Control of Shrinkage and Final Conversion of Vinyl Ester Resins Cured in Low-Temperature Molding Processes

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ABSTRACT: Vinyl ester resin is a major thermoset polymer used in low-temperature composite manufacturing processes such as the Seemann composite resin infusion-molding process (SCRIMP). Volume shrinkage and residual styrene are important concerns for composites produced in such processes. A low-shrinkage additive (LSA) is a typical agent added to control the volume shrinkage of vinyl ester resins during molding. In this study, the effects of LSA content and the temperature profile (the temperature gradient and peak temperature) on the volume shrinkage control of a vinyl ester resin were investigated. The reaction kinetics of the resin system were also studied. We achieved good volume shrinkage control if we raised the curing temperature slowly to allow sufficient time for phase separation and if the curing temperature reached a high value after phase separation to allow microvoid formation. On the basis of experimental results, we designed an improved SCRIMP to increase resin conversion, reduce resin shrinkage, and produce composites with better properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1486–1496, 2003

Key words: vinyl ester; resins; additives; phase separation; thermosets

INTRODUCTION

Unsaturated polyester (UP) resins and vinyl ester (VE) resins are two of the most successful materials used in the fabricated composite industry. VE resins have excellent chemical and corrosion resistance coupled with outstanding heat performance, which makes them a good choice for fiber-reinforced polymer applications. The reactive unsaturation of VE resins is presented as terminal groups in the polymer, which can be crosslinked with vinyl monomers (e.g., styrene) in the same way as UPs. However, unlike conventional polyesters, UPs have no internal polyester linkages. Therefore, VE resins provide better corrosion resistance than UPs.[1–3] VE resins are amenable to most high-temperature processes, including the compression molding of sheet-molding compounds (SMCs), the injection molding of bulk-molding compounds (BMCs), and pultrusion. With a redox (reduction–oxidation) initiation system, VE resins can also be processed at ambient temperature via hand lay-up, spray-up, and vacuum-assisted resin-transfer molding (RTM) processes.

In recent years, many researchers have focused on the development of low-temperature and low-pressure fabrication techniques that can significantly reduce tooling costs. Techniques for low-cost composite manufacturing processes, such as the low-temperature, low-pressure compression molding of SMCs;[4,5] RTM; and vacuum infusion liquid composite molding [e.g., Seemann composite resin infusion-molding process (SCRIMP)[6,7]], have grown considerably in the industry. The molding temperature of these processes ranges from ambient temperature (e.g., SCRIMP) to 60°C (e.g., RTM) up to about 100°C (e.g., low-temperature SMCs). This range of temperatures is much lower than that of high-temperature processes, such as SMC compression molding (150°C) and BMC injection molding (≥ 150°C).

During curing, the typical volume shrinkage of VE resins is about 7–10%. The volume shrinkage resulting from polymerization reduces the dimensional accuracy of the molded products and may expose the fiber pattern on the composite surface. The fiber readout, together with other molding problems such as porosity, internal cracks, warpage, and poor dimensional accuracy, limits the usage of VE resin in many high-volume applications. The addition of low-profile additives (LPAs), that is, certain thermoplastics, can partially compensate or essentially eliminate the polymerization shrinkage of UP resins.[8] However, LPAs have been less effective with VE resins,[9] especially when curing occurs at low temperatures. Although thermoplastics used in VE resin systems do not show the same shrinkage-control efficiency as LPAs in UP resin systems, they can effectively reduce surface defects and internal stresses resulting from polymeriza-

tion shrinkage and improve the properties of the molded products. Therefore, they are usually called low-shrinkage additives (LSAs). Attempts have been made to improve the surface properties (reduced volumetric shrinkage) by the incorporation of special thermoplastics into the VE resin.[10] A saturated polyester formed from a dibasic acid and an ethylene oxide (EO)/propylene oxide (PO) block copolymer was developed for the shrinkage control of UP and VE resins.[10] The block copolymer had an EO/PO molar ratio ranging from about 0.1 to 0.9, and the polyester had an acid value of greater than about 10 thicken the SMC paste well. The authors concluded that for good physical properties and shrinkage control, the EO/PO block copolymer-based polyester was equally effective in the formulation of all VE resins, UP resins, or any combination of the two in high-temperature SMC processes. In the presence of filler, the volume shrinkage could be lower than 1% at 150°C. Other authors[11] found that volume shrinkage of the VE resin with filler and styrene–2-hydroxyethyl methacrylate copolymer (weight-average molecular weight = 220,000, an LSA with a specified hydroxyl, carboxyl, or amino functional group) could be reduced to 1.0%, and the cured sample showed no warpage. Although these studies demonstrated good shrinkage control of VE resins in high-temperature molding processes, there has been little work on the low-temperature curing of VE resin systems.

In addition to shrinkage control, residual styrene content or final conversion is recognized as an important issue in the low-temperature cure of VE resins. A low residual styrene content is important for both health considerations and the physical properties of the cured composite. When VE resins are cured at a low temperature by a redox (reduction–oxidation) initiation system, they cannot be fully cured under ambient conditions because of the low mobility of the crosslinked polymer chains. The reaction exotherm, due to polymerization at ambient temperatures, may cause a rise in the resin temperature, which accelerates the curing reaction.[12] A higher final conversion was obtained with high levels of peroxide in polyester resins cured at room temperature.[13] However, a high initiator content may sacrifice the molecular weight and mechanical properties of the cured resin and may shorten the gel time. A substantially long gel time is very important for mold filling and fiber wetting. Recently, more effort has been given to the design of efficient curing systems to achieve desired performance (i.e., high final conversion, long pot life, and short cycle time) in low-temperature molding processes.[14,15]

Generally, curing agents, like inhibitors or retarders, are needed to prevent premature gelation and provide a sufficiently long time for mold filling. However, in room-temperature processes where no external heat is applied, the addition of inhibitors or retarders results in a low curing rate and a long cycle time. The low curing rate prevents the accumulation of reaction exotherm, which in turn may lead to low resin conversion. Such a conflict (i.e., a long gel time in mold filling versus a high curing rate in mold curing) is a very critical issue in composite fabrication, especially for manufacturing large parts.

