Polymer Vol. 39 No. 23, pp. 5677–5687, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(98)00074-3

Shrinkage control of low-profile unsaturated polyester resins cured at low temperature

Wen Li and L. James Lee*
Department of Chemical Engineering, The Ohio State University,
Columbus, OH 43210, USA
(Received 26 February 1997; revised 4 December 1997; accepted 16 January 1998)

With the development of new manufacturing processes, such as low-pressure compression moulding of sheet moulding compound (SMC), resin transfer moulding (RTM) and vacuum infusion liquid composite moulding (e.g. SCRIMP) processes, low-shrinkage moulding compounds which can be processed at low temperatures have attracted considerable interest from the composite industry. In this paper, an integrated rheology–kinetics–morphology–dilatometry study on an unsaturated polyester resin (UPE) mixed with different low-profile additives (LPAs) was carried out to investigate the shrinkage control mechanism of LPA under low-temperature cure. The reaction rate was determined by a differential scanning calorimeter, while a scanning electron microscope and a Rheometrics dynamic analyser were employed to follow the morphological and rheological changes respectively. The volume change of the resin mixture during the curing process was measured by a dilatometer. It was found that the shrinkage behaviour of the resin mixture strongly depends on the competition of the shrinkage induced by the resin polymerization and the expansion induced by microvoid formation. The results also showed that LPAs with higher molecular weight and lower LPA content seem to work better under low-temperature cure. Several moulding experiments were conducted to verify the dilatometry results. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: unsaturated polyester resin; low-profile additive; shrinkage control)

INTRODUCTION

Low-profile additives (LPAs) are thermoplastic materials that generally serve as non-reactive additives in unsaturated polyester (UPE) and vinyl ester resins. They are initially soluble or form a stable dispersion in the styrene and resin mixture before cure, but become incompatible with the cured resin during the curing process. Common LPAs include poly(vinyl acetate), poly(methyl methacrylate), thermoplastic polyurethanes and polyesters. LPA has been found to be highly effective in eliminating the polymerization shrinkage of UPE resins in high-temperature moulding processes such as compression moulding of sheet moulding compounds (SMCs) and injection moulding of bulk moulding compounds (BMCs).

The effects of LPA type, molecular weight and concentration on resin shrinkage, surface quality and dimensional control of moulded polymer composites have been studied by many researchers[1–4]. The effects of cure conditions on LPA behaviour, including temperature, pressure and thermal history, have also been investigated[5–7]. Most studies of LPA mechanism focused on the curing at high temperatures, since LPAs found most of their applications in high-temperature and high-pressure processes. Although the detailed high-temperature LPA mechanism is still a subject of controversy, it is now generally agreed that the most important features for LPA to work in high-temperature processes are thermal expansion, phase separation and inversion between LPA and cured UPE resin, and microvoid formation along the interface or inside the LPA phase[2,3,8–11]. During moulding, the compound is first heated to the mould temperature. The resin and LPA would thermally expand in this stage. The free-radical copolymerization of UPE molecules and styrene monomers is initiated by the decomposition of initiators. The increase in molecular weight and the change in polarity of the reacting UPE resins cause the once homogeneous system to become locally heterogeneous. The reacting UPE tends to phase out and a second phase is formed. The thermal expansion of unreactive LPA partially compensates the polymerization shrinkage. As the curing process goes on, a phase inversion would occur where the increasing amount of reacted UPE becomes the continuous phase and the LPA is forced to a discrete phase (in some cases, a co-continuous phase structure may form). The LPA-rich phase contains mostly LPA and styrene with some unreacted UPE resin. As the polymerizing material continues to shrink, the stress between the two phases is induced. Microvoids may form at the interface or throughout the LPA-rich phase. The stress is relieved and polymerization shrinkage compensated. More microvoids may form during demoulding and cooling to compensate the thermal shrinkage.

Recently, because of the growing interest of new manufacturing processes, such as low-pressure/low-temperature SMC moulding, resin transfer moulding (RTM) and vacuum infusion liquid composite moulding like Seemann composites resin infusion moulding process (SCRIMP), low-shrinkage moulding compounds with the ability to be processed at low temperature and low pressure have attracted considerable interest from the composite industry. Therefore, further understanding of the low profile mechanism at low temperature is important.

Since the resin thermal histories in the high-temperature processes such as SMC compression moulding and in the

---

* To whom correspondence should be addressed

low-temperature processes such as SCRIMP are totally different, the performance of LPAs may vary from process to process. In a typical SMC processing, the compound is first heated from room temperature to the mould temperature, which is typically 150°C. Then, there is a strong reaction exotherm, which will further increase the compound temperature to possibly 200°C. The temperature decreases after the exothermic peak. Finally, the moulded part is cooled down during demoulding. Therefore, there is a large temperature variation during moulding. Correspondingly, the volume change of the moulded material during moulding can be divided into three stages: thermal expansion during heating, polymerization shrinkage and thermal expansion/contraction during curing, and further thermal contraction during demoulding and cooling. To achieve the maximum shrinkage control in SMC processing, a large thermal expansion of the LPA during heating and reaction and microvoid formation during cooling are essential. In contrast, SCRIMP is conducted at room temperature. There is little temperature variation during curing and the curing cycle is usually long. Obviously, thermal expansion of LPA can no longer be counted for in this low-temperature moulding process.

The objective of this study is to determine LPA performance and to provide a better understanding of the low-profile mechanism at low-temperature cure.

EXPERIMENTAL

Materials

The unsaturated polyester (UPE) resin used in this study is Q6585 from Ashland Chemical, which 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. The low-profile additives used are three poly(vinyl acetate)-based thermoplastics (LPA-A, LPA-B and LPA-C) with different molecular weights (M_w = 190 000, 160 000 and 90 000 g mol^{-1}, respectively) from Union Carbide.

All the samples being tested were formulated to provide a styrene (St) double bond to UPE double bond ratio of 2.0. The initiator used was 1.5% methyl ethyl ketone peroxide (MEKP) with 0.5% cobalt octoate. The compositions and cure conditions are listed in *Table 1*. *Figure 1* shows the ternary phase diagrams of UPE/LPA/St, which were obtained by observing the cloud point when various amounts of styrene were added to the mixture at a constant temperature (35°C). The three LPAs shared a similar phase diagram.

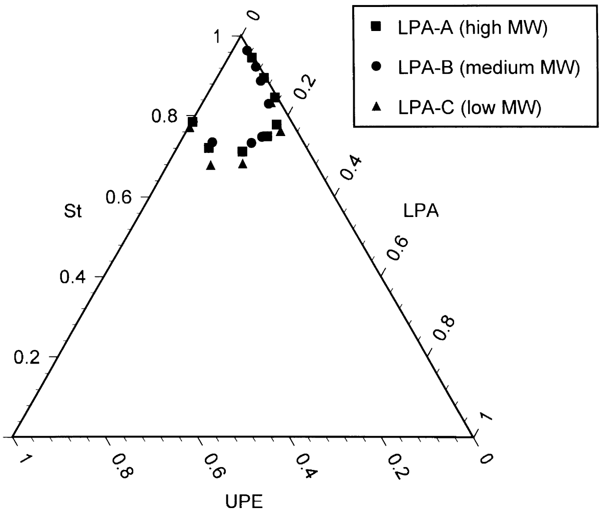

Figure 1 Phase diagram of styrene–UPE–LPA ternary systems

Instrumentation and procedures

In the rheological measurements, a Rheometrics Dynamic Analyzer-700 (RDA) in the oscillatory mode was employed to test the viscosity change during reaction. The frequency used was 1 rad s^{-1} and the strain was set at 10%.

