

# Comparison of Unsaturated Polyester and Vinylester Resins in Low Temperature Polymerization

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**ABSTRACT:** Many composite products are produced at low temperatures in processes such as resin transfer molding (RTM), vacuum infusion molding (e.g., Seemann Composite Resin Infusion Molding Process—SCRIMP), and hand lay-up. These processes are widely used for marine, civil infrastructure, transportation and defense applications. Unsaturated polyester and vinylester resins are two major resins used in these processes due to their low cost, good performance, and processibility. In this study, the reaction kinetics and rheological changes of these two resins cured at low temperatures were studied. Effects of resin type, initiator, promoter, inhibitor and retarder on the reaction kinetics and rheological behaviors were examined using a Differential Scanning Calorimeter (DSC) and a Rheometrics Dynamic Analyzer (RDA). A model was developed to quantify the effects of resin type, temperature, and different curing agents on the gel time for both polyester and vinylester resins cured at low temperatures. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1230–1242, 2001

**Key words:** unsaturated polyester resin; vinylester resin; reaction kinetics; rheological behaviors; low temperature polymerization; SCRIMP

## INTRODUCTION

In recent years, Vacuum-Assisted Resin Transfer Molding (VARTM) processes have gained attention in the composite industry, because they can yield large-sized composite products at low cost. VARTM processes can reduce styrene emissions and attain high fiber contents, which are only slightly lower than those of prepreg fabrics.<sup>1</sup> The Seemann Composites Resin Infusion Molding Process (SCRIMP) is a new type of VARTM. Composites made by SCRIMP are replacing large steel, wood, and concrete structures in boxcars, ferries, highway bridges, and other applications.

However, the process is time-consuming and requires large quantities of raw materials. For proper design and optimization of SCRIMP, the reaction kinetics and rheological behaviors of different types of resins need to be studied in depth.

Unsaturated polyester resins are step-growth products formed by unsaturated and saturated diacids or anhydrides with difunctional alcohols.<sup>2</sup> They have good mechanical properties and weather resistance, and are widely used in the composite industry. They can be easily handled, pigmented, filled, and fiber-reinforced in liquid form. The oxide process using various epoxides and ethylenically unsaturated monocarboxylic acids results in vinylester resins, which have greater toughness and excellent chemical/corrosion resistance.<sup>2</sup> Vinylester resins have terminal carbon–carbon double bonds, and hence, are more reactive than unsaturated polyester resins, which

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contain internal carbon-carbon double bonds. Both resins are usually diluted by adding a low molecular weight comonomer (i.e., styrene) to adjust the viscosity of the mixture. The reaction in these two resins is a free radical chain-growth copolymerization between the styrene monomer and the unsaturated vinylene molecules. The crosslink through the C=C double bonds produces a three-dimensional network structure.

To cure polyester and vinylester resins at room temperature, initiators and promoters are used to generate free radicals through redox mechanisms. The most common source of free radicals, which are needed to initiate the curing reactions in polyesters and vinylesters, is methyl ethyl ketone peroxide (MEKP). The polyester-grade MEKP contains monomer, dimer, and hydrogen peroxide, while the vinylester-grade MEKP is predominantly the dimer because MEKP monomer and hydrogen peroxide tend to cause foaming if used with vinylesters.<sup>3</sup> Promoters, usually cobalt octoate or cobalt naphthenate, are required to cure polyester or vinylester resins at low temperatures because they decompose the initiators rapidly at ambient conditions.

Inhibitors and retarders are also used in SCRIMP. Inhibitors consume free radicals and delay the onset of curing reactions, thus increasing the storage life of resins. Commonly used inhibitors include hydroquinone, 1,4-benzoquinone, *t*-butyl catechol and oxygen. The function of retarders is to reduce the curing rate. A commonly used retarder for vinylesters is 2,4-pentanedione (2,4-P). The difference in the reaction mechanisms between the ideal inhibitors and retarders is that inhibitors destroy the free radicals after their formation, while retarders slow the rate of radical generation.<sup>4</sup>