In a study of the redox initiation of t-butyl hydroperoxide in chlorobenzene,[16] the decomposition of the initiators was retarded by the addition of a millimolar amount of substances that provided strongly complex metal ions. For example, 2,4-pentanedione (2,4-P; acetylacetone), an enolizable β diketone, was incorporated into the redox initiation system at a level of 0.05–0.3% to retard the gelation of VE resins at low temperatures.[17–19] The gel time was extended by as much as 10-fold without adversely affecting the final cure and corrosion resistance of the finished composites.[17]

Also, the function of 2,4-P in UP and VE resins was found to be dependent on resin acidity.[14,19] For less acidic VE and UP resins, 2,4-P functioned as a retarder in the redox initiation. The nonacidic resin and 2,4-P may interact with the transition metal cations (e.g., cobalt ions) to form a six-membered chelate. This chelate ring is more stable than cobalt naphthenate (CoN). Consequently, the redox reaction between peroxide and cobalt ion becomes more difficult.[14] However, 2,4-P is a copromoter for acidic VE and UP resins because of the acid liability of cobalt acetylacetonate compounds. As a good retarder for nonacidic resins, 2,4-P is capable of extending the gel time for mold filling. When acid is added externally to nonacidic resins, 2,4-P functions as a copromoter. A resin design based on this concept was proposed,[14] in which 2,4-P was added to the resin system at a high content (i.e., 0.15%) to achieve a long resin gelation time. An acid, such as maleic anhydride (MA), was sprayed on the fiber mat. After mold filling, the acidity of the impregnated resins was changed, thereby altering the function of 2,4-P from a retarder to an accelerator. A shorter cure time and a higher final resin conversion were achieved through this method for both VE and UP resins.

In this study, the effects of LSAs and curing conditions on the shrinkage control of VE resin systems cured at low temperatures were investigated. To achieve this goal, we performed an integrated analysis, including a study of reaction kinetics, morphology, and volume change. We designed a low-temperature SCRIMP resin system to achieve good shrinkage control, long gel time, and a high final conversion.

EXPERIMENTAL

The VE resin used in this study was VER-E (Dow Chemical, Freeport, TX) with a high-polarity back-

bone. It was a methacrylated bisphenol and contained 50 wt % styrene, offering a styrene-to-VE C≡C bond ratio of about 4.2. The LSA was a low-molecular-weight polyurethane-based polymer. Methyl ethyl ketone peroxide (MEKP; Witco HiPoint 90, Greenwich, CT) and CoN (OMG Americas, Inc., Cleveland, OH) (Cobalt Octoate, CoOct, Pfaltz Bauer Chemicals, Waterbury, CT) were used as the low-temperature initiator and the promoter, respectively. N,N-dimethy-laniline (DMA) was used as the accelerator, and 2,4-P was added to provide adequate sample preparation time. The external acid applied during the SCRIMP was an acidic VE resin, VER-780 (Dow Chemical). The pH values of VER-E and VE-780, as measured in 10 wt % methanol solutions, were 6.6 and 2.9, respectively.

The volume shrinkage of the samples was measured by a dilatometer constructed in-house. The sample, weighing 5–6 g, was sealed in a polyethylene pouch and degassed *in vacuo*. A small hole was made at the edge of the pouch, and air bubbles inside the pouch that had been formed *in vacuo* were squeezed out. The pouch was heat-sealed again and placed inside the sample chamber of the dilatometer. The measurement was taken under a pressure of 0.69 MPa (100 psi) and at a prespecified temperature. More details regarding the construction and operation procedures of the dilatometer can be found elsewhere.[20,21]

The reaction kinetics were measured by a differential scanning calorimeter (DSC2910, TA Instruments, New Castle, DE). The sample was sealed in a hermetic aluminum sample pan, which could withstand a 2-atm internal pressure after sealing. After the reactant was mixed, about 10 mg of the sample was placed in a differential scanning calorimetry (DSC) pan. Isothermal runs were conducted at 35°C for a long enough time until no further reaction exotherm could be detected. The samples were then thermally scanned from 30 to 300°C at a heating rate of 5°C min^{-1} to determine the residual heat. The measured heat-flow data were then converted into conversion and reaction rates as a function of time, with constant thermophysical properties assumed.

The rheological changes during curing were measured with a Rheometrics mechanical spectrometer (Rheometric Scientific RMS-800, now part of TA Instruments, New Castle, DE). A set of parallel plates with an air oven as a heating chamber was employed. The diameter of the plates was 50 mm with a gap between them of 1 mm. The viscosity was measured under isothermal conditions (35°C) and at a shear rate of 1.0 s^{-1}. The *gel point* is defined as the point at which the reduced viscosity (η_r) reaches 10^3 Pa s ($\eta_r = \eta/\eta_0$, where η is the instantaneous viscosity and η_0 is the initial viscosity).

For the morphological measurements, a Philip XL-30 scanning electron microscope was used. The effective source or crossover of the field emitter (tung-
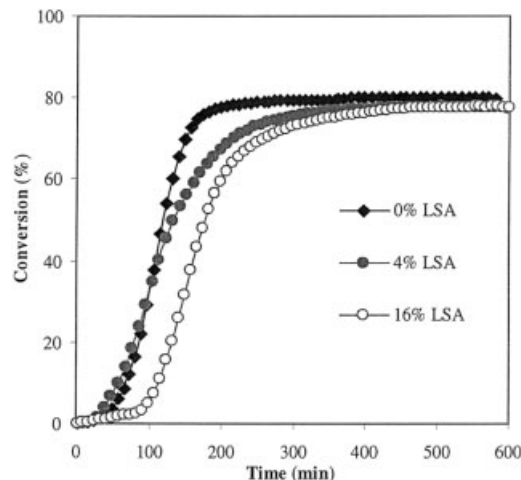
Figure 1 Conversion profiles of VER-E with various LSA concentrations cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

sten fiber) was about 10 nm. The sample cured in the dilatometer without solvent etching was gold-coated for morphological measurements. The fracture surfaces were observed under 10 kV of power. The magnification in this study varied from 2000 to 10,000× depending on the surface structure.

The surface quality of the molded samples was measured with a Federal's Surfanalyzer 4000 profilometer. The chosen tracing length was 25.4 mm. The *average roughness* (R_a), which is the arithmetic average height of surface irregularities measured from the mean line within the sample length, was used as a quantitative standard to compare the surface quality.