A differential scanning calorimeter (d.s.c., DSC2910, TA Instruments) was used to measure the reaction kinetics. The sample was sealed in a volatile aluminium sample pan which may withstand 2 atm internal pressure. Isothermal runs were followed by scanning the cured sample from room temperature to 250°C to determine the residual heat with a heating rate of 10°C/min. The scanning run was then repeated to obtain the baseline.

Sample volume change during reaction was measured at 0.69 MPa by a dilatometer developed earlier in our laboratory. The sample was sealed in a polyethylene pouch, then degassed under vacuum. A small hole was poked at the edge of the pouch, and air bubbles inside the pouch, formed under vacuum, were squeezed out. The pouch was heat-sealed again, and placed inside the sample chamber of the dilatometer. The sample chamber contained

Table 1 Formulations used in this study (based on weight)

Material/conditions	1	2	3	4	5	6	7
	3.5% LPA-A	3.5% LPA-B	3.5% LPA-C	6% LPA-A	10% LPA-A	3.5% LPA-A	3.5% LPA-A
Q6585	63.63	63.64	63.64	61.98	59.34	63.63	63.63
LPA-A	9.46	–	–	16.22	27.03	9.46	9.46
LPA-B	–	8.75	–	–	–	–	–
LPA-C	–	–	8.75	–	–	–	–
Styrene	26.91	27.61	27.61	21.80	13.63	26.91	26.91
MEKP	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Cobalt octoate	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Benzoquinone	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Temperature (°C)	35	35	35	35	35	55	80
Pressure (psi)	100	100	100	100	100	100	100

both the sample pouch and the encapsulating fluid (Dow Corning 200 fluid, 500 cst). First, the cure heating cycle was performed on the fresh sample, and then the same heating cycle was repeated on the cured sample to determine the thermal response of both the cured sample and the dilatometer. The percentage volume change due to the polymerization shrinkage was determined by subtracting the second curve from the cure curve, counting for the sample volume and also the dilatometer geometry. More details regarding the dilatometer design and operation can be found elsewhere[6].

The sample cured in the dilatometer, without etching by any solvent, was gold-coated for morphological measurements. The scanning electron microscope used was Hitachi S-510 with 25 kV power.

Samples cured in the dilatometer were also subjected to the BET internal surface area measurement[7] using a Micromeritics 2100E Accusor system. Krypton was used as the absorbate, and the sample was outgassed around 35°C for at least 72 h before the surface area measurement was performed.

RESULTS AND DISCUSSION

Rheology and kinetics

Although the addition of LPA may significantly influence the volume change and microstructure of the UPE resin, its effect on kinetic and rheological changes appeared to be minor. The effect of LPA molecular weight on gel time is small as shown in *Figure 2a*. The increase of LPA concentration slightly delayed the gelation, as shown in *Figure 2b*. *Figure 2c* shows that the increase of temperature shortened the gel time as expected.

As shown in *Figure 3a*, the molecular weight of LPA seemed to have no influence on the conversion profile. An increase of LPA concentration slightly decreased the final conversion, according to the data in *Figure 3b*. *Figure 3c* shows the temperature effect on reaction. Final conversion increased as the temperature was increased, as expected. For all the samples, the gel conversion was less than 5%.

Dilatometry

Effect of LPA molecular weight. *Figure 4* is a plot comparing the percentage volume change *versus* time for the UPE resin with different LPAs (3.5%) cured at 35°C. For all the cases, the samples showed slight expansion when heated to 35°C, followed by a sharp polymerization shrinkage. The shrinkage curves in these two regions showed only slight differences, probably due to their similar reaction kinetics, as shown in *Figure 3a*.

The differences between the three samples showed at the later stage of cure. At 314 min, the sample with 3.5% highest molecular weight LPA (i.e. LPA-A) exhibited an expansion, which continued until the end of the cure. The sample with 3.5% LPA-B behaved in a similar way, except

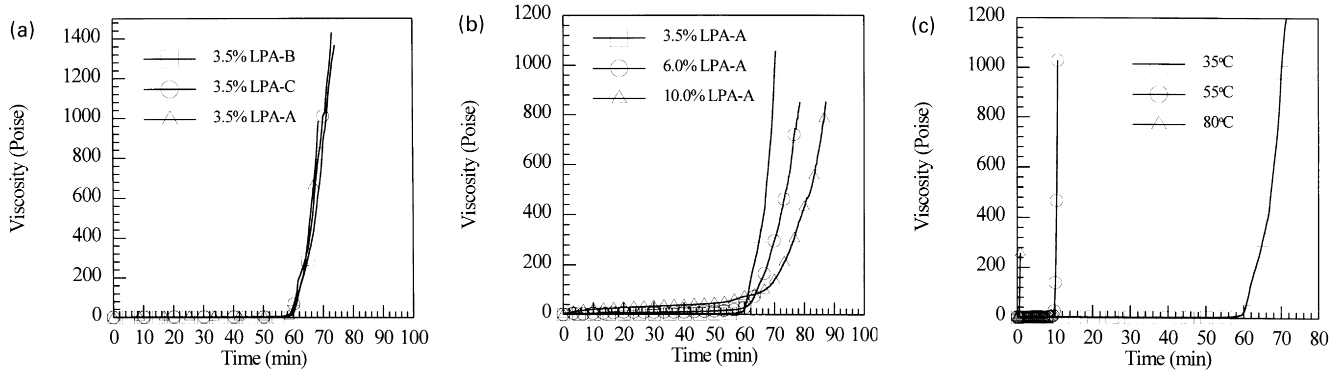

Figure 2 Viscosity *versus* time data obtained from RDA measurements: (a) samples with different LPAs cured at 35°C; (b) samples with various LPA concentrations cured at 35°C; (c) temperature effect on the sample with 3.5% LPA-A

