Development of a Dilatometer and Its Application to Low-Shrink Unsaturated Polyester Resins

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SYNOPSIS

Two dilatometers are presented here that were developed for the use with, but not limited to, low-shrink unsaturated polyester resins. One of the dilatometers, made from a glass syringe and two aluminum plates, was limited to lower pressures. The other dilatometer, similar in design to the first, was made from a hydraulic cylinder and was capable of pressures to 500 psi. The dilatometers were calibrated and tested by the polymerization of styrene. Several low-shrink unsaturated polyester resins were cured in the dilatometers and the results of these experiments are given. The interactions of volume change, rheology change, conversion, and microstructure formation were also measured. Finally, the effect of pressure was considered.

INTRODUCTION

A dilatometer is a device used to measure the pressure–volume–temperature (or PVT) relationship of materials. Most dilatometers were not designed for use with reacting systems, but a few have been designed to accommodate. In the past, several dilatometers were developed by different researchers to follow conversion of reacting systems,[1-3] as polymers shrank on curing. However, many problems existed in using a dilatometer, such as temperature control and viscosity interference, that made dilatometry less popular when thermal analysis and spectroscopy became widely accepted in kinetic measurements.[1,4-7]

Reactive dilatometry is of the greatest interest here. It should be noted that dilatometry of reactive systems is much more difficult than dilatometry of nonreactive systems. For example, in nonreactive systems, temperature control is not a problem, but in reactive systems, the heat of reaction must be dissipated quickly in order to avoid measuring thermal expansion. For some reactive systems, the conversion, α, may be found by the volume change data because volume change and conversion are inversely proportional. For many other reactive systems, this

may not be true and the conversion needs to be determined by use of other means, such as differential scanning calorimetry (DSC). In other words, four variables (P, V, T, and α) need to be considered instead of three (P, V, T). Finally, for reactive systems, the heating time must be kept to a minimum to avoid measuring both thermal expansion and reaction shrinkage simultaneously. Ideally, a dilatometer should be able to operate at low and high temperatures and pressures, be isothermal, accurate to a fraction of a percent, have a quick thermal response, not interfere with the reaction mechanism, and be safe. One that is limitless has not been invented yet, but there have been several systems applicable to special situations.

Most of the dilatometers used in the literature for reactive systems were noncommercial devices. They were of two basic categories: capillary type and plunger type. The capillary type[1-3,8-14] of dilatometer was a variation of a thermometer. The sample remained in a bulb (or some type of containing system) and a fluid (either the sample or a containing fluid such as mercury or oil) filled a capillary. As the reaction progressed, the volume change was monitored by following the fluid in the capillary. Obviously, this method of dilatometry was restricted to slow reactions, low conversions, and low-viscosity systems. Also, excellent temperature control was necessary; otherwise, the measurement would reflect an interaction of volume change due to conversion and

volume change due to thermal effects. The plunger type[8,15–17] of dilatometer used something similar to a syringe to contain and pressurize the sample. The plunger of the syringe was monitored to follow the volume change.

In this study, a dilatometry technique (based on the plunger type) was developed. Its application to low-shrink unsaturated polyester resins was demonstrated. Low-shrink unsaturated polyester resin is an unsaturated polyester resin that contains a low-profile additive (LPA). An LPA is a thermoplastic such as poly(vinyl acetate) (PVAc) that can reduce resin shrinkage and, consequently, provide a better surface quality to molded parts. Presently, there are several low-profile additives used in industry: PVAc, polyurethane (PU), poly(methyl methacrylate) (PMMA), and polystyrene (PS) are just a few. Some commercial LPAs contain unsaturated bonds and thus take part in the reaction. Variables of interest when considering an LPA are type, molecular weight, and amount to be used. Also to be considered are the molding conditions such as reaction temperature and molding pressure that may affect LPA performance. The LPA mechanism is still not well understood and details can be found elsewhere.[8,17–20]

Low-shrink unsaturated polyester resins are widely used in industry in sheet-molding compound (SMC), bulk-molding compound (BMC), resin-transfer molding (RTM), and others. The processing conditions (pressure, temperature, and reaction rate) are dependent on the process used. For example, RTM is generally a low-pressure (< 100 psi), low-temperature (< 100°C) process, whereas SMC is a high-temperature (150°C mold temperature), high-pressure (500–1000 psi) application. Also, the surface quality of a molded SMC or RTM part is directly related to the shrinkage of the resin. The less the shrinkage, then the better the surface quality.[8] To characterize resins used for various processes, the desired dilatometer must be able to cover a broad range of temperature and pressure. This was the primary motive of this study.

EXPERIMENTAL

Materials

To simplify the reaction system, only resins (unsaturated polyester and styrene), low-profile additives, and curing agents (initiators) were considered in this study. Although the type of unsaturated polyester (UPE) as well as the ratio in which UPE

and styrene are mixed, the initiator type, and the use of inhibitor may all affect volume change and surface quality, the most important ingredient for shrinkage control is believed to be the LPA and it is the only one varied in this study.

The unsaturated polyester used was provided by Ashland Chemical Company. The resin was a 1 : 1 mixture of maleic anhydride and propylene glycol, which has an average of 10.13 vinylene groups per polyester molecule. The number average molecular weight of the unsaturated polyester was 1580 g/mol and the equivalent molecular weight/mol C=C was 156 g/mol. All dilatometry runs were done at 80°C with a resin having a styrene-to-UPE molar ratio of 2.0 and 15% LPA by weight; 1.1% PDO was used as the initiator.

It would be impossible to try all the LPAs available at all the conditions of interest, so for this study only two LPAs were considered: two different molecular weights of PVAc from Aldrich Chemical Co. The two molecular weights available for PVAc LPA were 105,500 and 174,000 (weight average) as measured by gel permeation chromatography (GPC). Characterization of other types of LPA was given in a separate publication.[20]

Dilatometer

In this study, two dilatometers were developed. A schematic of the first dilatometer is shown in Figures 1 and 2. This dilatometer is a variation of a dilatometer from the literature.[19] The sample was heat-sealed (air-free) in a pouch made out of a laminated PE material (Seal-a-Meal plastic boiling bags). This pouch was contained between two screens, in a 4-in. (10.2 cm) cavity honed in two 5-in. (12.7 cm) aluminum disks. The two disks were bolted together and sealed with an O-ring. Holes were drilled in the center of both plates, and a 30 mL glass syringe was cut in half and glued into the holes, as shown in Figure 1.

To aid in heat transfer, the sample geometry chosen was that of a thin disk. This yielded the highest surface area-to-volume ratio. A thermocouple wire was run from inside the sample (contained in the pouch), through the cavity, and out of the dilatometer through a slit in the O-ring. Another thermocouple was placed in the dilatometer cavity, but not inside the sample. This was done to detect a change in sample temperature due to heat of reaction or slow dissipation of heat.