RESULTS AND DISCUSSION

### Volume shrinkage and the final conversion of vinyl ester resins with LSA

Effect of LSA content

To study the effect of LSA concentration on the shrinkage control and final conversion of the VER-E resin cured at low temperatures, a series of reactions was carried out isothermally at 35°C. All of the samples were cured with 0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP to ensure the desired reaction rate and with a long induction time for sample preparation in the dilatometry experiment. Figure 1 shows the resin conversion profiles versus time at various LSA concentrations. The reaction rates of the resin systems with more LSA were lower, but the final conversions at different LSA concentrations were about the same at around 80%. The dilatometry profiles in Figure 2 show that the volumetric shrinkage decreased as the LSA concentration increased. All of the samples (with varying amounts of LSA) exhibited different degrees of shrinkage but followed the same shrinkage pattern.
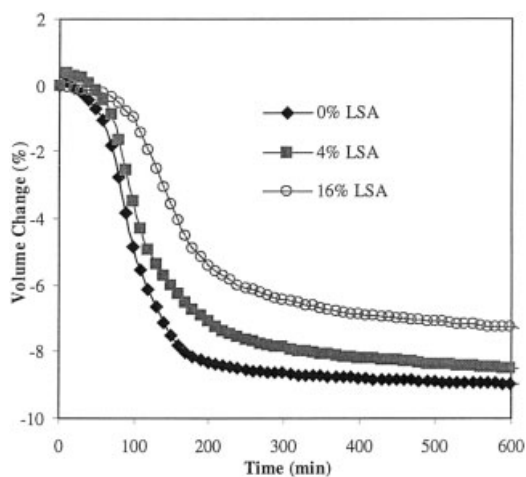
Figure 2 Volume change profiles of VER-E with various LSA concentrations cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

The sample without LSA had a final shrinkage of 9.07%. If LSA is considered a filler only, its effect on the volumetric change of VER-E resin is shown as the dashed line in Figure 3. The effect of LSA on the final shrinkage of samples cured isothermally at 35°C was only slightly better than that of the filler. In other words, the LSA acted almost like a filler. All of the samples with different LSA concentrations cured in the dilatometer at 35°C were translucent, implying that there were few microvoids inside the sample and, consequently, poor shrinkage control.[21] Figure 4 shows the SEM micrograph of the VER-E resin with 10% LSA cured isothermally at 35°C. The sample had a two-phase structure, where the continuous phase was a flake-like region and the dispersed phase consisted of small droplets with diameters ranging from 1 to 2 μm. Inside the droplets, tiny particles with diam-
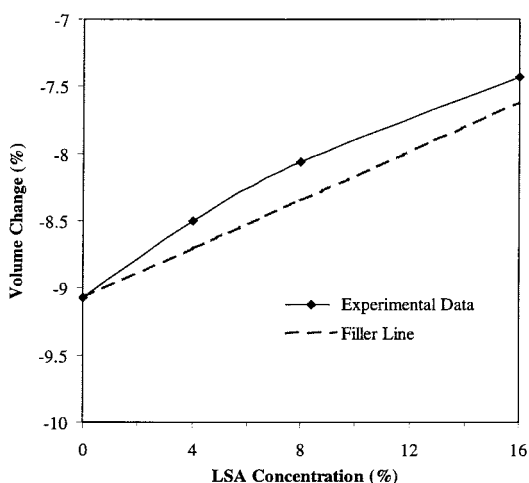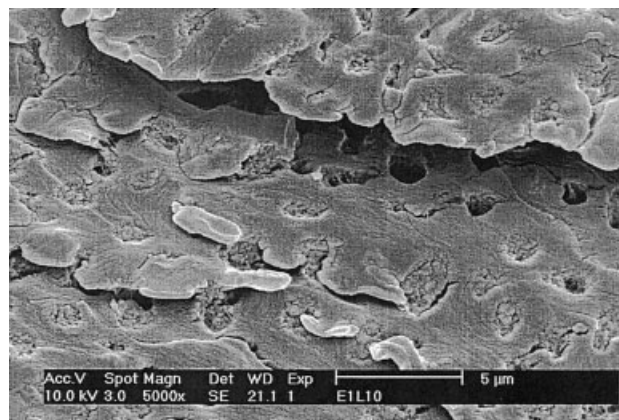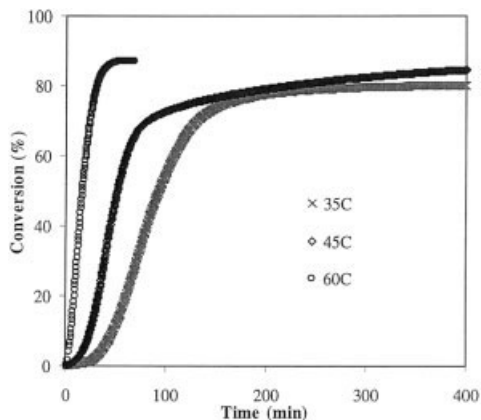

Figure 4 SEM micrograph of VER-E with 10% LSA cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

eters of less than 1 μm were found tightly packed and coagulated. The droplets were LSA-rich, whereas the flake-like region was VER-rich. As shown in the micrograph, the region where the LSA was effective was very small at this concentration level. This may be the reason why the volume shrinkage control was poor at these cure conditions.

The structure of UP and VE resins is important for shrinkage control.[22] Generally, the propylene glycol–maleic anhydride (PG–MA) type of UP resin responds well to LSAs. However, for UP resins containing orthophthalic acid or isophthalic acid units, LSAs are less effective. The VE resins, produced by the reaction of epoxy-resin-based bisphenol A with an unsaturated carboxylate, are considered the most difficult resins to interact with LSAs. The VER-E resin used in this study belonged to this group, and the experimental results confirm that the LSA was ineffective when the resin was cured isothermally at low temperatures. It was, therefore, a challenge to design proper curing conditions to improve the efficacy of the LSA in the VE/LSA system.

Effect of curing temperature

The effect of temperature on the shrinkage of the VER-E resin system with 10% LSA was investigated by dilatometry at various temperatures, that is, 35, 45 and 60°C isothermally. Figure 5 shows the conversion profiles of the resin system at different temperatures. As the reaction temperature increased, the final conversion reached a higher value, from 79.8% to 87.2%. The reaction also took place earlier, and the time required to reach the final conversion was reduced. However, early occurrence of the reaction is undesirable for mold filling and fiber wetting during the molding process. As seen in Figure 6, the volumetric shrinkage of the samples decreased slightly when the temperature was increased from 35 to 60°C. The volume change of the cured sample at 35°C was −7.83%,