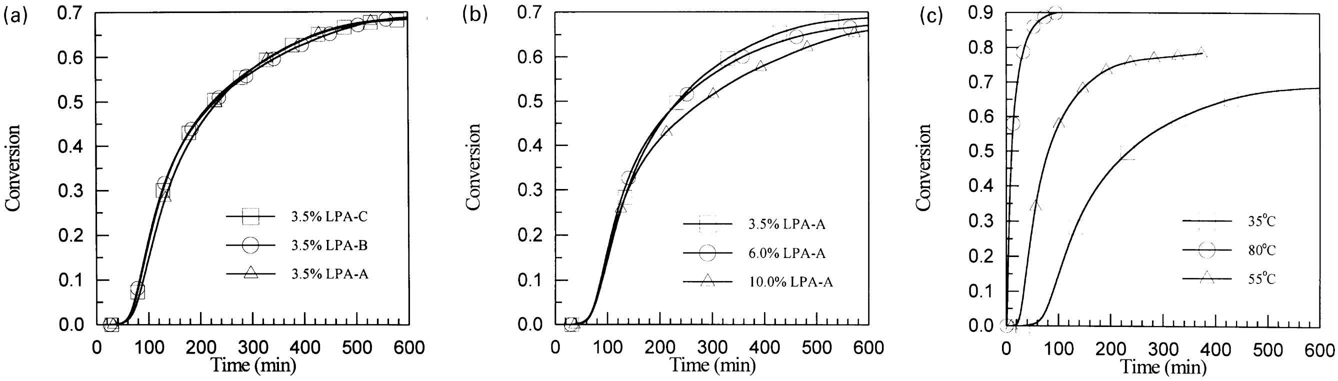

Figure 3 Conversion *versus* time data obtained from d.s.c. measurements: (a) samples with different LPAs cured at 35°C; (b) samples with various LPA concentrations cured at 35°C; (c) temperature effect on the sample with 3.5% LPA-A

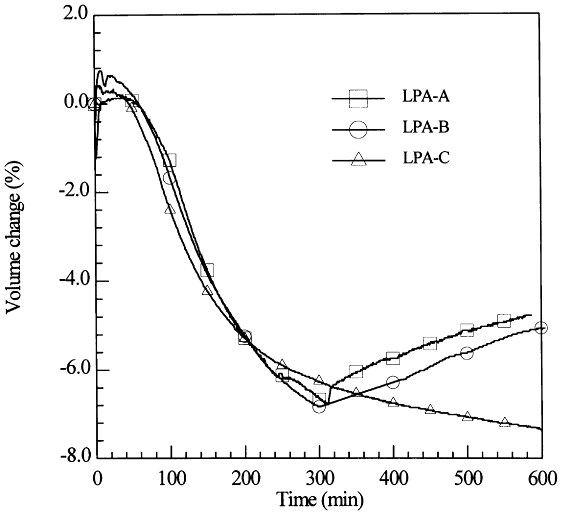

Figure 4 Comparison of volume change *versus* time of samples with different LPAs (3.5%) cured at 35°C

that the shrinkage control performance was slightly worse than that of 3.5% LPA-A. No expansion was observed for the sample with 3.5% LPA-C, and this sample had the highest shrinkage. At the point when the expansion started, the gelation has long been reached. Here, the conversions of the sample with LPA-A and LPA-B were 59 and 58%, respectively. Compared with the final conversion of 69% for both samples, the major observation for the first 58–59% conversion increase was shrinkage, while for the second half of the experiments, expansion was observed with only about 10% conversion difference. The sample appearance was also quite different for the three samples. The two cured samples with the expansion were stark white (opaque) in appearance and the one without expansion was translucent. Thus, we may conclude that good low-profile performance corresponds to the stark white appearance.

To further investigate the relationship between shrinkage control and sample opacity, the dilatometry test of the sample with 3.5% LPA-A was repeated. Here, the metal lower part of the dilatometer was replaced by a transparent part made by Plexiglas. The opacity change of the sample during cure was observed and videotaped. Three stages of

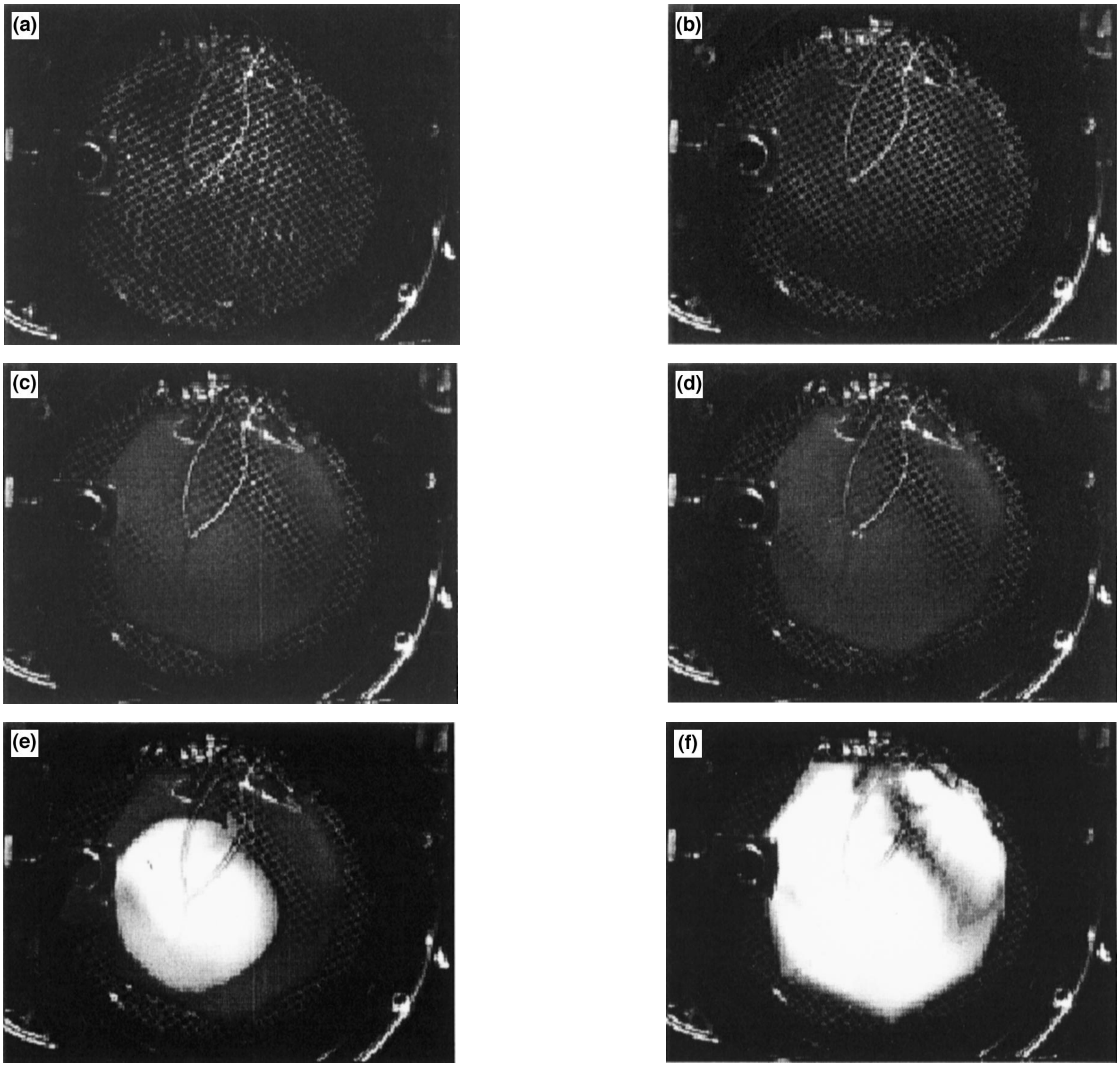

Figure 5 Change in opacity during curing of 3.5% LPA-A sample at 35°C: (a) 0 min; (b) 51.67 min; (c); 272.1 min; (d) 314 min; (e) 314.15 min; (f) 314.33 min