After installing the sample, the cavity was filled with silicon oil (Dow Corning 550 fluid) and the syringe plunger was inserted into the upper part of
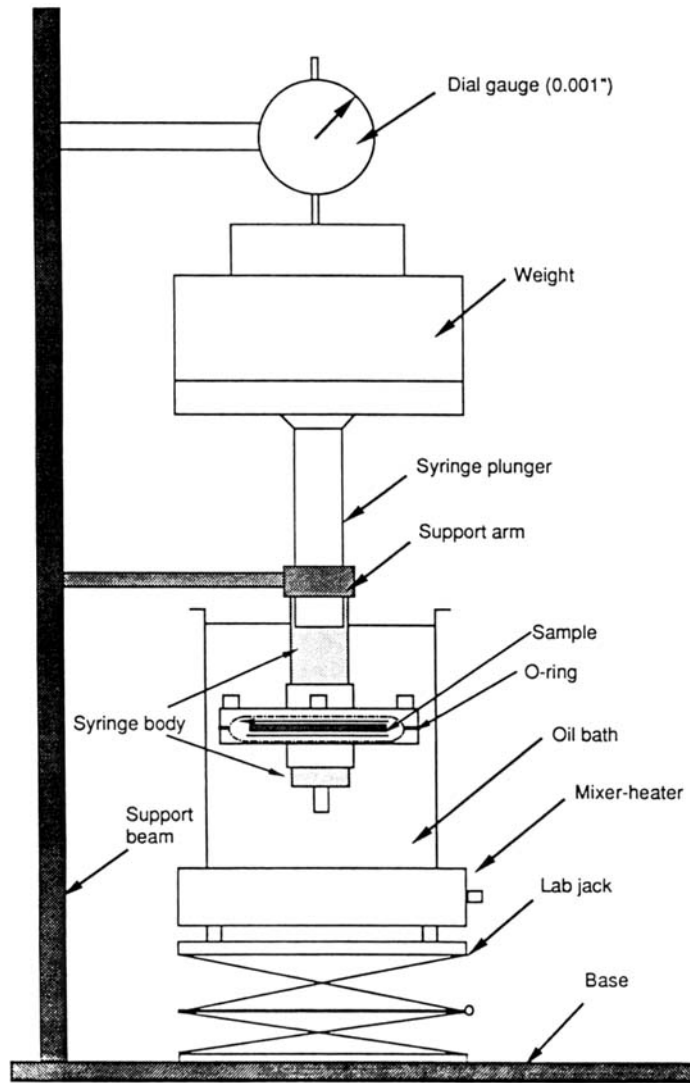
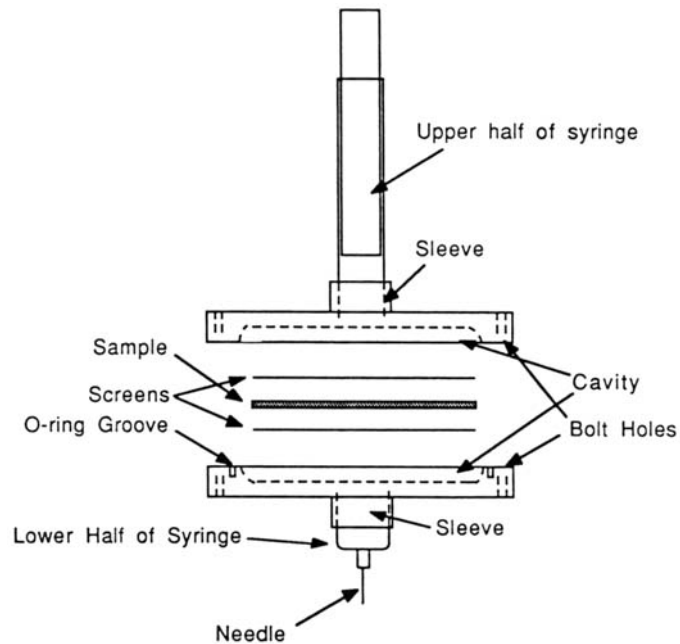**Figure 1** Schematic of glass syringe dilatometer.

Figure 2 Schematic of dilatometer sample cell.

the syringe body. All the air bubbles were removed from the needle at the bottom by turning the dilatometer upside down and the needle was corked.

The dilatometer was then mounted onto a support beam and weights were balanced onto the syringe plunger. The weights provided a constant pressure of approximately 45 psig. The pressure could be varied by changing the amount of weight used. As the sample expanded or shrank, the weight would move up or down. Either a dial gauge or a linear variable differential transformer (LVDT) was mounted on the support beam to follow the movement of the weights. By knowing the syringe plunger diameter (22.65 mm), the volume change was calculated as a function of time.

After assembly and mounting, a cooling bath was raised to the sample cell (submersing the cavity containing the sample and the part of the syringe containing silicon oil) and was kept there until the thermocouples in the dilatometer registered the same temperature and were constant. At that point, the initial plunger position was recorded and the cooling bath was removed. A heating bath was then raised into place. Temperature from both thermocouples and the plunger position were recorded vs. time until the reaction was believed to be complete. The heating bath was then lowered and put aside and the cooling bath was again installed. The dilatometer was cooled until both thermocouples read the same constant initial temperature. To determine the expansion effects due to the oil and the dilatometer, the entire heating and cooling process was repeated on the reacted sample (similar to a base-line determination). This also helped to determine if the dilatometer was leaking or if the sample was not completely cured.
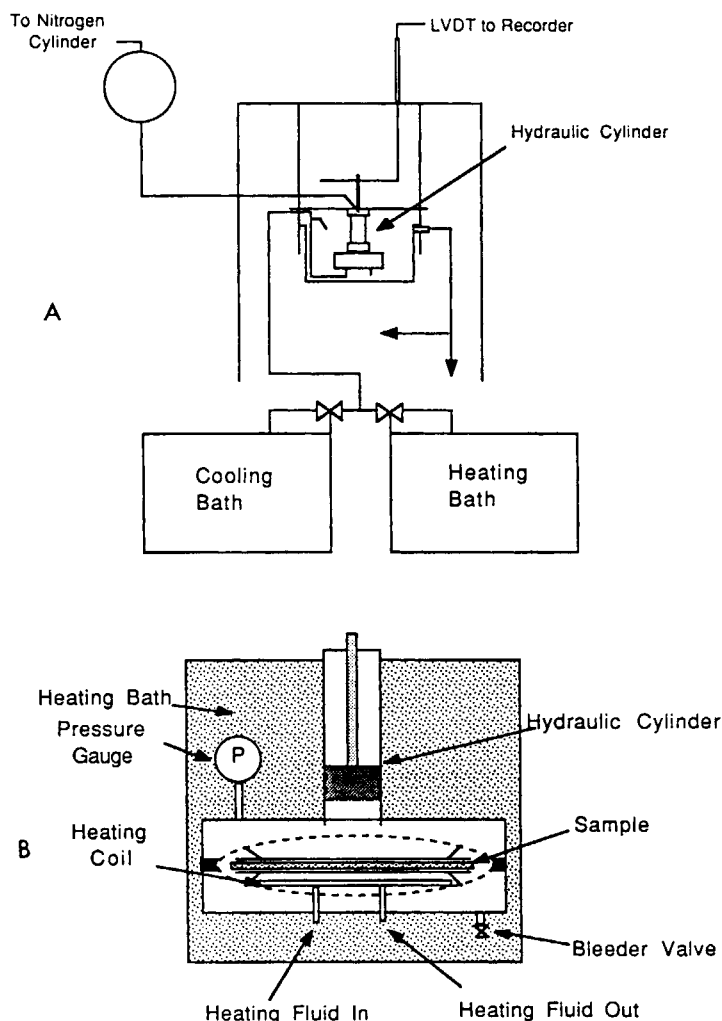

Figure 3   High-pressure dilatometer: (a) setup; (b) sample cell.