Figure 3 Final volume change versus LSA concentration of VER-E cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).
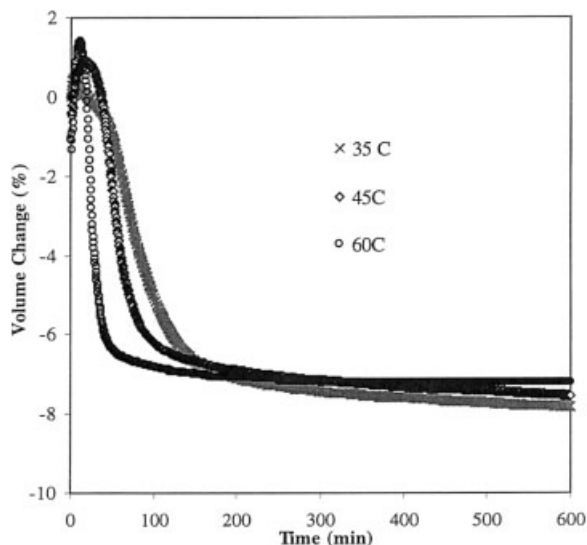
Figure 5 Conversion profiles of VER-E with 10% LSA cured at different temperatures (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

whereas that at 60°C was −7.21%. However, when the resin system was cast in a 35°C oven, it showed a significant change in appearance (it turned white) compared to the sample cured at 35°C isothermally in the dilatometer (it remained translucent). To determine the volume shrinkage of the sample cured in the oven, a density measurement method was applied in this study. The density of the cured sample (ρ_s) and the volume change were calculated according to the following equations:

$$\rho_s = \rho_{H_2O} \times W_s / (W_s - W_w)$$

$$\text{Volume change (\%)} = (\rho_{s0}/\rho_s - 1) \times 100$$

where ρ_{s0} is the theoretical density of the resin system before cure, ρ_s is the density of the resin system after

Figure 6 Volume change profiles of VER-E with 10% LSA cured at different temperatures (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

TABLE I
Comparison of the Final Volume Changes for VER-E with Various LSA Concentrations Cured at 35°C Taken with Density and Dilatometry Measurements

	Volume change (%)	
LSA (%)	Density measurement	Dilatometry measurement
0	−8.4	−9.07
4	−7.6	−8.51
10	−6.8	−7.96
16	−5.4	−7.43

2,4-P = 0.045%, DMA = 0.2%, CoN = 0.1%, and MEKP = 0.5%.

cure, ρ_{H_2O} is the density of water at 25°C, and W_s and W_w are the sample weights in air and in water, respectively. Table I summarizes the volume change of the VER-E resin with different LSA contents cured at 35°C, determined by both the dilatometer and the density measurement methods. The final volume change measured by the density method was slightly less than that measured with dilatometry, but the trend was similar. Therefore, the density measurement method could be used as a characterization method to quantify the final volume change of the cured samples.

The volume change of the sample cured at 35°C in the oven was only −2.4%, whereas it was −6.8% when the sample with the same formulation was cured in the dilatometer at the same temperature (both were measured by the density measurement). The major difference between the two cases was the temperature profile. For samples cured in the dilatometer, the temperature was kept constant at 35°C. While in casting, the sample temperature was not controlled and could reach as high as 110°C in the center. This difference in thermal history may explain why the samples exhibited very different volume shrinkage control.

To investigate the effect of temperature profile on curing, an isothermal mode and a ramp mode were combined in a dilatometer experiment to create a temperature profile similar to that in the casting process. The results are shown in Figure 7. The volume of the sample decreased first because of polymerization shrinkage. When the temperature reached the maximum value (at 40 min), a volume expansion was observed. This expansion compensated for most of the polymerization shrinkage, and the VE resin with LSA ended with only 3.20% final shrinkage (instead of 8–9% as in the isothermal cases). The final shrinkage determined by the density measurement was 2.60%, which agreed fairly well with the dilatometry result. Therefore, the efficiency of the LSA depended greatly on the thermal history of the resin system.

To further understand the effect of thermal history during sample curing on the shrinkage control of the

resin system, we measured the volume change of samples that had the same formulation but were cured at different ramping rates and peak temperatures. All of the samples were sealed in thin plastic pouches (0.05 mm thick) and heated from room temperature to a prespecified temperature (40, 60, or 80°C) in a water bath at different heating rates from 0.34 to 14°C min^{-1}. The temperature was then maintained at the prespecified value, and the resin was allowed to react for 5 h. As shown in Table II, the samples cured at a low heating rate turned cloudy (i.e., phase separation) before the temperature reached the peak temperature, and these samples showed good shrinkage control (i.e., low volume shrinkage). The larger the temperature difference was between the cloudy point and the peak temperature, the better the shrinkage control was.

SEM micrographs of all of the samples are shown in Figures 8–10. At a prespecified curing temperature of 80°C, the samples had a particulate structure independent of the heating rate. However, when the heating rate was 12°C min^{-1}, the particles tended to coagulate tightly in many cases. Some samples showed a loosely packed particulate structure (Fig. 8). When the samples were cured at 60°C at different heating rates, the sample morphology was also particulate-like, except the particle size and packed patterns were different (Fig. 9). At a high heating rate, the particles became smaller and were packed together more tightly, whereas at a low heating rate, the particles were larger and more loosely packed.

The morphology of the samples cured at 40°C was different from the samples cured at 60 and 80°C. The particles were less identifiable (Fig. 10). However, the samples cured at a low heating rate still provided good shrinkage control. From these results, more uniform and loosely packed particulate structures could be developed at a low heating rate. At high heating
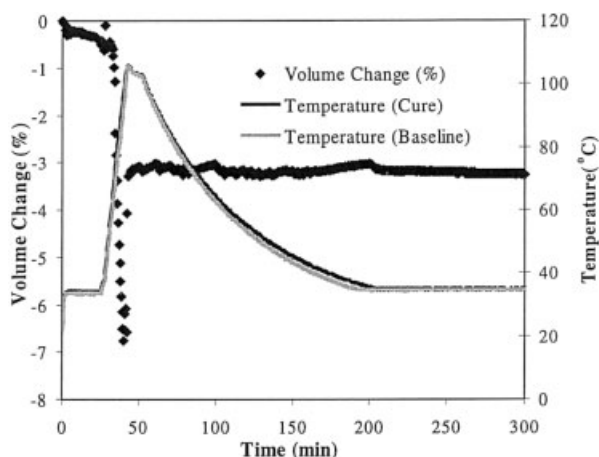
TABLE II
Volume Shrinkage of VER-E with LSA Under Various Temperature Profiles