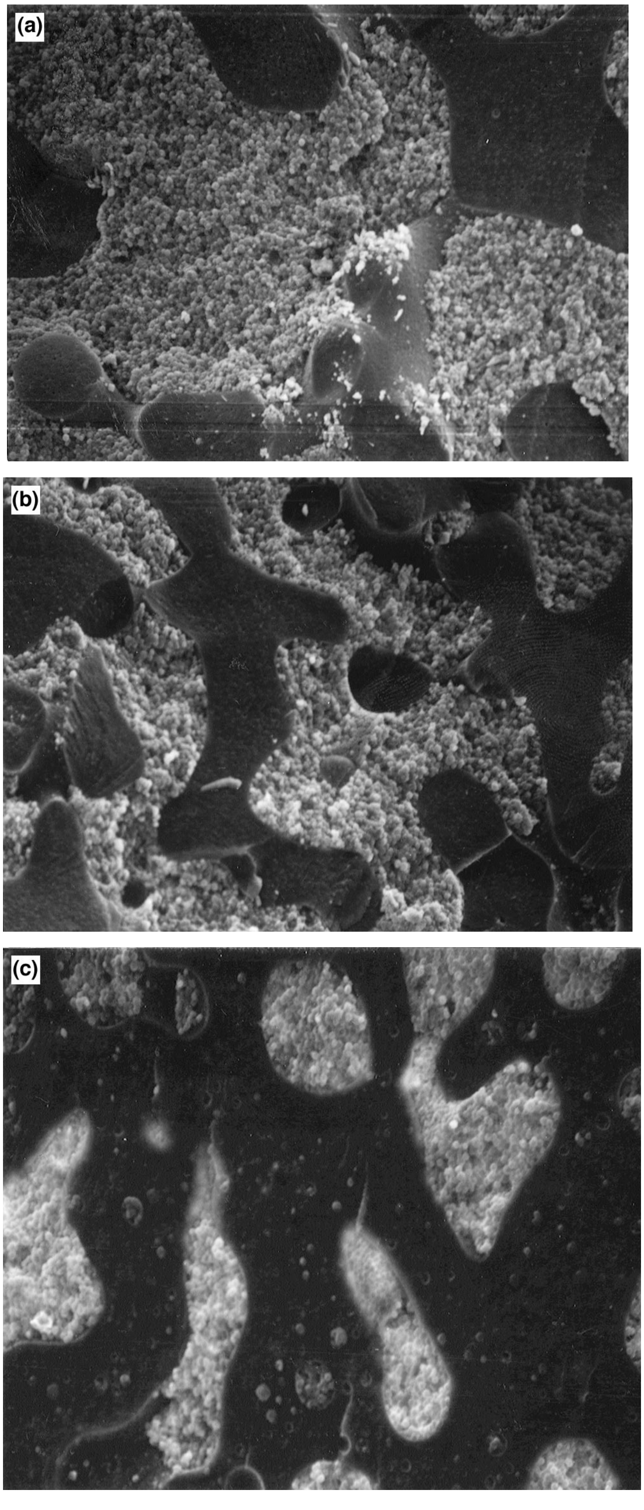

Figure 6 Scanning electron micrographs of UPE resins with different LPAs (3.5%) cured at 35°C: (a) LPA-A; (b) LPA-B; (c) LPA-C

opacity change were found during reaction: transparent in the beginning, turning translucent during the shrinkage period, and turning opaque when the second expansion occurred. In the first stage, the sample was transparent. Therefore, it was invisible in *Figure 5a*, suggesting that the UPE resin was compatible with LPA and styrene. *Figure 5b* and *Figure 5c* correspond to the second stage. In this stage, the copolymerization of UPE molecule and styrene monomer was initiated. The sample became more and more translucent. At the beginning of the third stage (t = 314 min), which was exactly the point when the expansion started, the sample turned opaque. As recorded by the videotape, a white spot first emerged at the centre of the sample, and then in less than 30 s, it grew and covered the whole sample (*Figure 5d–f*). The volume jump measured by the dilatometer matched very well with such morphological changes. The opacity increased as the expansion continued. It is believed the whitening is caused by the formation of microvoids inside the sample.

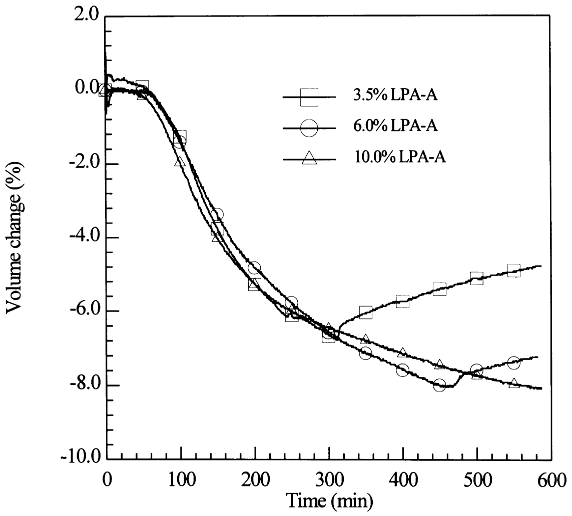

Figure 7 Comparison of volume change *versus* time of samples with various LPA concentrations cured at 35°C

The scanning electron microphotographs in *Figure 6* show the final morphology of the three samples. For all three samples, a coexistence of two distinct regions, a flake-like region and a particulate region, were found. According to the literature, the flake-like structure corresponds to a highly concentrated UPE region. The particulate region, on the other hand, is a co-continuous structure formed by UPE and LPA. The scanning electron micrograph of the sample with 3.5% LPA-B, as shown in *Figure 6b*, is similar to that of LPA-A (*Figure 6a*), except that the area of the particulate region is smaller in the latter. For the sample with LPA-C, *Figure 6c* shows that the particulate phase formed a dispersed region, while the UPE network formed the continuous matrix. This probably explained why LPA-C had relatively poor shrinkage control, since the LPA effective area was much smaller.

As mentioned earlier, microvoid formation may play an important role in LPA shrinkage control. Opacity measurement and scanning electron microscopy morphological measurement cannot provide quantitative information about the microvoid formed inside the sample.

