, the volumes of the three samples decreased much faster than the sample cured at 35°C, and followed the same route. At 2.5% PVAc-A level, no volume expansion was observed
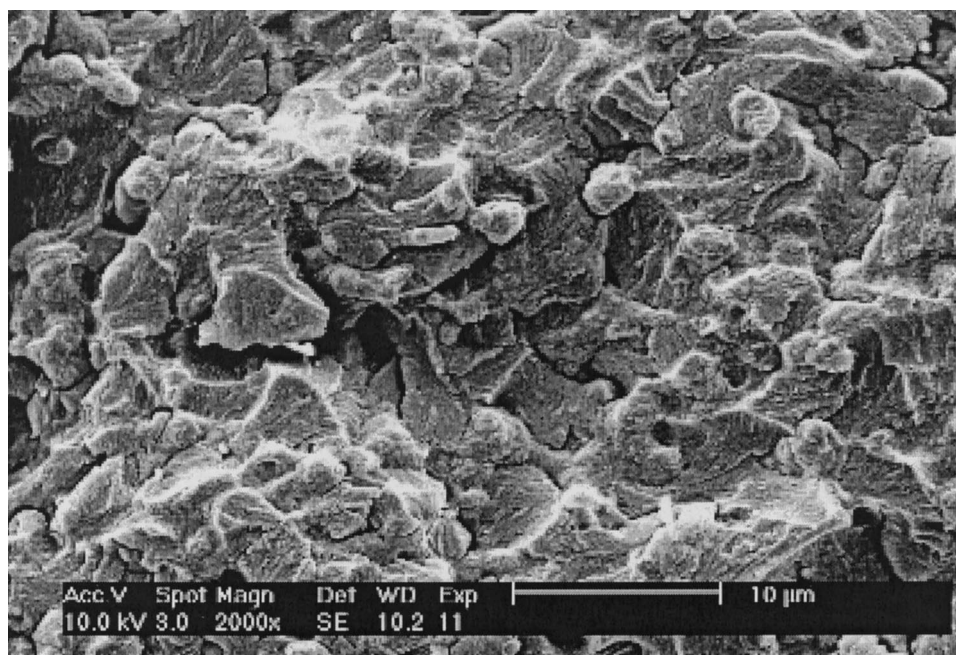

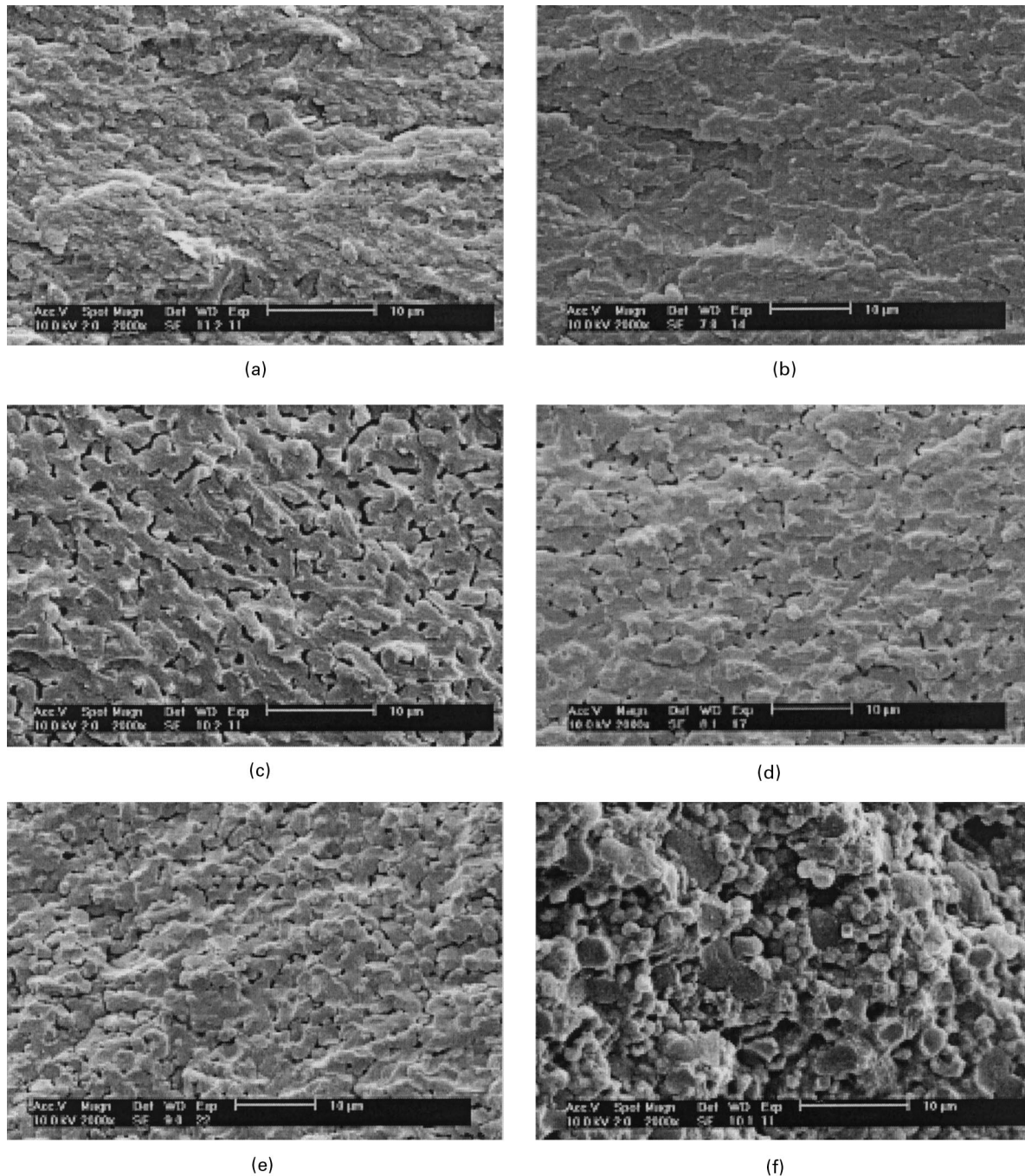Fig. 17. The SEM micrographs of Resin B with 3.5% PVAc-A cured at 35°C.