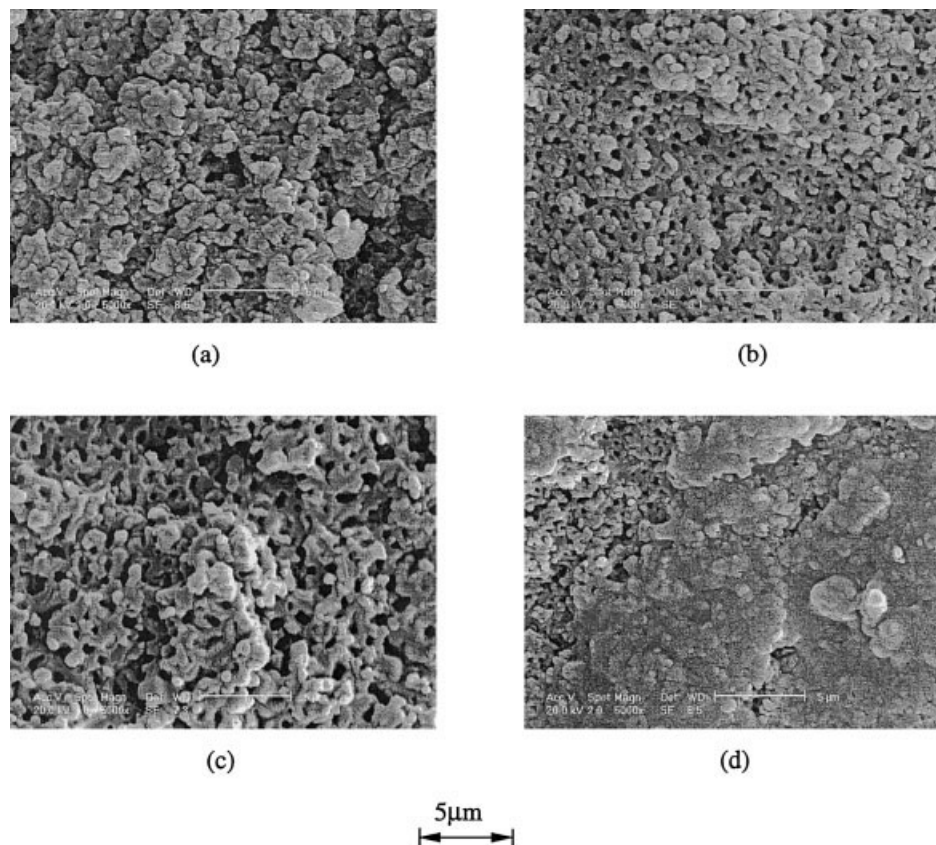| Peak temperature (°C)	Heating rate (°C min^{-1})	Cloudy temperature (°C)	ΔT (°C)	Volume change (%)
80	1.7	50	60	3.00 ± 0.0
	4.5	55	25	3.00 ± 0.0
	6.4	70	10	3.00 ± 0.0
	12	80	0	−4.19 ± 0.42
60	4.7	55	5	1.9 ± 0.29
	8.5	60	0	0.39 ± 0.05
	14	60	0	−2.99 ± 0.01
40	0.34	33	7	3.00 ± 0.0
	0.92	38	2	1.75 ± 0.02
	2.54	40	0	−0.94 ± 0.21

ΔT = temperature difference between the peak temperature and the temperature when the sample turned cloudy.
LSA = 10%, DMA = 0.2%, CoOct = 0.3%, and MEKP = 1.0%.

rates, the reaction rate may be too high to achieve a well-developed particulate structure. The LSA used in this study was a low-molecular-weight polyurethane-based polymer, which had a glass-transition temperature lower than room temperature. Therefore, the thermal expansion of the LSA during polymerization may have played a very important role. At low heating rates, the temperature gap between the onset of phase separation and the peak temperature was large, which allowed the LSA's large thermal expansion within a large and loosely packed particulate structure in the LSA-rich phase to initiate and propagate microcrack during polymerization.[20] This provided good volume shrinkage control. The temperature ramping also provided a higher level of polymerization-induced internal stresses than in isothermal cases because of the fast reaction facilitating microcrack formation. The detailed mechanism of volume shrinkage control needs to be further investigated.

SCRIMP

The above experimental results show that good volume shrinkage control could be achieved if the temperature was raised slowly to allow phase separation and if the temperature reached a high value after phase separation to allow microvoid formation. However, in actual low-temperature molding processes such as SCRIMP, it is not easy to achieve such a temperature profile because there is no external heating source. The temperature profile depends mostly on the resin reaction kinetics. It would be desirable if the reaction exotherm could be accumulated in the composite. In this way, a higher temperature could be reached during curing, accelerating the curing rate of the composite. This would then produce more heat and a high peak temperature, which would not only


Figure 7 Volume change profile of VER-E with 10% LSA cured nonisothermally in the dilatometer (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

Figure 8 SEM micrographs of VER-E with 10% LSA cured at 80°C at heating rates of (a) 1.7, (b) 4.5, (c) 6.4, and (d) 12°C min^{-1} (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

benefit the shrinkage control of the resin system but would also drive the reaction to completion. However, the SCRIMP is typically used for making large composite parts. Therefore, the resin gel time needs to be long for complete mold filling and good fiber wetting. To prevent premature gelling, a certain amount of inhibitor or retarder is often added to the resin system to prolong the resin gel time. This results in a low curing rate, which prevents the accumulation of reaction exotherm because of heat dissipation to the surroundings. Consequently, poor shrinkage control, low resin conversion, and high residual styrene would result. It would be desirable if the resin system could be designed in such a way that the gel time was long during mold filling, the curing rate was low initially but became high later and the system could reach a high temperature during curing.

In nonacidic VE or UP resin systems, 2,4-P was found to function as a retarder that provides a longer gel time but a lower reaction rate.[14,19] However, 2,4-P works as a copromoter in acidic resin systems, which results in a shorter gel time but a higher reaction rate. The addition of external acids into the nonacidic resins to change the acidity of the resin system may also turn 2,4-P from a retarder to a copromoter. Some researchers applied this concept to the design of a better low-

temperature resin system by spraying an external acid on the fiber mats instead of premixing the acid with the matrix resins.[14] The gel time can be extended by the addition of 2,4-P as a retarder in a nonacidic resin. Once the resin flows through the fiber reinforcement, it dissolves the presprayed acid. The dissolved acid can then increase the acidity of the resin system, changing the function of 2,4-P from a retarder to a copromoter. We adopted this idea to develop a low-temperature SCRIMP resin system that allowed good surface quality (shrinkage control) and low residual styrene of molded VE composites.