Table 2 Summary of BET surface measurements

	Sample						
	1	2	3	4	5	6	7
Surface area ($m^2\ g^{-1}$)	0.43	0.23	0.05	0.42	0.36	0.32	0.42
Sample appearance	Opaque	Opaque	Translucent	Opaque	Opaque	Opaque	Opaque

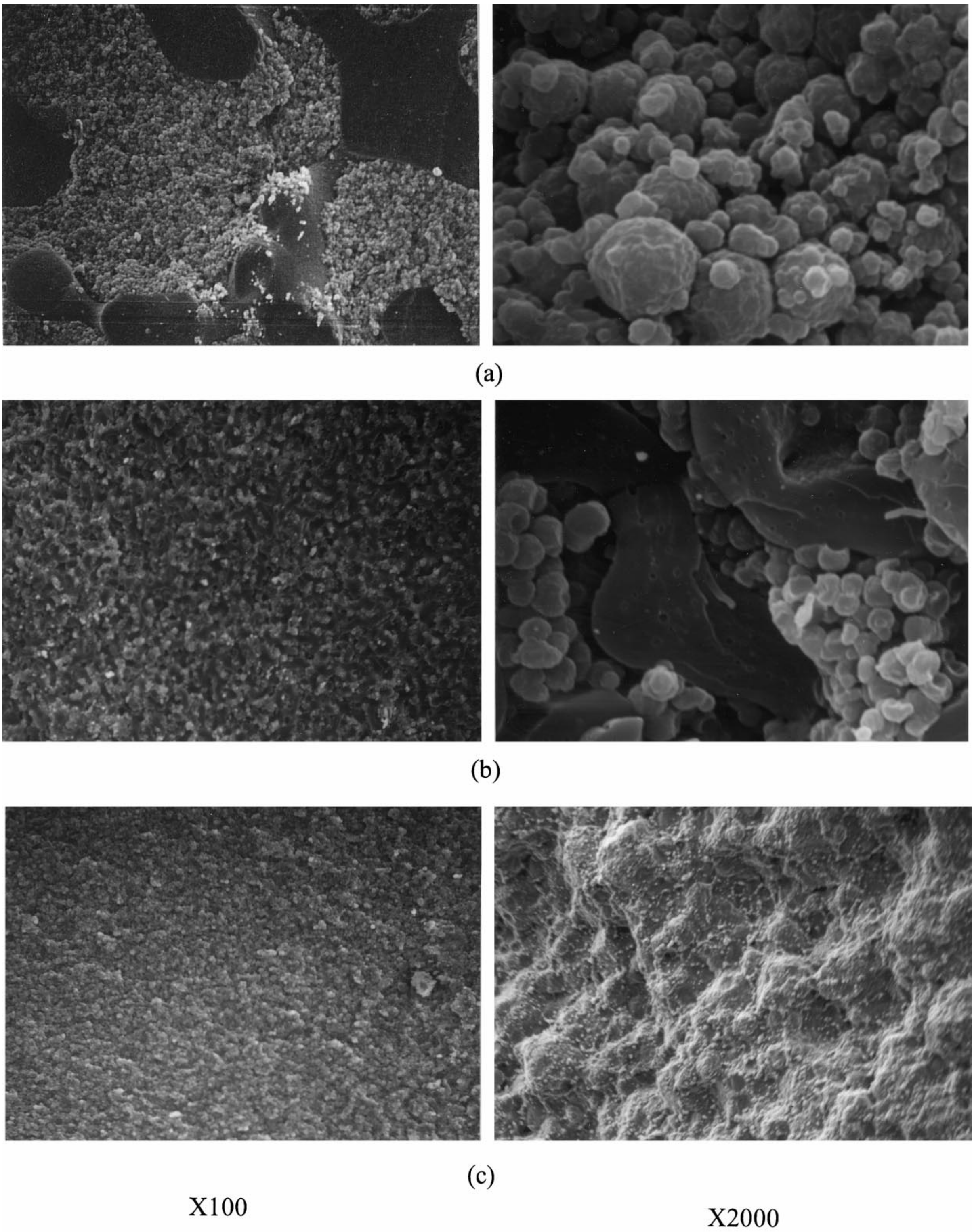

Figure 8 Scanning electron micrographs of UPE resins with different LPA contents cured at 35°C: (a) 3.5%; (b) 6.0%; (c) 10.0%

A direct way is to use the BET surface area measurement technique.

The BET technique is most commonly used to measure the internal surface area of porous materials (i.e. catalytic particles). It requires the pores inside the sample to be continuous, so that the adsorbate gas may penetrate into the pores. The results of the BET studies are summarized in *Table 2*. The internal surface area of opaque samples, which had expanded, was high. On the other hand, the value for the translucent sample, which did not exhibit expansion, was extremely low and is consistent with the scanning electron micrographs. The shrinkage results, sample opacity and the internal surface area data are well correlated, that is the sample with good shrinkage control has a high internal surface area measured by BET, and is always opaque. This observation confirms that the opacity increase during sample expansion is the result of microvoid formation.

Effect of LPA concentration. To investigate the effect of LPA concentration, LPA-A was chosen since it provides the best shrinkage control. Dilatometry runs of samples with 3.5, 6 and 10% LPA-A were carried out at 35°C. *Figure 7* shows the shrinkage behaviour of various resin mixtures. The volume change followed nearly the same path for all three samples, except that expansion of the sample with 3.5% LPA-A started at 314 min and that of the sample with 6% LPA-A started at 460 min. No expansion of the sample with 10% LPA-A was observed in the experiment for more than 15 h. Cured samples with 3.5% and 6% LPA-A were opaque, while that with 10% LPA-A was translucent.

The effects of varying LPA concentration on the resin morphology are shown in *Figure 8*. At the 3.5% level, as shown in *Figure 8a* at a low magnification (×100), the structure was distinctly inhomogeneous. Flake-like areas, consisting mainly of cured UPE resin, alternated with particulate-like co-continuous structures formed by UPE and LPA. The particles inside the particulate region were up to 7–8 μm and loosely packed as shown at high magnification (×2000). At 6% LPA, the structure was still quite inhomogeneous. The size of the flake-like region, however, was much smaller, in comparison with that in *Figure 8a*, and the two regions formed another co-continuous structure. The particle size of the particulate phase decreased to 2–3 μm. Further increasing the LPA concentration to 10% resulted in only particulate structure. The particles, however, were coagulated and cannot be clearly identified. From these results, we may conclude that a particulate structure alone does not guarantee the formation of microvoids. The individual particle size and how the particles are packed play important roles.

Effect of cure temperature. The effect of cure temperature on shrinkage control was conducted for the resin with 3.5% LPA-A. As shown in *Figure 9*, the time that the second expansion occurred was 10, 35 and 314 min for 80, 55 and 35°C cure respectively. Obviously, the expansion period shifted strongly with temperature. The final shrinkage results did not vary too much: 4.6% for 35°C cure, 5.5% for 55°C cure, and 4.7% for 80°C cure.

Comparing *Figure 9* with *Figure 3c*, it is seen that for all three cases, the resin conversions where the second expansion occurred were close and around 55–60%. The final conversion, however, depended on cure temperature (i.e. 69, 79 and 91% for 35, 55 and 80°C cure respectively). For the other two cases, the 3.5% LPA-B and 6% LPA-A samples cured at 35°C, the conversions when the expansion occurred were also within this range. This implies that a certain reaction stage must be reached before the microvoid formation could start.