After studying the limitations of the glass syringe dilatometer, a second, more versatile, dilatometer was designed. This higher-pressure dilatometer was designed for better temperature control, quicker heating and heat dissipation, higher pressure and temperature capabilities, and easier use. A schematic of it is shown in Figure 3. It can be seen that the basic design is very similar for both dilatometers, except that instead of using a glass syringe a small hydraulic cylinder (Cylinders and Valves Inc., Cleveland, OH) with a 0.75-in. (1.905 cm) diameter and a 0.375-in. (0.953 cm) rod, capable of 500 psi and 400°F (204°C), was used. The cavity dimensions were the same as those of the glass syringe dilatometer, and the same pouch material was used. Also, note that there was a heating coil welded into the high-pressure unit [Fig. 3(b)]. This was done because the heating was slow on the glass syringe dilatometer.

Assembly of this dilatometer was done by vacuum techniques: A vacuum was pulled at the bleeder valve, removing the air. The valve was then closed and a tube filled with degassed oil was installed at the valve. The valve was then opened and oil flowed into the cavity. This was repeated until no air remained. To use this technique, the sample must be degassed first to avoid bubble formation. This dilatometer was constructed of copper to lessen the heating time. The method of pressurization is shown in Figure 4. Silicon oil was used on both sides of the hydraulic cylinder and on some of the tube leading into the top of the cylinder. An accumulator was used to prevent changes in pressure due to volume changes and to maintain a steady pressure. Note that because of the presence of the rod on the top side of the piston the pressure on the other side of the piston would be lower and the ratio of the two pressures was related to the ratio of the areas (i.e., 1 : 0.75). The pressure in the dilatometer cell was calibrated by measuring both the pressure in the cell (as shown in Fig. 3) and the pressure in the pressurization system. The high-pressure cell was mounted in a stand and a photograph of it is shown in Figure 5. Again, a method of first cooling to an initial temperature, heating, and then cooling to the original temperature was used. Note that the heating fluid was pumped into both the heating tank and directly into the sample cell heating coil. This was done to speed the heating process. The result was that this dilatometer yielded a better temperature and pressure range, faster heating and better temperature control, and steady pressure and higher
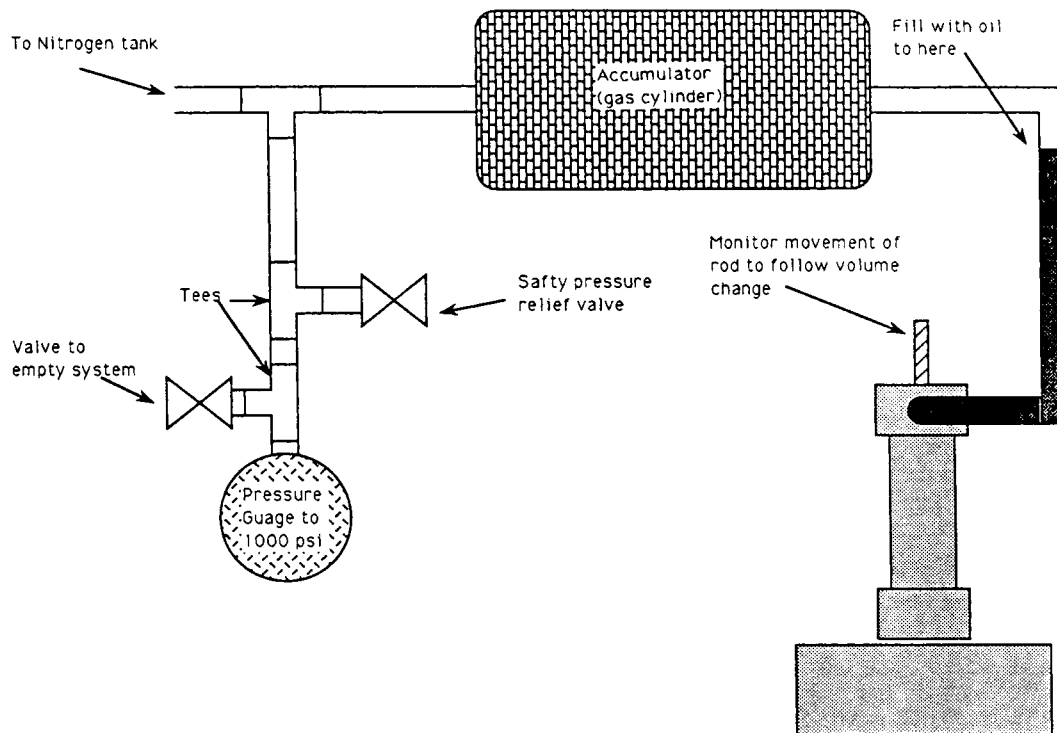

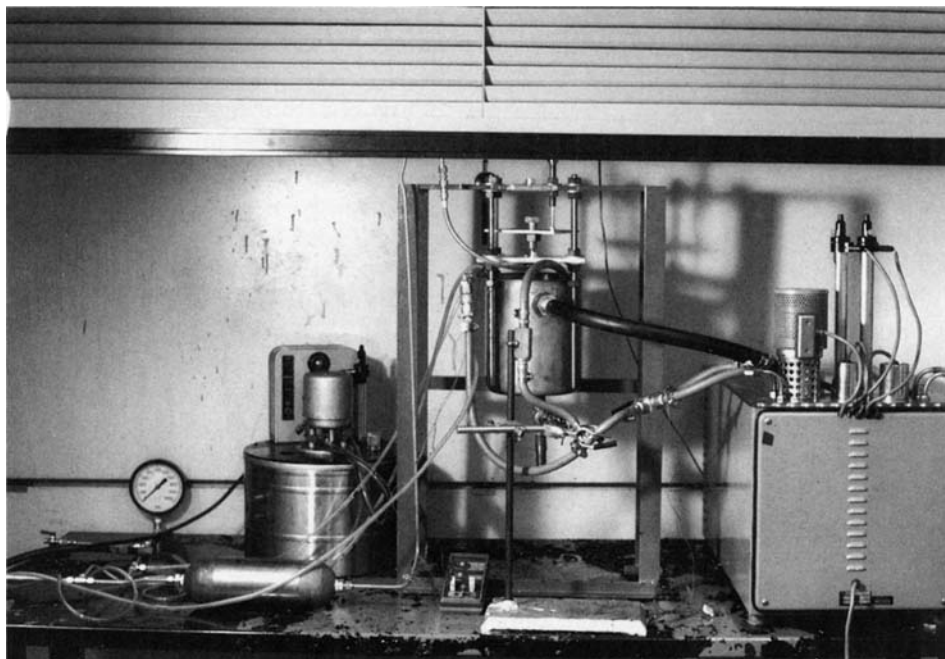**Figure 4**   Method of pressurization for high-pressure dilatometer.