VER-E was a nonacidic resin (pH = 6.6 measured in a 10% methanol solution). The effect of the 2,4-P content on the reaction rate was studied by DSC at 35°C isothermal cure. As shown in Figure 11, the initial reaction rate decreased as the content of 2,4-P increased. Although the maximum reaction rate tended to be slightly higher when 2,4-P was added, the gel time increased as more 2,4-P was added. As shown in Figure 12, the gel time of the resin system was extended from 19 to 32 min when 0.15% 2,4-P was added into the resin system. It is clear that 2,4-P could be used as a retarder to adjust the gel time and initial reaction rate of the VER-E resin.
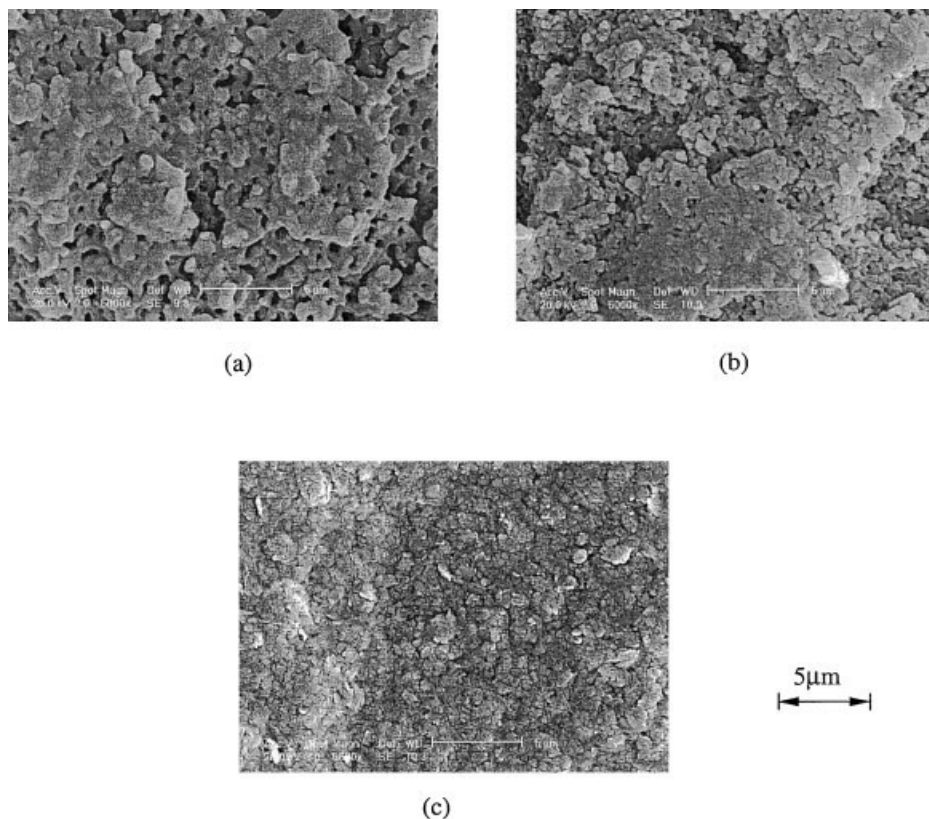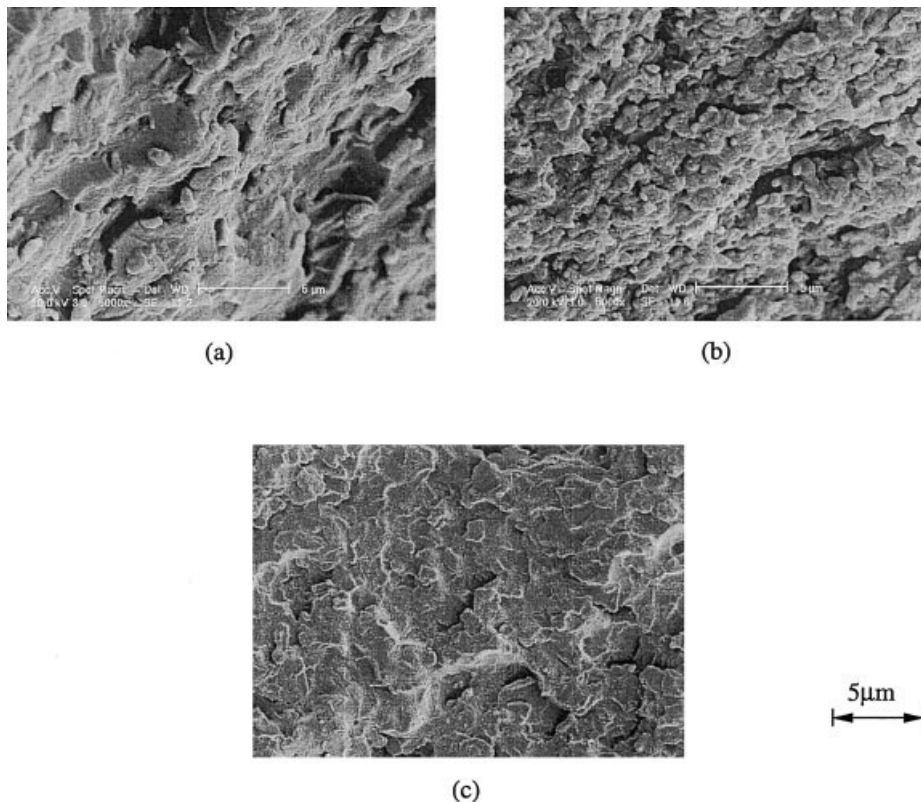
Figure 9 SEM micrographs of VER-E with 10% LSA cured at 60°C at heating rates of (a) 4.7, (b) 8.5, and (c) 14.0°C min^{-1} (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

Figure 13 shows the resin system cured at 35°C with 0.1% 2,4-P but with different external acids: MA (Aldrich Chemical, Milwaukee, WI) and VER-780 (Dow Chemical, Freeport, TX). These two acids were chosen because they dissolved in the VER-E resin easily. MA is a small-molecule acid, whereas VER-780 (solid) is an epoxy-based dimethacrylate VE prepolymer with a grafted acid functional group. The results show that the initial reaction rate increased if either of these two acids was added into the resin system. As more MA was added into the resin system with 2,4-P, the reaction rate became higher. Also, the addition of VER-780 was not as effective as the addition of MA. This was because VER-780 is a prepolymer with a lower acid number per unit mass than MA. As shown by the results presented in the previous section, a slow reaction before phase separation and a high temperature after phase separation were essential for good volume shrinkage control of the VER-E resin. On the basis of these observations, a new SCRIMP design was developed, in which 2,4-P was added to the nonacidic VE resin (with a LSA) to serve as a retarder. This design provided a long gel time for mold filling and a low initial reaction rate for phase separation. An external acid, VER-780, was distributed on the fiber mats uniformly during preform preparation to serve as a binder. As the resin was infused into the mold and the

VER-780 binder was slowly dissolved into the VER-E resin, the resin acidity increased. 2,4-P then became a copromoter during curing to fasten the curing rate. This could lead to a higher peak temperature, which is critical for good shrinkage control. The resin conversion could also increase (i.e., less styrene residue) because of the higher reaction exotherm.