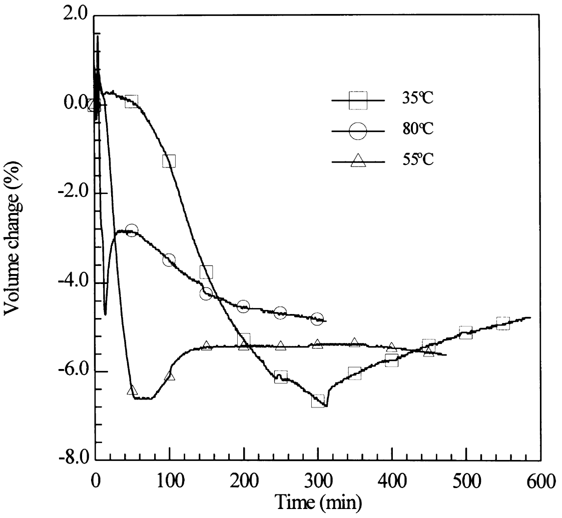

Figure 9 Effect of cure temperature on shrinkage behaviour of the sample with 3.5% LPA-A

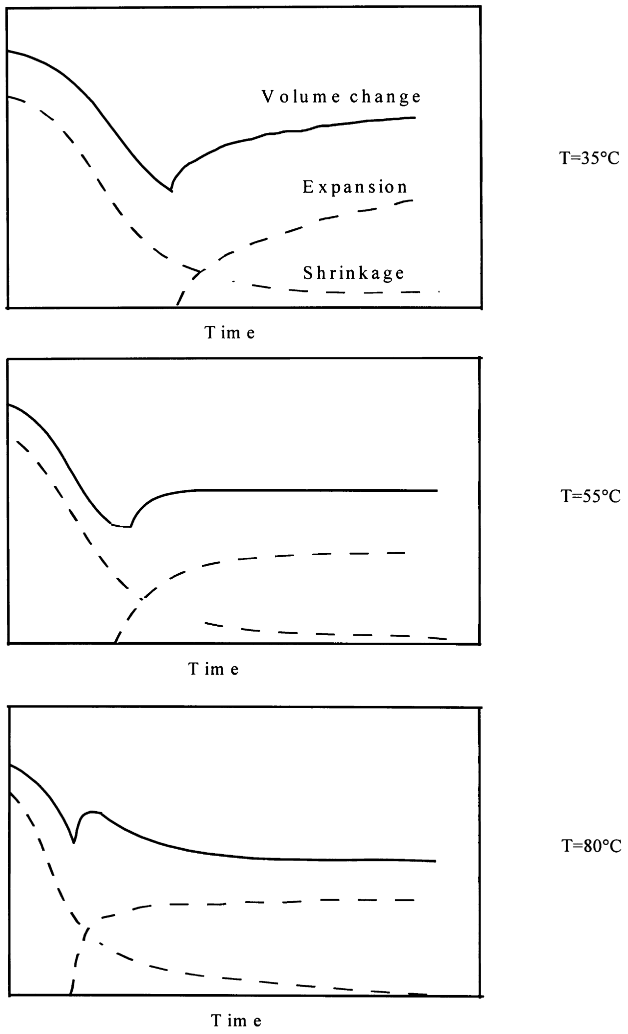

Figure 10 Competition between polymerization (shrinkage) and microvoid formation (expansion)

The shape of the volume change curves at different temperatures can be explained by the competition of two factors: shrinkage caused by polymerization and expansion induced by microvoid formation. As shown in *Figure 10*, the overall volume change curve can be decoupled into a shrinkage curve and an expansion curve. These two factors, however, may occur at different times and with different rates. The shrinkage curve strongly depends on resin conversion. In other words, a higher conversion would result in a larger shrinkage. The combination of these two factors may result in different volume change profiles. At 35°C, there was only 10% conversion change after the expansion started, which means that the polymerization shrinkage was small in this case. Consequently, the expansion dominated after the sample turned opaque. At 55°C, the conversion difference between the starting point of expansion and the final conversion was 25%, which suggests a larger polymerization shrinkage in this stage. This explains why, after a certain expansion, the sample

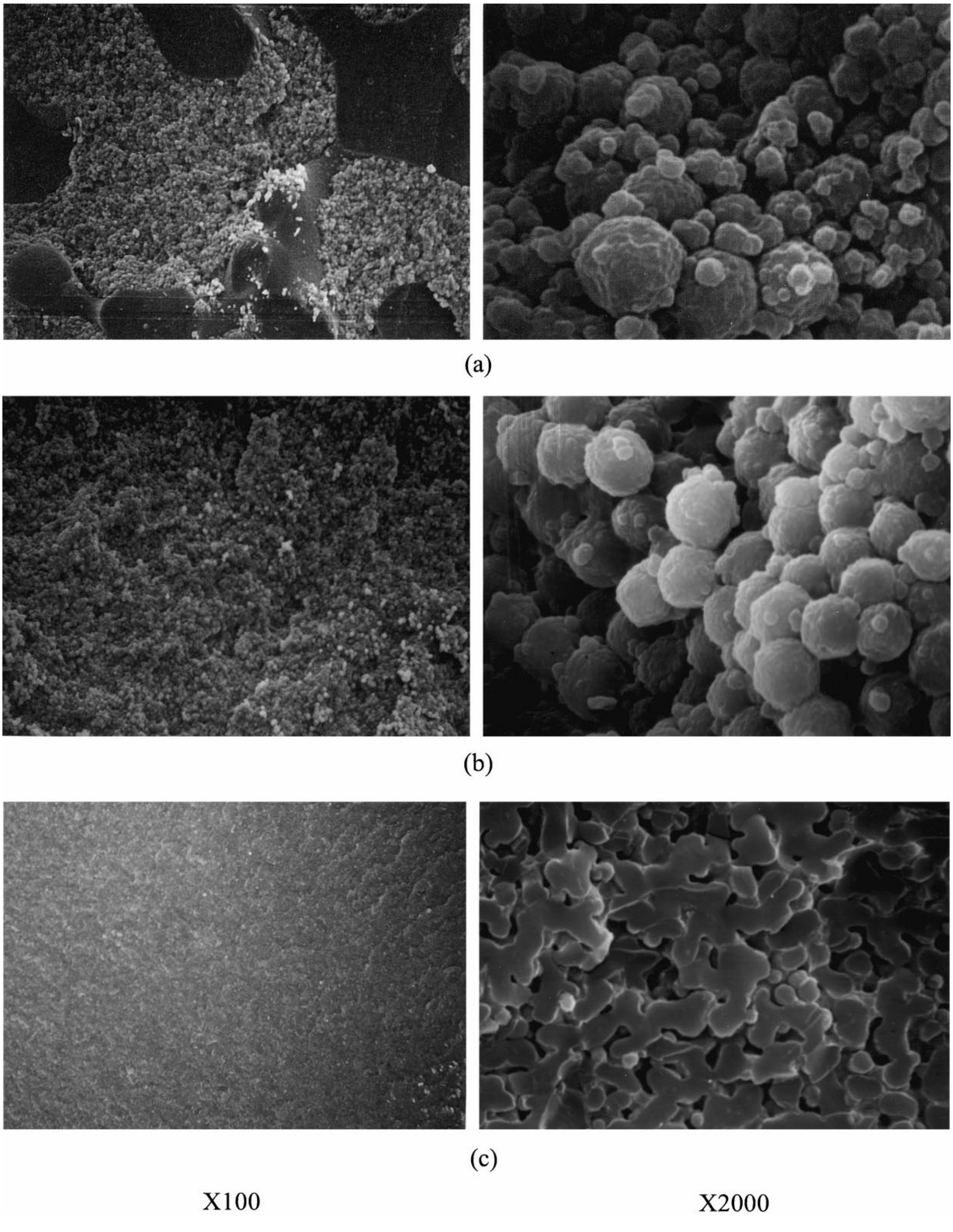

Figure 11 Scanning electron micrographs of UPE resins with 3.5% LPA-A cured at different temperatures: (a) 35°C; (b) 55°C; (c) 80°C

volume reached a plateau region, which implied that the expansion was counteracted by the shrinkage. For 80°C cure, the conversion difference was larger than 30% between the starting point of expansion and the final conversion. Therefore, after a short expansion period, the sample shrank again.