Figure 5   High-pressure dilatometer.

resolution (because the plunger diameter was smaller than the syringe diameter).

Differential Scanning Calorimeter (DSC)

The DSC used was a Perkin-Elmer DSC-2. The DSC was used to follow the rate of reaction exotherm. A sample of about 10 mg was placed into a volatile sample pan (a small aluminum pan, of about 25 mg, sealed and able to withstand an internal pressure of 2 atm). The sample pan and an empty reference pan were either heated at a programmed rate or kept isothermal. By measuring the difference in the amount of energy required to heat the sample vs. the empty pan as a function of time, heat of reaction, reaction rate, and conversion as a function of time were calculated.[6] By modeling the temperature pro-
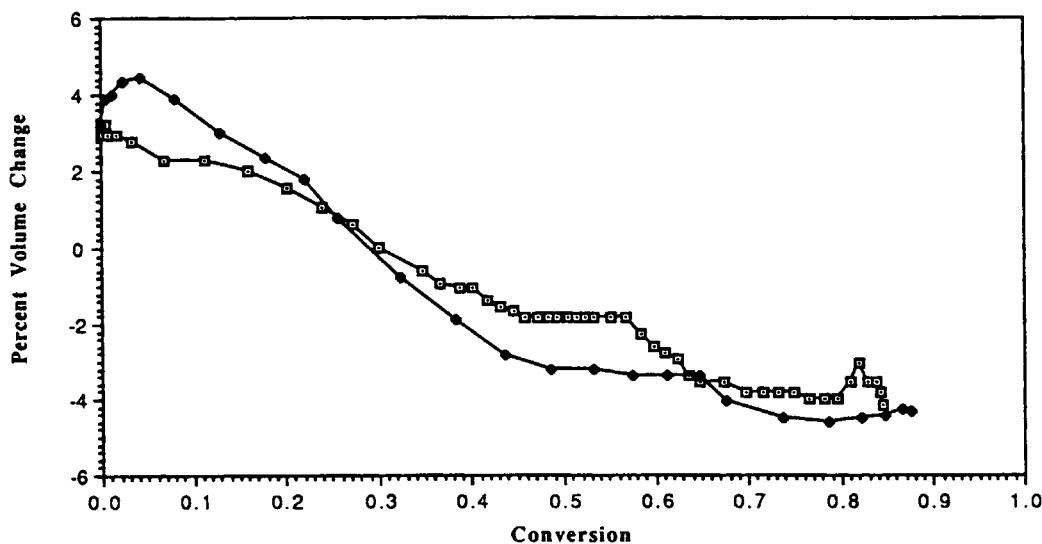

Figure 6   Test of repeatability, glass syringe dilatometer.

file of the dilatometer with the DSC, conversion was found with respect to the volume change.

Rheometrics Dynamic Analyzer (RDA)

A Rheometrics dynamic analyzer (RDA-700) was used to follow rheological changes and gelation in the oscillatory mode. The sample cell in an RDA is basically a set of serrated disposable aluminum par-

allel plates with a 25 mm diameter. Again, the temperature could either be programmed or be kept isothermal, so modeling of the dilatometer temperature profile was possible. The gap between the plates was set at 1.1 mm and the frequency used was 10 radians/s. The strain ratio was 10%. Storage modulus (G') and loss modulus (G'') were calculated and liquid-to-solid transition was implied when G' and G'' crossed in this study.
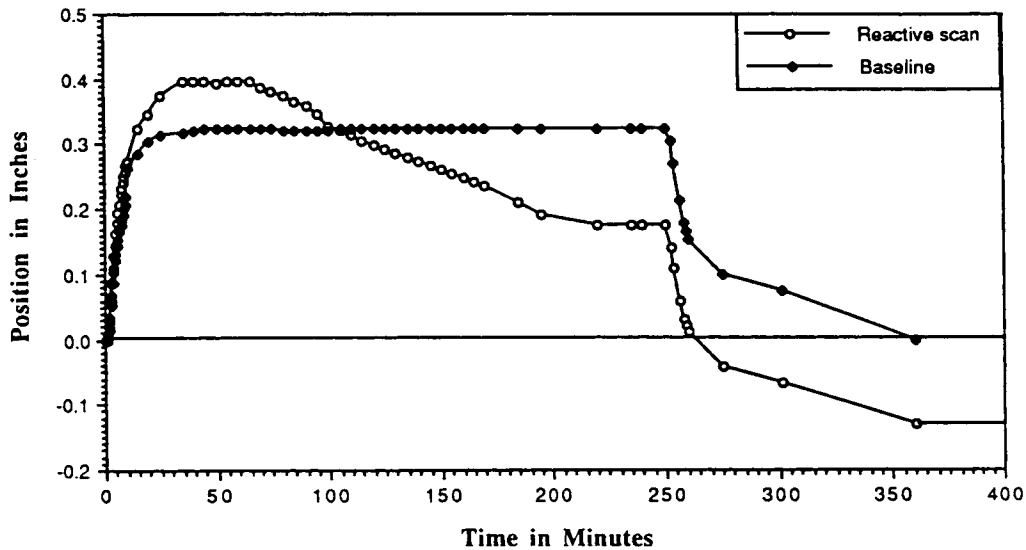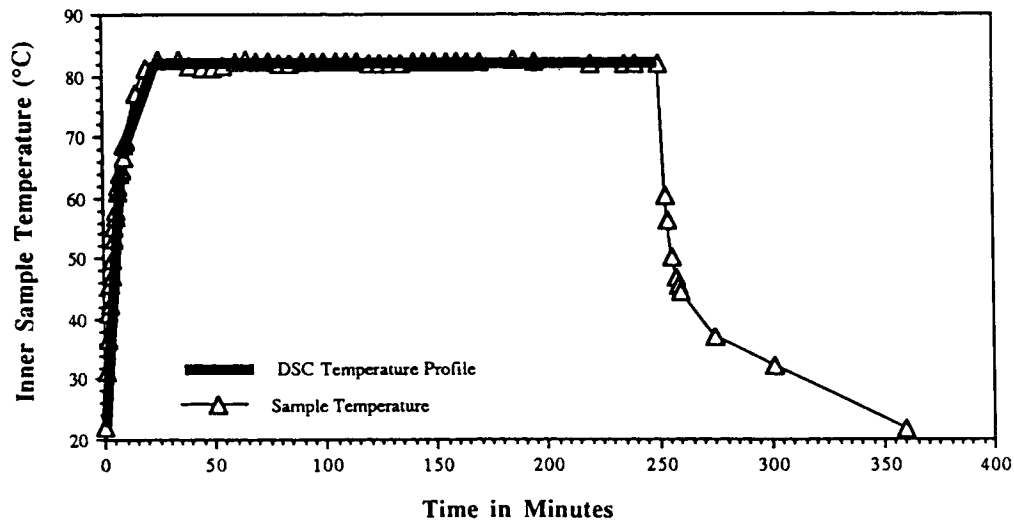
Figure 7   Results of styrene polymerization from syringe dilatometer: (a) cure and baseline profiles; (b) sample temperature profile and DSC temperature programming.
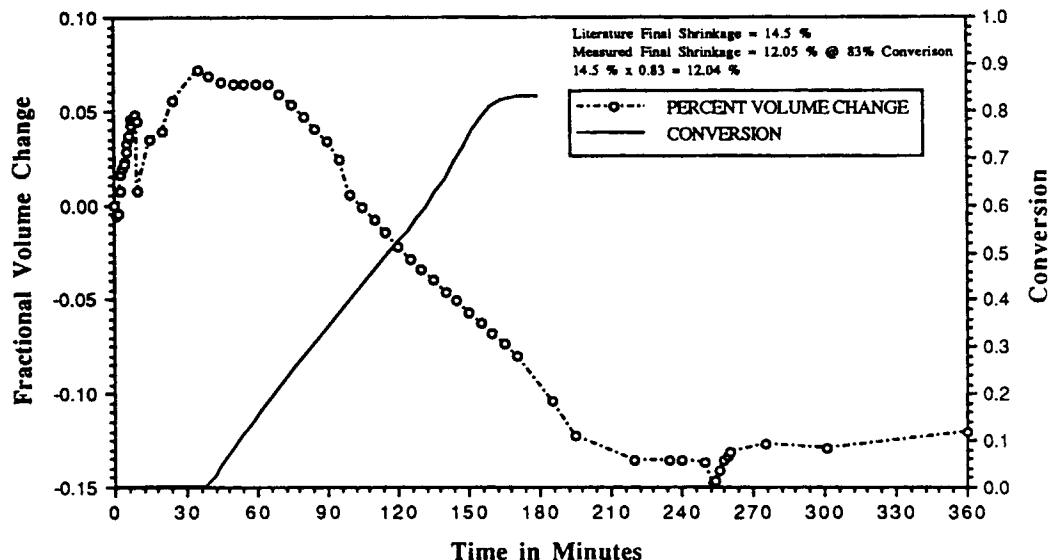
Figure 8   Fractional volume change and conversion vs. time for styrene polymerization.