To verify this design, a series of SCRIMP experiments were carried out. Two molding temperatures were chosen: one was room temperature (26°C), and the other was 42°C to simulate the molding temperature in the summer. The experimental set-up is shown in Figure 14. Ten layers of dry glass fiber mats (QM6408 from Brunswich Technologies, Inc., Brunswick, ME) were laid upon a glass plate. The fiber stack was covered by a polyester film to form a vacuum bag whose outer edges were sealed by tacky tape. A resin inlet and a vacuum outlet on opposite ends of the mold were also formed. The resin was first stored in a tank. The initiator was added to the resin system immediately before mold filling. During molding, a vacuum was applied through the outlet, which forced the bag to press tightly against the fiber stack. The liquid resin was introduced into the inlet through a supply line and cured in the vacuum bag for 24 h. The gel time of each resin system was measured at molding temperatures in a vial (25 mm in diameter) con-

Figure 10 SEM micrographs of VER-E with 10% LSA cured at 40°C at heating rates of (a) 0.3, (b) 0.9, and (c) 2.54°C min^{-1} (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, and 0.5% MEKP).

taining 10 g of sample. The residual activity of the molded composite parts was examined 2 days after molding by DSC in the scanning mode at 5°C min^{-1} from room temperature to 300°C on the basis of a total reaction exotherm of about 360 J/g. Three samples were taken at the surface of each part, and the average value was calculated. In the cases where an external acid was introduced into the molding system, 5 wt %

VER-780 based on the resin weight of the molded panel was distributed uniformly on the fiber mat. First, the prepolymer VER-780 was dissolved in acetone, and the fiber mats were soaked in the solution for 24 h. The mats were then dried in a vacuum oven at 40°C for 24 h to remove the acetone.
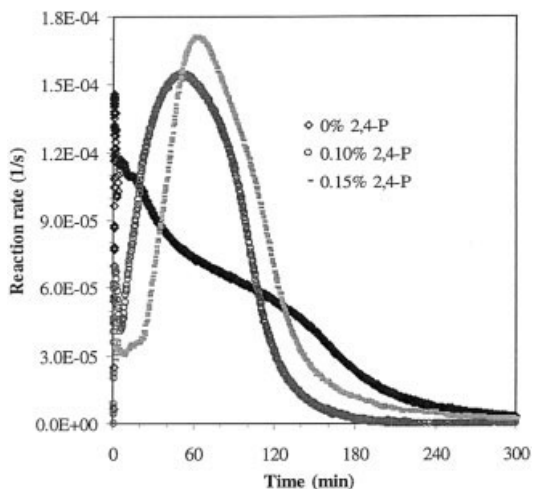
Figure 11 DSC isothermal reaction rate profiles of VER-E with different 2,4-P concentrations cured at 35°C (0.3% CoOct and 2.0% MEKP).
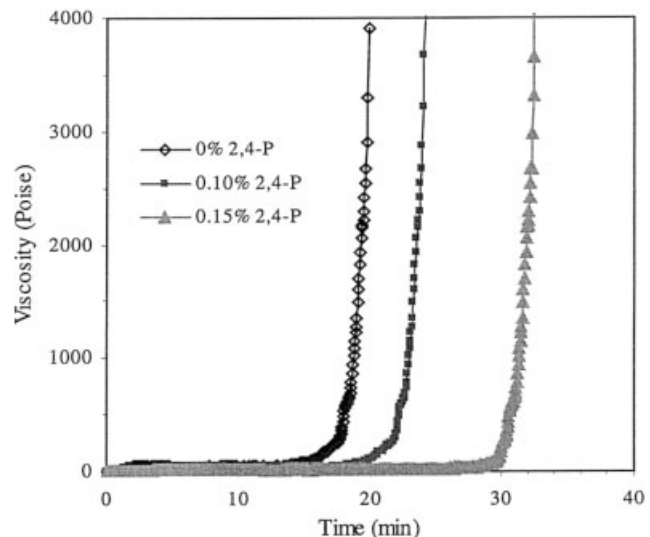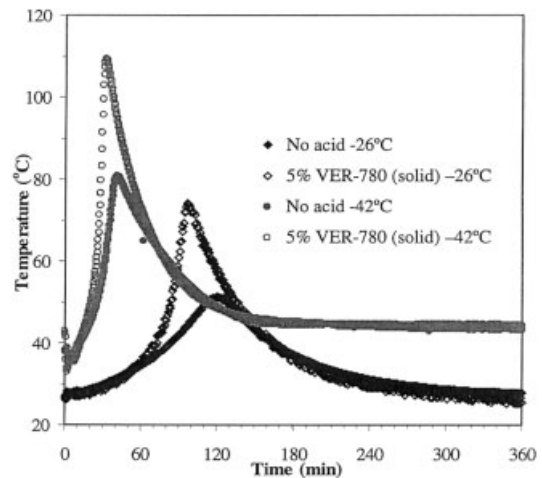

Figure 12 Viscosity change of VER-E with different 2,4-P concentrations cured at 35°C (0.3% CoOct and 2.0% MEKP).
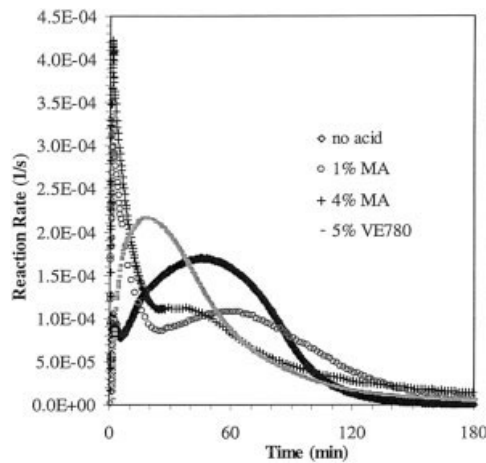
Figure 13 Effect of external acid on the DSC isothermal reaction rate profiles of VER-E with 0.1% 2,4-P cured at 35°C (0.3% CoOct and 2.0% MEKP).

Figure 15 Effect of VER-780 on the temperature profiles in the SCRIMP of VER-E resins (0.1% 2,4-P, 0.3% CoOct, and 2.0% MEKP).