Rheological behaviors of polyester and vinylester resins are important because the composite manufacturing processes of thermosetting resins require knowledge of rheological behaviors of resins such as viscosity change, gelation, and network formation. Before the free radical polymerization proceeds, the resin is a viscous liquid. During the curing reaction, the chain length of the resin molecules grows through the crosslinking reaction of functional groups, and the resin becomes more viscous. As the curing advances further, the reacting system forms a highly crosslinked network, which results in a quick increase in the resin viscosity. The gel point is defined as the point when covalent bonds connect

across the molecules and form an infinite network. After the gelation, the diffusion rates are relatively low due to the increased viscosity, which reduces the bimolecular termination.<sup>5,6</sup> Therefore, the reaction rate increases due to higher concentration of free radicals. Usually, a maximum reaction rate is observed at this stage (Trommsdorf effect). As the reaction proceeds further it reaches the glassy state because of vitrification, and further reaction is prohibited due to the immobility of the monomers and the propagation radicals.<sup>7</sup>

In this study, effects of temperature, initiator, promoter, inhibitor, and retarder on the reaction kinetics and rheological behaviors of an unsaturated polyester and a vinylester resin, which are the typical SCRIMP resins, were studied using a Differential Scanning Calorimeter (DSC) and a Rheometrics Dynamic Analyzer (RDA). The differences of these factors on the two resins were compared.

## EXPERIMENTAL

### Materials

The unsaturated polyester resin used in this study is a low-shrink dicyclopentadiene (DCPD) polyester resin (UP551) from Cook Composites and Polymers (CCP). DCPD polyesters, which are inexpensive and offer low shrink and excellent cosmetics, can be cured rapidly and completely without any air inhibition effect. The major disadvantage of DCPD resin is low failure strain, which may cause cracking problems.<sup>3</sup> DCPD polyesters are widely used in gel coats, auto parts, casting marbles, bath fixtures, and boat-building industry.

The vinylester resin used in this study is DERAKANE 411-350 (VE350) from Dow Chemical. VE350, which is based on the bisphenol A epoxy resin, provides good resistance to a wide range of acids, alkalis, bleaches, and solvents. DERAKANE resins have superior creep resistance, and can be cured rapidly and consistently. Applications of DERAKANE vinylester resins include FRP storage tanks, vessels, ducts and on-site maintenance projects.<sup>8</sup>

These two resins are the major resins currently used for SCRIMP applications in the composite industry. The main properties of these two resins are listed in Table I. To maintain a similar vis-

**Table I Properties of Unsaturated Polyester and Vinylester Resins Used in This Study**

Resin Type	Viscosity at Room Temperature (CP)	Styrene Content (wt %)	Molecular Weight per Double Bond	$M_n$ (g/mol)	$M_w$ (g/mol)	Styrene/Unsaturated Vinylene Double Bond Ratio
DCPD polyester resin (UP551)	205	33	320	508	1568	1.52
Vinylester resin DERAKANE 411-350 (VE350)	350	45	485	970	—	3.8

cosity for mold filling, the weight fraction of styrene monomer differs in polyester (33%) and vinylester (45%) resins. This results in a molar ratio of styrene to unsaturated vinylene C=C of 1.52 and 3.8 for polyester and vinylester resins, respectively. At room temperature, the viscosity is 205 centipoise for the polyester resin and 350 centipoise for the vinylester resin. The number average molecular weight is 508 for the polyester resin and 970 for the vinylester resin. The molecular weight per double bond is 320 and 485 for the polyester and vinylester resins, respectively. This means that the average degree of unsaturation is 2 for the vinylester resin and less than 2 for the polyester resin.

Methyl ethyl ketone peroxide (MEKP) from Fluka and cobalt octoate (Co) from Pfaltz & Bauer were used as the low-temperature initiator and promoter for both resins. To adjust the reaction rate and gel time of the two resins to a similar range, different amounts of initiator and promoter were used. For the polyester resin, 0.8 wt % MEKP and 0.1 wt % Co were used as the initiator and promoter, respectively, while 1.6 wt % MEKP and 0.2 wt % Co were used for the vinylester resin. 1,4-Benzoquinone (BQ) and 2,4-Pentanedione (2,4-P) from Aldrich Chemical were used as the inhibitor and retarder (or co-promoter), respectively.