Scanning Electron Microscopy (SEM)

The SEM microscope used in this study was a Hitachi S510 with an accelerating voltage of 25 kV and sample magnification from 200X to 4000X. The cured sample was first washed in a mixture of inhibitor (benzoquinone) and solvent (dichloromethane) to prevent any further reaction and to remove any of the nonreacted resin and LPA. It was then dried and coated with a thin layer of gold. The advantage of using SEM was that the microstructure formation of the nonsoluable cured UPE resin was easy to see. SEM was also used for partially cured samples around the liquid–solid transition point (by pulling a sample out of the RDA at the $G' = G''$ point or at a set time near that point) to monitor microstructure formation.

Table I   Summary of Volume Changes for Resins with and without LPA

	PVAc		
	Low	High	No LPA
$\overline{M_n}$	33,800	56,020	—
$\overline{M_w}$	150,500	174,000	—
Volume change	−1.8%	−3.0%	−6.5%

RESULTS AND DISCUSSION

Dilatometer Calibration

Several runs were made to determine if the dilatometers worked correctly. First, they were run without a sample to determine if there were any leaks and to get a feel for the data. Next, several runs were made with a reacting unsaturated polyester (UPE) resin to determine limitations of the system. It was found that the sample size should be on the order of 7 ± 3 g for both dilatometers. Any larger heat of reaction would not be dissipated quickly enough, causing a large temperature rise and bubble formation (due to styrene boiling) in the sample. Any smaller resolution would be lost. Furthermore, the temperature must be low enough (i.e., less than 90°C) for the syringe dilatometer to keep the reaction slow and to avoid a large temperature rise and bubble formation in the sample.

Third, it was desired to see if the data were repeatable. Figure 6 shows the results of two syringe dilatometry runs of the same resin cured at identical conditions. The plot is of percent volume change vs. conversion (to get conversion, the DSC was run at a similar temperature profile as the inner sample temperature in the dilatometer). As shown in Figure 6, the data agreed with each other quite well, especially at the final conversions. The deviations in the plot were due to temperature differences in the
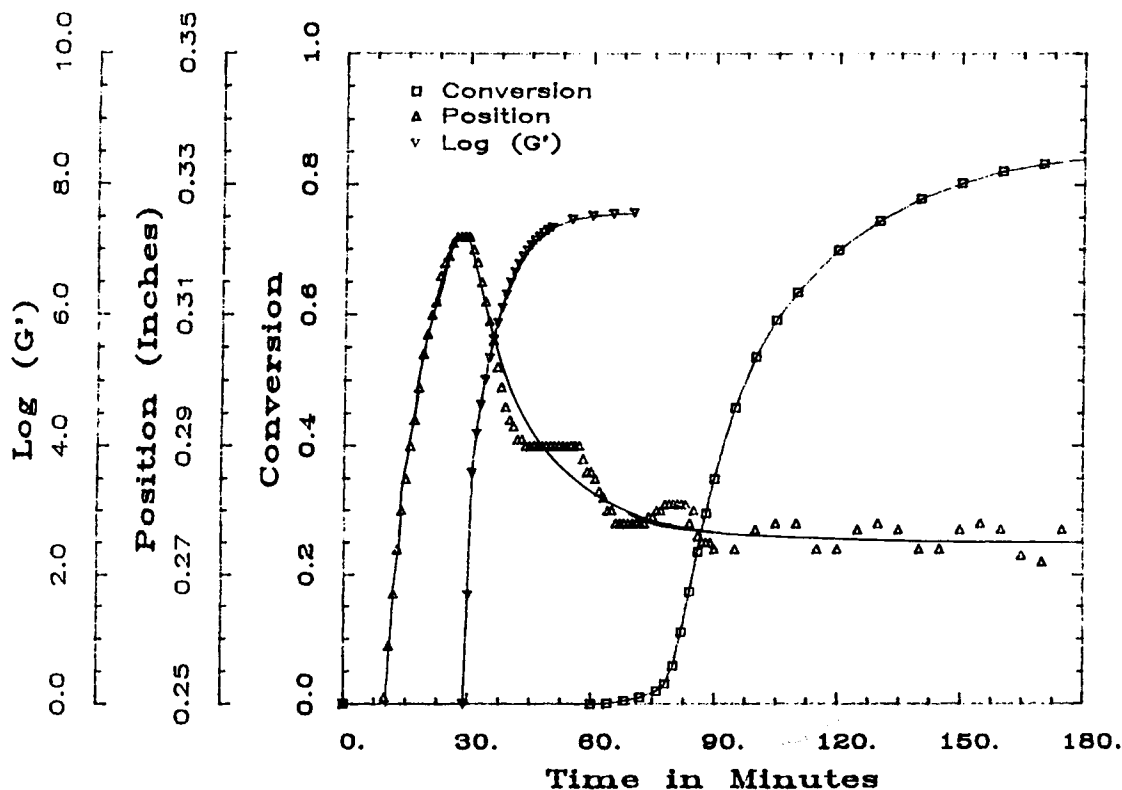
Figure 9 Interactions of gelation, conversion, and volume change of UPE resin with low molecular weight PVAc LPA.

heating bath between runs. (The heating bath used held the temperature constant ±2–3°C in the syringe apparatus, enough to cause the differences shown in Fig. 6.) For the high-pressure dilatometer, similar tests were performed. The repeatability was better because of better temperature control.