Increase of cure temperature also caused a remarkable change in sample morphology. Unlike the two-phase structure at 35°C cure (*Figure 11a*), a homogeneous particulate structure was resulted for the sample cured at 55°C (*Figure 11b*). Further increase of the cure temperature to 80°C caused a large change in appearance (*Figure 11c*). The particles were highly packed and deflated. Thus, only sample morphology cannot provide enough information to determine the shrinkage control performance.

Effect of fibre presence. Glass fibre is one of the principal ingredients in composite materials. It is used to achieve the necessary dimensional control and mechanical properties, reduce the coefficient of thermal expansion, and

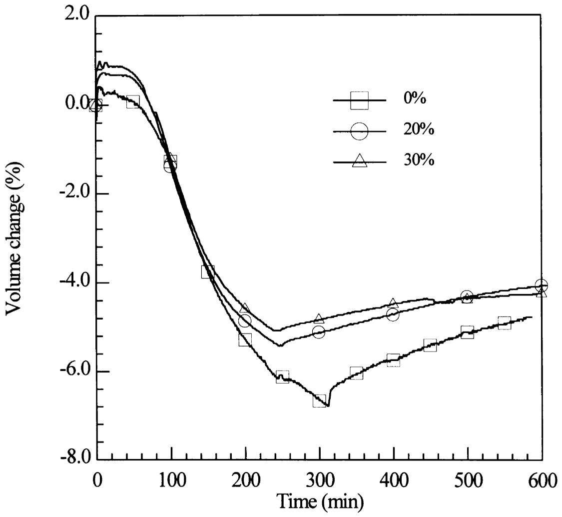

Figure 12 Effect of fibre presence on shrinkage control (3.5% LPA-A, 35°C)

increase the heat distortion temperature of moulded parts. To study the effect of glass fibre presence on LPA behaviour, dilatometry of two samples, one with 20% fibre by weight and the other 30% fibre by weight, was compared with that of neat resin mixture. The fibre used was a glass fibre mat (plain weave). All other aspects of the formulation and sample preparation were unchanged as in Sample 3 in *Table 1*, and the same cure conditions were followed.

Figure 12 shows the volume change *versus* time based on the neat resin mixture. The general trend remained the same. The second expansion was still observed, except it occurred earlier with the presence of fibre mats. During polymerization, fibres resist cure shrinkage, thereby setting up stresses at the interface of the fibre and the polymer matrix. Such stresses may have caused an early formation of microvoids. As observed in the experiment using the transparent mould, the microvoids first grew along the fibres, and then migrated into the resin phase as cure progressed. Changing the fibre content does not seem to have a strong influence on volume change, since the two curves almost overlapped with each other as shown in *Figure 12*.

MOULDING EXPERIMENTS

Two series of room-temperature moulding experiments were accomplished using the same formulations listed in *Table 1*. The first series followed the ASTM standard for linear shrinkage measurement (ASTM D2566-86). The mould was 254 cm long with 1.27 cm internal radius. The resin mixture was cured at room temperature and the change in specimen length was measured by a calliper gauge. The moulding process was also videotaped. *Figure 13* shows the case of 3.5% LPA-A. The material started as a homogeneous mixture. After about 20 min, the sample turned cloudy and became more translucent as time passed. At 55 min, the dark area indicated a gap had been formed between the mould wall and the specimen. The width of the gap grew larger in the next picture, and the white area showed the beginning of whitening. As the white area gradually developed and covered the whole specimen, the width of the gap decreased. At the end of the moulding, the gap almost disappeared. The observation here is identical to the dilatometry results. The sample with 6% LPA-A gave similar results to that with 3.5% LPA-A. For the sample with 10% LPA-A, the gap formed was larger than with 3.5% LPA-A, the specimen was translucent, and no gap width decrease was observed. The cure process of the sample without LPA showed only shrinkage, and the specimen was transparent.

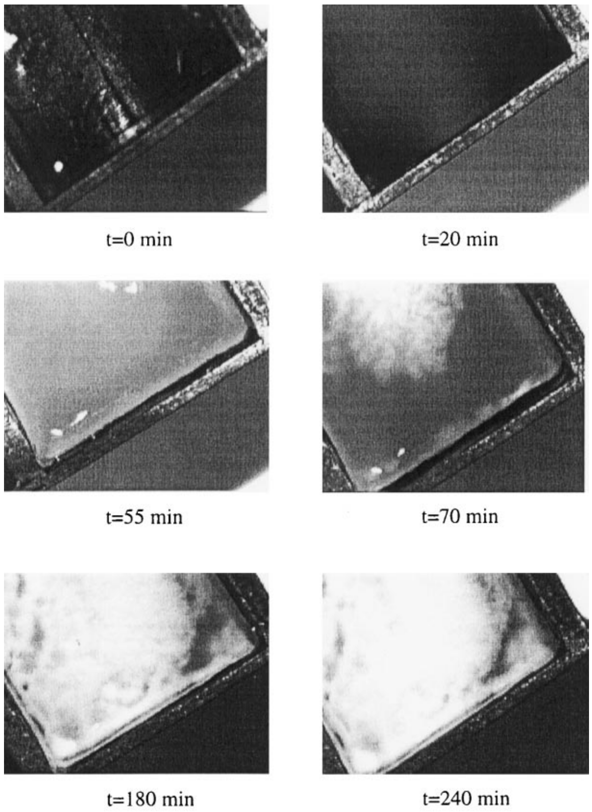
t=0 min
t=20 min
t=55 min
t=70 min
t=180 min
t=240 min

Figure 13 Sample change during linear shrinkage measurement

In the second series of moulding tests, a vacuum infusion technique similar to the SCRIMP process was used. Before moulding, four layers of dry glass-fibre mats were laid upon a steel plate which has a chrome-coated surface finish. A vacuum bag was used to cover the fibre stack, and the outer edges of the bag were sealed. A resin inlet and a vacuum outlet on each end of the mould were also formed. During moulding, vacuum was applied through the outlet, which forced the bag to press tightly against the fibre stack. The liquid resin was introduced to the inlet through a supply line. After mould filling and curing, the moulded part was removed by peeling away the vacuum bag. The surface quality of the moulded samples was measured by a profilometer, Federal's Surfanalyzer 4000. It provides the profile of surface, roughness, and waviness. Most commonly, a roughness average (*Ra*) is used as a quantitative standard to compare the surface quality. *Ra* is the arithmetic average height of surface irregularities measured from the mean line within the sample length.

As listed in *Table 3*, the result confirmed the trend exhibited by the dilatometry test: a higher molecular weight and a relatively lower concentration of poly(vinyl acetate) can provide better shrinkage control.