Fig. 18. The SEM micrographs of Resin B with different amounts of PVAc-A cured at 55°C: (a) 2.5%; (b) 3.25%; (c) 3.5%; (d) 4.25%; (e) 4.5%; (f) 6%.

and the sample shrank continuously with the reaction. Increasing the PVAc-A content to 3.5%, an expansion was noticed around 65 min, followed by a plateau region. The sample volume slightly decreased after the plateau, reaching a final shrinkage of 5.8%. This final shrinkage is substantially lower than that of 2.5% PVAc-A sample. Further increasing PVAc-A concentration to 6% PVAc-A level, the expansion vanished.

The pattern of shrinkage profile of samples cured at 80°C was virtually the same as that cured at 55°C, as shown in

Fig. 15. At 3% PVAc-A level, there was no volume expansion. However, at 4% PVAc-A level, expansion was observed around 26 min. The difference of the final shrinkage between the two samples was significant, i.e. 4.06%. Again, a further increase in the PVAc-A content (i.e. 8%) led to the disappearance of the volume expansion. The volume expansion occurred earlier at a higher cure temperature.

The final shrinkage data obtained from the 55 and 80°C tests are plotted versus PVAc-A concentration as shown in
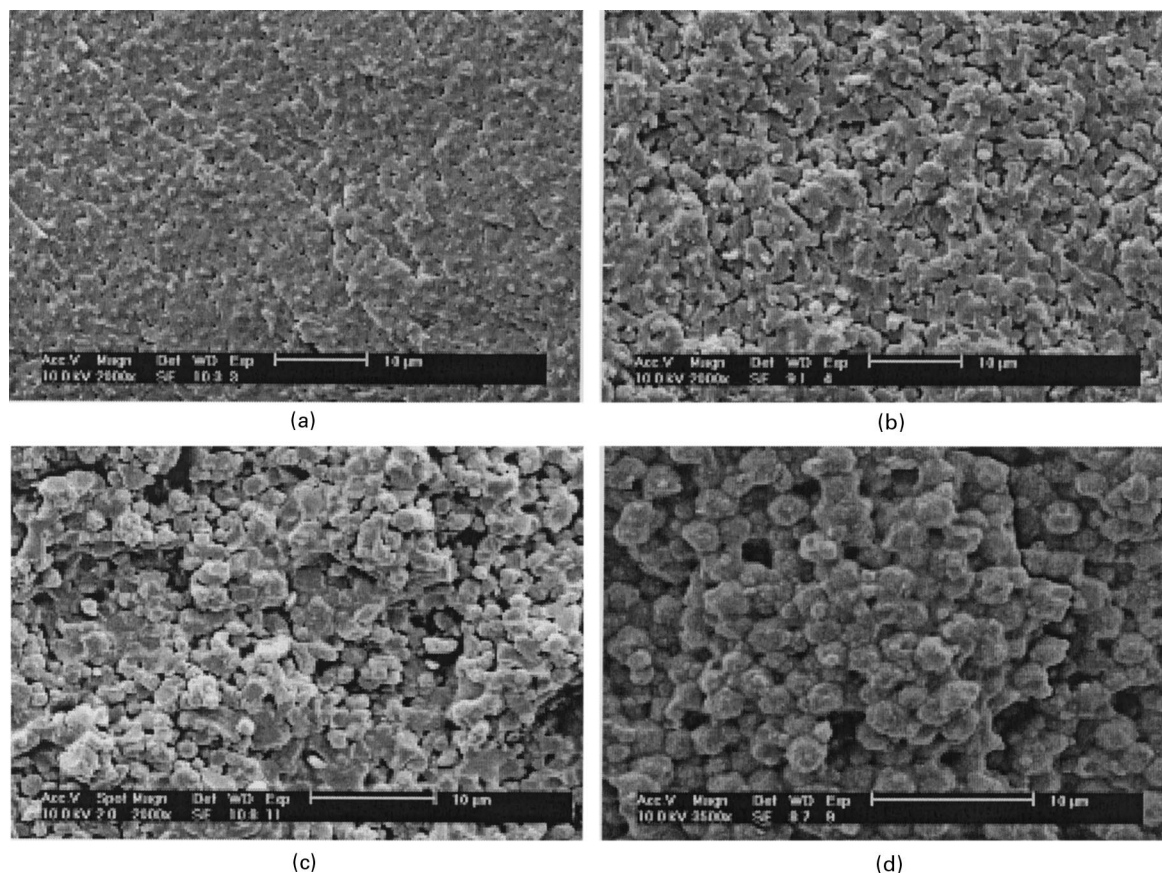
Fig. 19. The SEM micrographs of Resin B with different amounts of PVAc-A cured at 80°C: (a) 3%; (b) 4%; (c) 6%; (d) 8%.