Finally, as a test of accuracy, an experiment was run on a well-documented reaction: styrene to polystyrene. Approximately a 10 g sample of styrene initiated with 6.7% benzol peroxide and inhibited with 0.23% benzoquinone was run at 80°C in the syringe dilatometer (inhibitor was used to delay the reaction until the dilatometer reached its operating temperature). Figure 7(a) is a plot of plunger position vs. time for both reaction and base line. For reaction, there was first an expansion due to heating of the dilatometer, oil, and sample. After heating, the position leveled off until the reaction started at around 50 min. On reaction, the volume change of styrene should be inversely proportional to conversion, and a shrinkage was measured between 50 and 200 min. After the reaction was completed, the plunger position leveled off. At 250 min, the heating bath was removed and the cooling bath installed. The dila-

tometer was cooled to its initial temperature. The entire process was repeated on the reacted system without disturbance or disassembly to find the base line.

Figure 7(b) is a plot of the styrene temperature vs. time. First, note that the initial and final temperatures were the same. This was important to assure that the final volume change was accurate. To obtain conversion as a function of time, a DSC scan was done using a heating profile, as shown by the heavy lines over the temperature data in Figure 7(b). The scan consisted of three regions: a faster temperature ramp, followed by a slower temperature ramp, and then followed by isothermal ramp.

By subtracting the base line from the cure line in Figure 7(a) and multiplying by several factors (inverse of sample volume, area of plunger, etc.), fractional volume change was found as a function of time. Figure 8 is a plot of fractional volume change and conversion (from DSC) vs. time for the styrene reaction. Note that the volume change is nearly inversely linearly proportional to the conversion for this system. The final volume change for polymerization (at 100% conversion) was reported to be

−14.5% in the literature.[10] From Figure 8, a final volume change of −12.05% was found at a final conversion of 83%. Assuming that conversion and volume change are linear for this system, the literature value for volume change at 83% conversion would be .83 times −14.5% or −12.04%. Thus, the literature value and the experimental value were very close and the dilatometer worked correctly.

Cure of UPE Resins

The application of dilatometry to the cure of an unsaturated polyester resin with different molecular weights of PVAc as the LPA and with no LPA is presented. Table I lists the results of the final volume changes measured for resins with and without LPA. The data show that the resin without the LPA shrank −6.5%, more than did the resin containing an LPA (as expected). For the given conditions, low molecular weight PVAc LPA provided the best volume control, with a shrinkage of 1.8%. The temperature used here was more relevant to low-temperature processes such as resin transfer molding (RTM) or hand lay-up and was much lower than that used in sheet molding compound (SMC) or bulk-molding compound (BMC) molding (i.e., 150°C). At higher temperatures, the effect of LPA may vary.

In the next several paragraphs, all the dilatometry profiles for materials shown in Table I will be presented. Interactions between conversion, gelation, microstructure formation, and volume change are also of interest; they are considered first. A comparison of LPA performance is then presented.

(i) Interactions of Conversion, Gelation, Microstructure Formation, and Volume Change

The interactions of volume change, gelation, conversion, and microstructure formation are especially useful in modeling the system and understanding the LPA mechanism. Figure 9 is a plot of conversion (squares), log G' (reverse triangle), and plunger position of the syringe dilatometer (triangle) vs. time for the UPE resin with low molecular weight PVAc LPA. Recall that G' and conversion were determined by RDA and DSC, respectively, using the same heating profile of the dilatometer.

The first point of interest in Figure 9 is that G' increased rapidly before any measurable conversion occurred. This means that liquid–solid transition occurred very early and that most of the reaction occurred as a gel or solid. (Recall that gelation was

assumed near the intersection of G' and G''. G'' was not plotted here because of crowding. The two intersected at 30 min in this case.)

Figure 10 is an SEM micrograph of the gel fraction of this resin cured to different conversions. Fig-
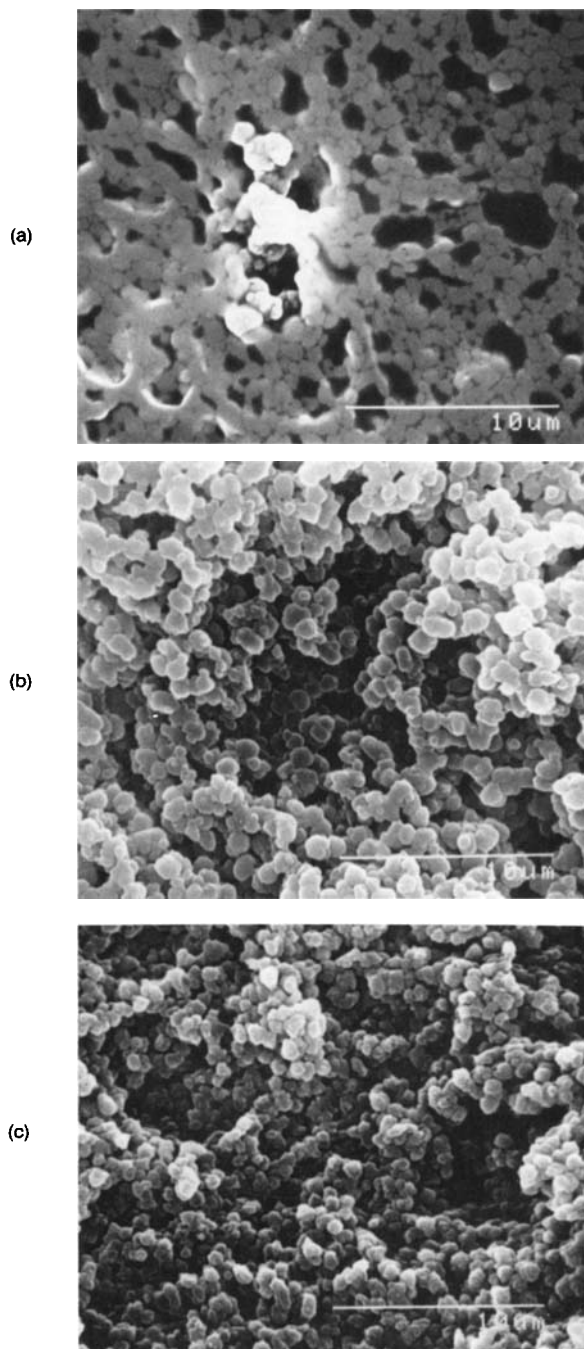

Figure 10   SEM micrographs of ST/UPE resins with 15% PVAc LPA: (a) before gelation, (b) at $G' = G''$ point, (c) final conversion.

ure 10 shows samples (a) before gelation, (b) at the $G' = G''$ point, and (c) after cure. Sample (a) was a nonuniform, translucent, fluidlike gel and sample (b) was a soft, translucent solid, whereas sample (c) was a rigid, opaque solid. Solvent etching dissolved nearly 90% of sample (a) and the remaining material formed a thin film on the bottom of the container. Solvent etching changed the shape of sample (b) slightly and dissolved 40–50% of the sample. Sample (c) was relatively inert to solvent etching with only a slight weight loss and little shape change.