#### Instrumentation and Procedures

A Differential Scanning Calorimeter (DSC, Model 2910, TA Instruments) was used to measure the overall reaction rate profiles. All of the reactions were conducted in volatile aluminum sample

pans, which are capable of withstanding at least 2 atm internal pressure after sealing. The sample weight was about 10 mg. Isothermal reactions were measured at different temperatures. It took about 1 min for the DSC to reach the desired temperature in the isothermal runs. Isothermal DSC runs were terminated when there was no further exotherm, and scanning runs of isothermally cured samples were carried out from room temperature to 300°C with a heating rate of 5°C/min to determine the residual heat. The total heat of reaction is the sum of the isothermal reaction heat and the residual heat. The reaction was also measured in scanning mode, ranging from an ambient temperature to 300°C at a heating rate of 2°C/min. The average total exotherm of the polyester resin and vinylester resin is 294 J/g and 362 J/g, respectively. The total exotherm under various thermal histories is consistent, with variations less than 5%.

A Rheometrics Dynamics Analyzer (RDA II, Rheometrics) was used to study rheological changes and gelation at isothermal conditions. A pair of parallel plates with a diameter of 50 mm was used as the sample cell. The samples were placed between these two parallel plates with a gap of approximately 1 mm between them. A water bath was used to control the temperature. It took about 1 min for RDA to reach the desired temperature in the isothermal runs. The temperature variation in RDA during the first minute was about  $\pm 0.1$ – $\pm 0.2$ °C. Isothermal tests were used to determine the gel point of the polyester and vinylester resins. In these tests the viscosity was measured as a function of time at a constant

shear rate. Because high shear rate may destroy or delay network formation, a low shear rate ( $1 \text{ s}^{-1}$ ) was applied in this study. The experiment was conducted until the viscosity started to rise sharply. For the steady shear method, the gel point is defined as the point where the relative viscosity  $\eta_r$  ( $\eta_r = \text{viscosity}(\eta)/\text{initial viscosity}(\eta_1)$ ) reaches  $10^3$ .<sup>9</sup>

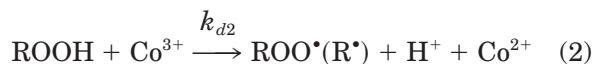
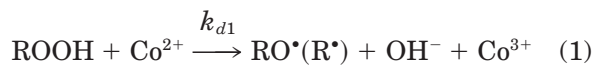
## RESULTS AND DISCUSSION

### Reaction Kinetics

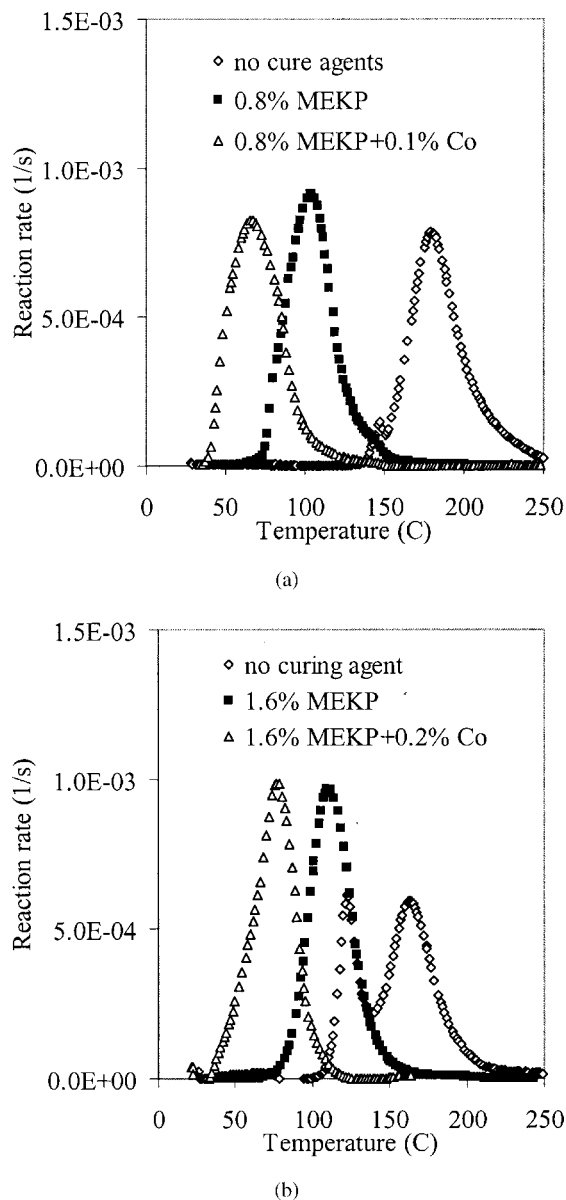
Figure 1 shows the DSC scanning curves of polyester and vinyl ester resins cured at a heating rate of  $2^\circ\text{C}/\text{min}$  under three different conditions: (1) without any curing agent, (2) with MEKP, and (3) with MEKP and Co. It was observed that without any curing agent, the reaction was mainly caused by the thermal decomposition of monomers at high temperature. For the polyester resin, the reaction occurred as the temperature reached  $140^\circ\text{C}$  and one exotherm peak was observed. For the vinyl ester resin, the reaction occurred at a lower temperature [i.e.,  $110^\circ\text{C}$  as shown in Fig. 1(b)], and two exotherm peaks were observed, one at  $125^\circ\text{C}$  and the other at  $160^\circ\text{C}$ .