Fig. 16. Similar to Resin A, two transitions are found at both temperatures. At 55°C, the two transitions are 3.5 and 6%, respectively, implying a fairly narrow shrinkage control effective range. At 80°C, the shrinkage control effective range is much wider, starting at 4% and ending at 8%. It is noted again that the final appearance of the sample inside the effective range is opaque, whereas it is translucent outside the range. This supports that microvoid formation is the main source of volume expansion. The results also demonstrate that, even though the two transitions exist in the Resin B system, the effective shrinkage control range is narrower in comparison with Resin A, and the shrinkage compensation is less efficient.

The final morphology of the samples cured in the dilatometry test was observed under SEM. Fig. 17 depicts the fracture surface of the sample containing 3.5% PVAc-A cured at 35°C. The microstructure was different from the particulate structure observed in the Resin A system. The change of the PVAc-A concentration did not alter the sample morphology significantly. No trace of the microcrack was noticed.

Samples cured at 55°C with different PVAc-A concentrations were also examined. At 2.5% PVAc-A level, a flake-like morphology was obtained (Fig. 18(a)). A branch-like structure was found at 3.25% level in Fig. 18(b). When the PVAc-A concentration reached 3.5% (the first transition

point), a uniform branch structure covered the entire sample surface. The length of the branch was around 3–4 μm. The cracks among the branches can be clearly identified (Fig. 18(c)), which agrees well with the dilatometry results. Further increasing the PVAc-A concentration to 4.25%, the branch structure was again observed, but became less clear (Fig. 18(d)). At 4.5% level, the structure changed to be more particulate-like (Fig. 18(e)). Compared with the Resin A/PVAc-A system, the particle is much smaller. Increasing PVAc-A amount to 6%, a clear particular structure similar to the Resin A system was obtained (Fig. 18(f)). However, the particles were found coagulated and fused together, which explained why the shrinkage control effect vanished at this percentage.

The microstructure of samples cured at 80°C shows the same pattern as that of the samples cured at 55°C (Fig. 19). For the sample showing no shrinkage control effect, i.e. 3%, the fracture surface was flake-like (translucent), as demonstrated in Fig. 19(a). An increase in the amount of PVAc-A to 4% resulted in a significant change, where a clear interconnected branch-like structure with large amount of microvoids was observed (Fig. 19(b)). A particulate morphology with fusion among particles was seen once the PVAc-A concentration was raised to 6 and 8% (Fig. 19(c)and (d)). The shrinkage control effect disappeared after these percentages.

In comparison with Resin A/PVAc-A system, the morphological transitions of Resin B/PVAc-A systems are less obvious. Nevertheless, the change of thermoplastic concentration results in a similar change of the microstructure. Microvoids are only observed when a critical thermoplastic percentage is reached, and the disappearance of the shrinkage control effect is again due to the fusion among the particles. High thermoplastic concentrations favor the formation of the particulate structure, however, the particulate structure is not a necessary requirement for microvoid formation, as at low temperatures (i.e. 35°C).

4. Conclusion

The study of the effect of thermoplastic type and concentration, and resin structure on shrinkage control suggests that there are two transitions for UP resins with thermoplastic additives cured at low temperatures. The thermoplastics are effective for shrinkage control only in the concentration range between the two transitions. The range depends on the thermoplastic type and its molecular weight. Similar results were observed in the two resin systems. The experimental results demonstrate that there is a close relationship between the microstructure and the microvoid formation. Further investigation of the microstructure formation is given in Part II [13].

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