All micrographs in Figure 10 show small compact particles covering the entire sample surface with particle diameter in the order of 0.5–1 micron. Particles could be seen even before the $G' = G''$ point. After the globule-type structures formed, the morphology of the sample showed little change during reaction except that the particles were more tightly packed in samples with higher conversions. The particle size remained relatively constant (0.5–1 micron) with a slight reduction (0.2 micron average) during cure.

Next, consider the plunger position curve. First, an expansion was measured. This was due to the heating period of the dilatometer. Note that the plunger position started at zero, but only the range of interest is plotted here. After heating, the position leveled off and started to decrease, meaning a shrinkage. Unlike the styrene reaction, the shrink-

age of UPE resin did not appear to shrink linearly with conversion. The periodic wave in the position was caused by the proportional temperature controller used on the heating bath. Comparing these shrinkages to the G' and conversion curves, one can see that the shrinkage, at first, was rapid and corresponded to the gelation and phase separation (i.e., particle formation), and, later, the shrinkage slowed, corresponding to the conversion. Note that at higher temperatures the G' and conversion curves may overlap and that the two stages may merge. However, more shrinkage should occur at the beginning of the reaction than toward the end. Similar results were also found when other types of LPA were used.[20]

To summarize, at 80°C, gelation and phase separation occurred very early in the reaction of UPE resins with LPA. The resins showed two phases of shrinkage during reaction: one that corresponded to the gelation and microstructure formation and one that corresponded to conversion.

(ii) Performance Comparison of Different LPAs at Low Pressures

Discovering that the UPE resin shrank nonlinearly (unlike the styrene results presented earlier), it would be interesting to compare different LPA systems, or lack thereof, and see how they affect the dilatometric profile. To begin with, a plot of the di-
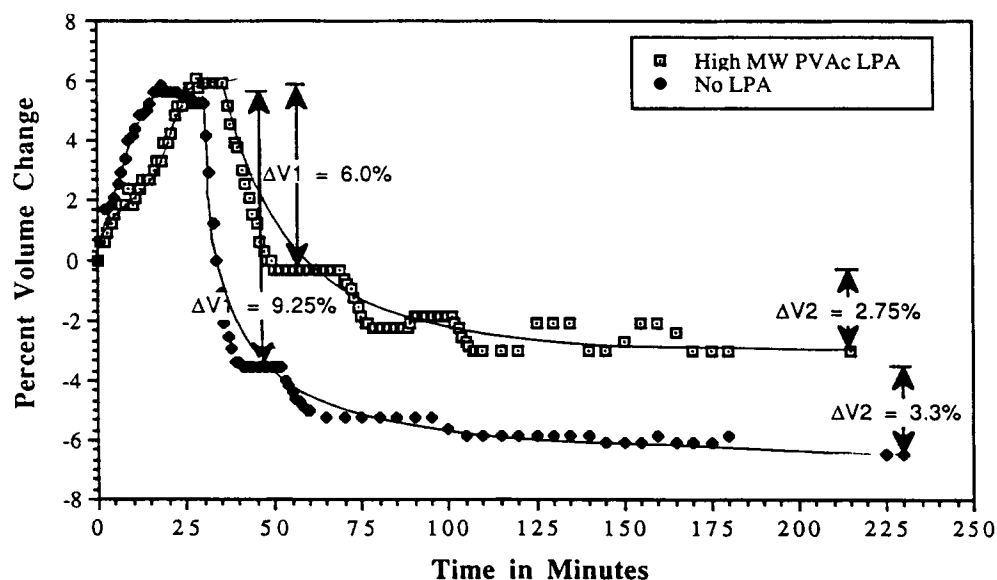

Figure 11   Comparison of dilatometric profiles of resin without an LPA and resin with high molecular weight PVAc LPA.

latometric profiles (percent volume change vs. time) of UPE without LPA and UPE with the high molecular weight PVAc is depicted in Figure 11. Again, both resins displayed the nonlinear shrinkage; nonetheless, substantial differences were apparent. Note that the volume change of each phase is given in Figure 11; $\Delta V1$ for the volume change corresponding to the initial shrinkage and $\Delta V2$ corresponding to the long-term shrinkage. While $\Delta V2$ was approximately the same for the two resins, $\Delta V1$ measured a significant difference of 3.25%, about the difference in final shrinkage measured. Figure 12(a) and (b) are SEM micrographs of UPE with and without an LPA. Note that without an LPA, the cured polymer is flakelike, and with an LPA, phase separation and particle formation occurred. Recall from the previous section that the LPA caused a phase separation and particle formation near the $G' = G''$ point, which corresponded to $\Delta V1$ or to the initial shrinkage. Therefore, the differences in $\Delta V1$ was due to the phase separation that compensated part of the volume change. Thus, from the results in Figure 11 combined with the findings mentioned earlier, it can be implied that the LPA mechanism occurred mainly at the beginning of the reaction and did not influence the second shrinkage stage too much for this system.

To compare high and low molecular weight PVAc LPAs, a plot of percent volume change vs. time is shown in Figure 13. One can see that the difference between the two resins occurred mainly in the early reaction (i.e., gelation and phase separation). Figure 12(b) and (c) are the SEM micrographs of the high and low molecular weight PVAc at $G' = G''$. Comparing the two micrographs, the high molecular weight PVAc yielded better phase separation and better-defined particles, yet from Figure 13, one can see that the volume control was better for the low molecular weight LPA. This contradicts the thought that better phase separation and particle formation yielded better volume control. Note, however, that the phase separation is an important, but probably not the only, factor in shrinkage control. Other researchers[17] have pointed out that several properties of LPA such as glass transition temperature, thermal expansion coefficient, and polarity all play important roles on the LPA mechanism.