LPA MECHANISM

Based on the data presented in this work, a low-temperature LPA mechanism is proposed as shown in *Figure 14*.

In step 1, the system starts as a homogeneous mixture

Table 3 Surface roughness and linear shrinkage measurements

	No LPA	3.5% LPA-C	3.5% LPA-A	6% LPA-A	10% LPA-A
Ra (mm)	1.9	0.65	0.38	0.43	0.6
$\Delta L/L$ (%)	2.40	1.83	~0	–	1.00

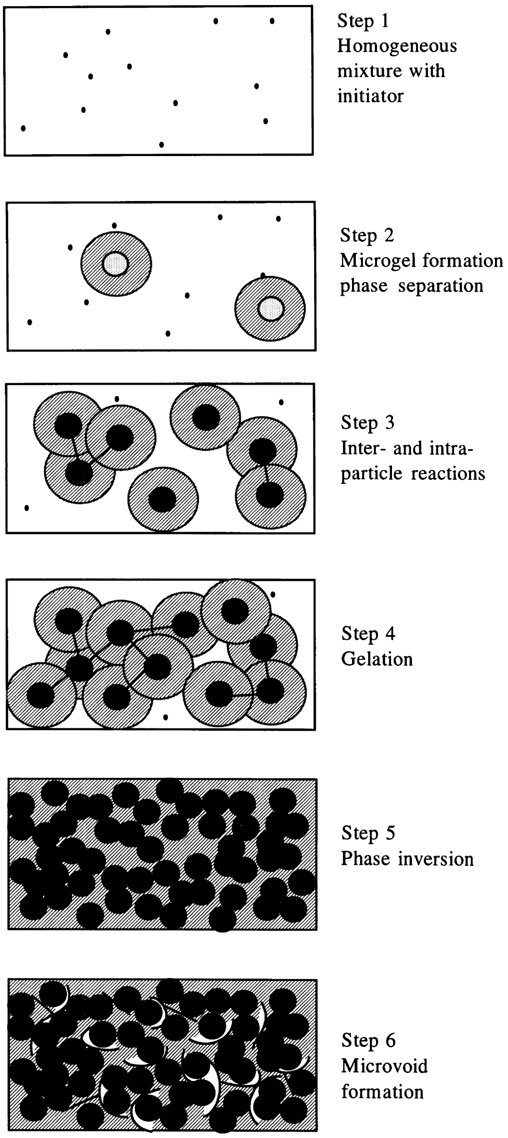

Figure 14 Illustration of LPA mechanism at low-temperature cure

consisting of UPE, LPA, styrene and initiator. In step 2, the reaction starts, where the UPE molecules are linked by either an inter- or an intramolecular reaction. Because of the increase of UPE molecular weight and change of polarity, the compatibility of reacting UPE with both LPA and styrene decreases. Localized phase separation occurs. According to the mass balance, the microgel must be surrounded by an LPA-rich layer. Further reaction in steps 3, 4 and 5, which includes inter- and intraparticle reactions, results in gelation and phase inversion between the LPA-rich and the UPE-rich phases. In these steps, the reaction mixture turns cloudy and translucent. The viscosity starts to increase, and the system keeps shrinking. In further reaction, i.e. step 6, stress may build up internally because of the possible difference of the two phases in reaction rate and modulus. At a certain point, a local crack may be initiated and propagate along the interface or inside the weaker phase (LPA-rich phase). Microvoids are formed and stress is released; consequently, the polymerization shrinkage is compensated. Here, the reaction mixture turns opaque and expansion starts.

In general, the low-temperature LPA mechanism is quite similar to the high-temperature LPA mechanism, except for the effect of thermal history. In high-temperature processes, as mentioned earlier, the thermal expansion/contraction resulting from the large temperature gradient during moulding plays the most important role in compensating shrinkage. Therefore, LPAs with high thermal expansion coefficient and low glass transition temperature (i.e. lower molecular weight) are preferred. High concentration of LPA is also needed to provide more thermal expansion and to delay the phase inversion, so that the thermal expansion effect may last longer.

At low temperatures, on the other hand, the thermal effect is almost negligible. The reaction-induced microvoid formation turns out to be the major factor in reducing shrinkage. Therefore, factors that are related to reaction-induced stress and crack formation, such as the difference of the two phases in reaction rate and modulus, and the phase inversion, may have a strong influence on shrinkage control. This may explain why LPAs with higher molecular weight (i.e. higher glass transition temperature, higher modulus and less compatible with the resin) and lower concentration (i.e. earlier phase inversion) provide a better shrinkage control at low-temperature cure, which is totally opposite to that in high-temperature processes. Detailed relationship between process/material variables and the reaction-induced microvoid formation needs to be further studied.

CONCLUSIONS

The LPA performance under low-temperature cure was investigated with regard to kinetics, rheology, morphology and volume change. In the study of volume change, it was found that a second expansion occurred for the samples with good shrinkage control. The results indicated that microvoid formation at a later stage of curing is a critical factor for shrinkage control. The shrinkage result, sample opacity and internal surface area were well correlated. Two series of moulding experiments were also performed to compare the linear shrinkage and the surface roughness of the moulded samples with the dilatometry results. Again, the correlation is quite good. In general, the results showed that the high-molecular-weight LPAs works better than the low-molecular-weight LPAs, and relatively low-LPA concentration seems to be able to provide good shrinkage control. The detailed mechanism of microvoid formation and shrinkage control under isothermal conditions (i.e. no thermal expansion and contraction effects) is still not well understood and needs to be further studied.

ACKNOWLEDGEMENTS

The authors would like to thank Union Carbide Corporation for financial support and material supply, and Ashland Chemical Company for resin donation.

REFERENCES

1. Pattison, V. W., Hindersinn, R. R. and Schwartz, W. T., *J. Appl. Polym. Sci.*, 1974, **18**, 1027.
2. Atkins, K. E., *Polymer Blends*, ed. D. R. Paul and S. Newman. Academic Press, New York, 1978. Chapter 23.
3. Atkins, K. E., Low profile additives: shrinkage control mechanism and applications, in *Sheet Molding Compound Materials: Science and Technology*, ed. H. Kia. Hanser, 1993.
4. Melby, E. G. and Castro J. M., *Comprehensive Polymer Science*, Vol. 7. Pergamon Press, Oxford, 1989.
5. Ruffier, M., Merle, G. and Pascault, J. P., *Polym. Eng. Sci.*, 1993, **33**(8), 466.
6. Kinkelaar, M. and Lee, L. J., *Polym. Eng. Sci.*, 1992, **45**, 37.
7. Kinkelaar, M., Wang, B. and Lee, L. J., *Polymer*, 1994, **35**(14), 3011.
8. Bartkus, E. J. and Kroekel, C. H., *J. Appl. Polym. Sci.*, 1970, **15**, 113.
9. Bucknall, C. B., Davies, P. and Partridge, I. K., *Polymer*, 1985, **26**, 109.
10. Suspene, L., Fourquier, D. and Yang, Y. S., *Polymer*, 1991, **32**(9), 1595.
11. Hsu, C. P., Kinkelaar, M., Hu, P. and Lee, L. J., *Polym. Eng. Sci.*, 1991, **31**(20), 1450.