Figure 15 shows the temperature profiles during SCRIMP of the VER-E resin with and without VER-780. The temperature profiles showed little difference because of the presence of VER-780 on the fiber mats in the first 10 min at 42°C cure and the first 50 min at 26°C cure. This was because VER-780 needed time to dissolve into the matrix resin to change its acidity. The dissolved VER-780 then led to a rapid temperature rise because of the copromoter nature of 2,4-P in the acidic resin system. The maximum temperature increased from 52 to 73°C during SCRIMP at a 26°C initial temperature and from 80 to 109°C at a 42°C initial temperature. Because VER-780 was distributed on the fiber mats before mold filling, the gel time was not affected. As shown in Table III, the gel time for systems with and without VER-780 was the same, that is, 36 min at 26°C and 15 min at 42°C. In both SCRIMP cases, a higher final conversion was achieved when VER-780 was introduced into the molding system. The increase of the final conversion was the result of a higher cure temperature inside the mold. The surface quality of the molded panel was also improved by the addition of VER-780 at low-temperature molding;

however, no improvement was observed at 42°C. The higher cure temperature may have resulted in too-high initial reaction rate that affected the phase separation and microstructure formation as discussed earlier. Although a higher peak temperature was reached at a higher initial molding temperature, the microvoid formation for shrinkage compensation may have suffered if there was not a good enough phase separation in the early stage of curing. Among the four SCRIMP cases, the one with VER-780 cured at a low initial temperature provided the best surface quality, whereas the one with VER-780 cured at 42°C provided the highest resin conversion.

CONCLUSIONS

In this study, the shrinkage control of a VE resin with LSA cured at low temperatures was investigated. Volume expansion did not occur for samples cured isothermally with different LSA concentrations. However, a large volume expansion was observed for samples cured nonisothermally. These results suggest that
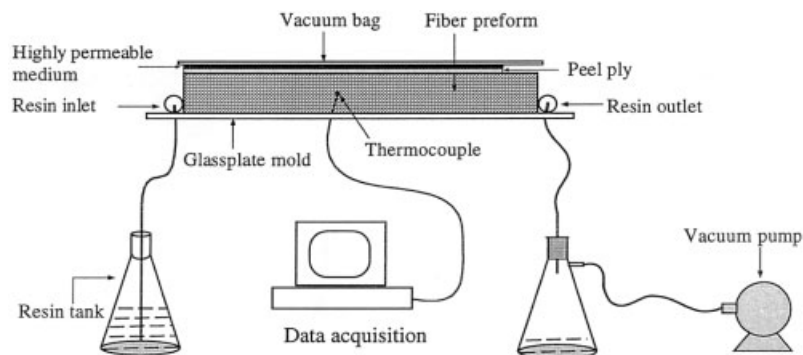
Figure 14 Schematic of experimental set-up for the SCRIMP.

TABLE III
Effect of VER-780 on the Final Conversion and Surface Quality of Molded Panels in the SCRIMP of VER-E Resins (0.1% 2,4-P, 0.3% CoOct, 2.0% MEKP)

	26°C		42°C	
	No acid	5% VE-780	No acid	5% VE-780
Gel time (min)	36	36	15	15
Peak temperature (°C)	51.1	73.3	80.3	108.9
Peak time (min)	123.3	98.3	43.8	31.7
Residual heat (J/g)	60.5	38.1	36.7	23.3
Final conversion (%)	83.2	89.4	89.8	93.5
R_a (μm)	0.70	0.22	0.30	0.36
SD (μm)	0.19	0.11	0.19	0.19

R_a: Average surface roughness. SD = standard deviation of R_a; 2,4-P = 0.1%, CoOct = 0.3%, MEKP = 2.0%.

the temperature profile had a strong effect on shrinkage control. The temperature gradient affected the rate and degree of phase separation, which was critical for microvoid formation and volume shrinkage compensation during curing. A low initial heating rate and a high peak temperature during curing were the most desirable for shrinkage control. This observation was applied to the design of a better SCRIMP resin system for VE resins. 2,4-P was added into the resin to achieve a long resin gelation time. An acidic resin, such as VER-780, was distributed on the fiber mat. After mold filling, the acidity of the impregnated resins was changed, which altered the function of 2,4-P from a retarder to an accelerator. This resulted in a high reaction exotherm, which led to a higher final resin conversion and better shrinkage control.

References

1. Bruins, P. F. Unsaturated Polyester Technology; Gordon and Breach Science: New York, 1976.
2. Juska, T. D.; Puckett P. M. Composites Engineering Handbook; Marcel Dekker: New York, 1996; Chapter 3.
3. Encyclopedia of Chemical Technology; Grayson, M.; Eckroth D., eds.; Wiley: New York, 1996; Vol. 19, p 654.
4. Gaspari, J. D. Plast Technol 1996, Jan., 21.
5. Atkins, K. E.; Behar, G.; Seats, R. L.; Reid C. G. Presented at the 51st Annual Conference of Reinforced Plastics/Composites Institute, Society of Plastics Industry, Cincinnati, OH, 1996; Section 2D.
6. Seemann, W. H. U.S. Pat. 4,902,215 (1990).
7. Lazarus, P. Int SAMPE Symp 1996, 41, 1447.
8. Arakawa, K.; Iwami, E.; Kirnura, K.; Momaguchi, K. 47th Annual Conference of Reinforced Plastics/Composites Institute, Society of Plastics Industry, 1992; Section 1A.
9. Lin, T. S. 45th Annual Conference of Reinforced Plastics/Composites Institute, Society of Plastics Industry, 1990; Section 6E.
10. Chang, K. K.; Tufts, T. A. U.S. Pat. 5,116,917 (1992).
11. Chiyou, I.; Watanabe, M.; Tanaka, S.; Hayashi, S. Jpn. Pat. 154,295 (2000).
12. Technical Information: Thermoset Polymers; Dow Chemical Co., Midland, MI, 1989.
13. Roskott, L.; Groenendaal, A. A. M. 33rd Annual Conference of Reinforced Plastics/Composites Institute, Society of Plastics Industry, 1978; Section 5B.
14. Li, L.; Lee, L. J. Polym Compos 2002, 23, 971.
15. Fujii, S. Jpn. Pat. 030,123 (2002).
16. Hiatt, R.; Irwin K. C.; Gould, C. W. J Org Chem 1968, 33, 1430.
17. Brinkman, W. H.; Damen, L. W. J.; Maira, S. Mod Plast 1968, Oct., 67.
18. Chetakian, E., U.S. Pat. 3,630,960 (1971).
19. Heck, H. G.; Moore, C. H.; Lingley, N. L. World Organization Pat. WO 84/00765 (1984).
20. Kinkelaar, M. R.; Lee, L. J. Polym Eng Sci 1992, 45, 37.
21. Li, W.; Lee, L. J. Polymer 2000, 41, 685.
22. Atkins, K. E. In Sheet Molding Compounds: Science and Technology; Kia, H., Ed.; Hanser: New York, 1993.