(iii) The Effect of Pressure

To measure the effect of pressure on the volume change, high-pressure dilatometry was done on two identical samples (containing low molecular weight

PVAc) at a system pressure of 100 and 300 psi. This converts to a sample pressure of 75 and 225 psi. Figure 14 is a plot of percent volume change vs. time for both runs. One can clearly see that the difference
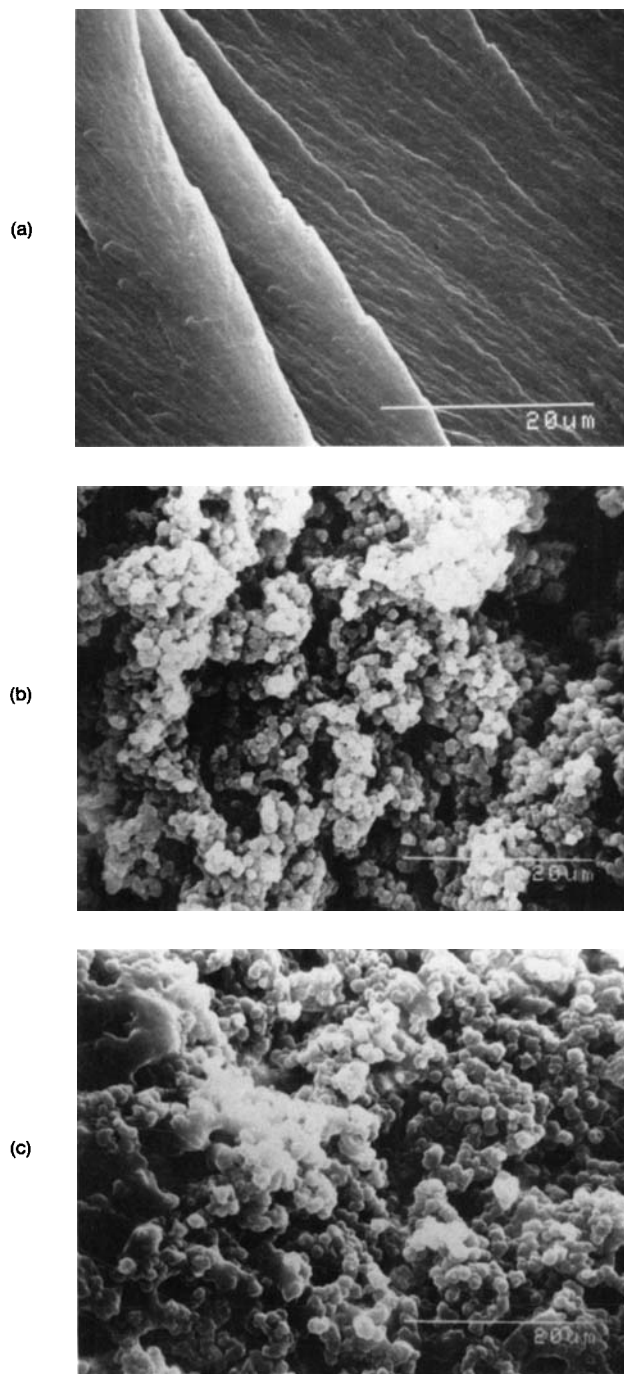
(a)

(b)

(c)

Figure 12   SEM micrographs of (a) resin without LPA, (b) resin with high molecular weight PVAc, and (c) resin with low molecular weight PVAc at $G' = G''$.
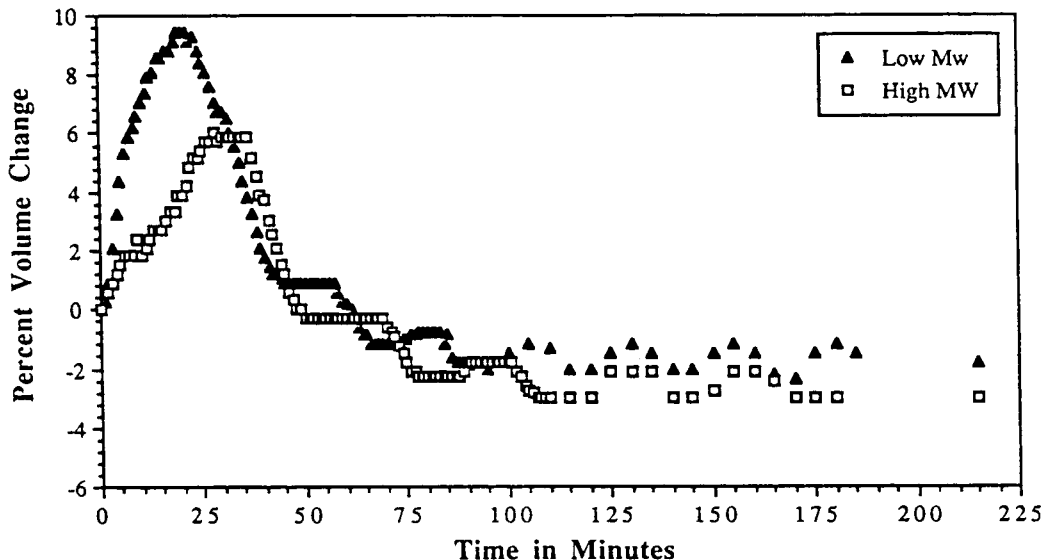
Figure 13   Comparison of dilatometric profile of resin with low molecular weight PVAc LPA and resin with high molecular weight PVAc LPA.

in pressure here did not cause too much difference in the data. The only difference is that the high-pressure run seemed to lag a little with respect to shrinkage starting time. This was a reported trend by other researchers.[21] A larger pressure difference may be needed to see a more significant difference in the data. Unfortunately, the current system is limited to 500 psi, as that is the upper limit on the hydraulic cylinder.

CONCLUSIONS

In this study, two dilatometers were presented: one made from a glass syringe and one made from a hydraulic cylinder. The limitations and advantages and calibration of each were given. The dilatometers were shown to be applicable to UPE resins. The effects of LPA and interactions between conversion,
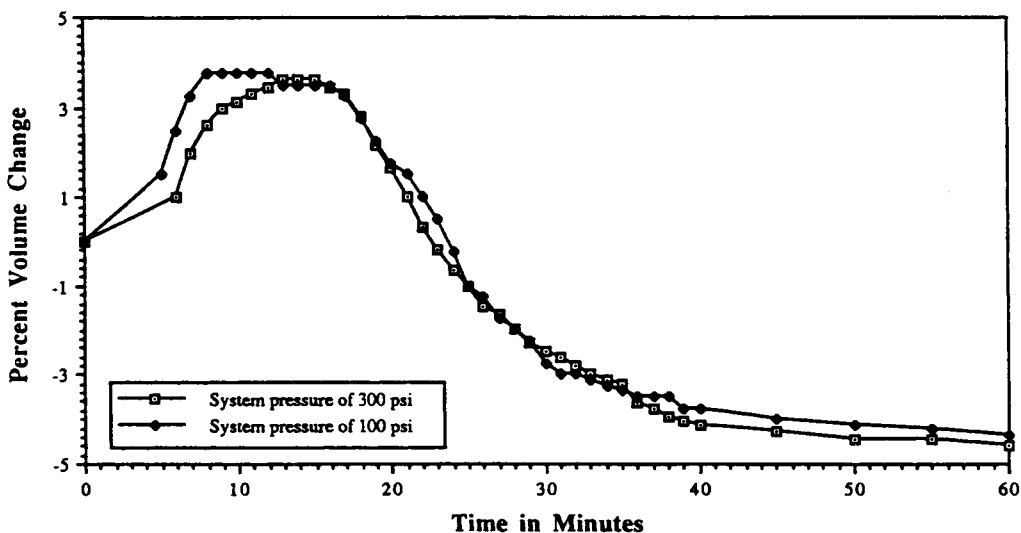

Figure 14   Comparison of dilatometer profiles at different pressure for resin with low molecular weight PVAc LPA.

microstructure formation, volume change, and rheological change were studied.

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