When MEKP was added into the systems, the thermal decomposition of peroxide created primary free radicals for polymerization, causing the reaction to start at a lower temperature. For the polyester resin, the reaction exotherm peak shifted from  $170$  to  $100^\circ\text{C}$ . For the vinyl ester resin, the two exotherm peaks combined into a higher exotherm peak at  $110^\circ\text{C}$ .

With the aid of a metallic promoter such as cobalt octoate, the formation of radicals may result from the redox decomposition of peroxide, allowing the reaction to occur at ambient temperature. The mechanism of the redox decomposition of peroxides is shown in equations (1) and (2).

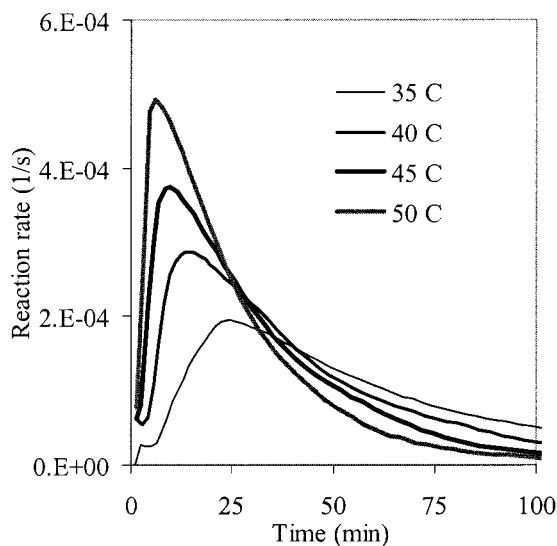


where ROOH is the initiator and  $\text{Co}^{2+}$  ( $\text{Co}^{3+}$ ) is the promoter,  $\text{R}\cdot$  represents primary free radicals

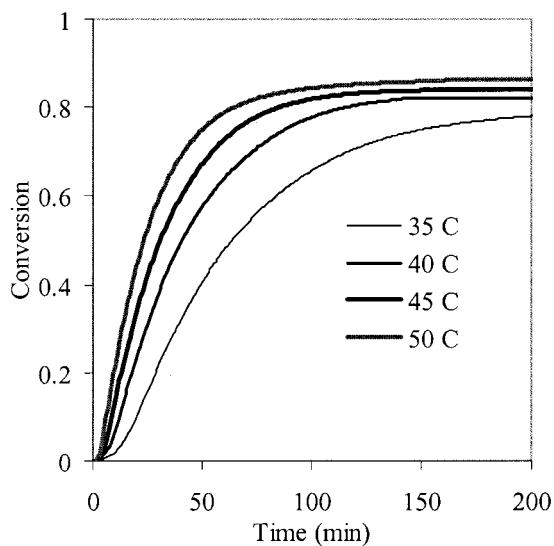


**Figure 1** Scanning reaction rate profiles under different conditions measured by DSC for (a) polyester resin, and (b) vinyl ester resin.

decomposed from the initiator.  $k_{d1}$  and  $k_{d2}$  are the rate constants of redox decomposition. Either  $\text{Co}^{2+}$  or  $\text{Co}^{3+}$  is able to generate free radicals in a redox (reduction and oxidation) cycle. Therefore, a small amount of promoter can induce a large amount of initiator because of the regeneration of cobalt ions. In this study, 0.1 and 0.2 wt % Co were used for the polyester and vinyl ester resins, respectively.



(a)



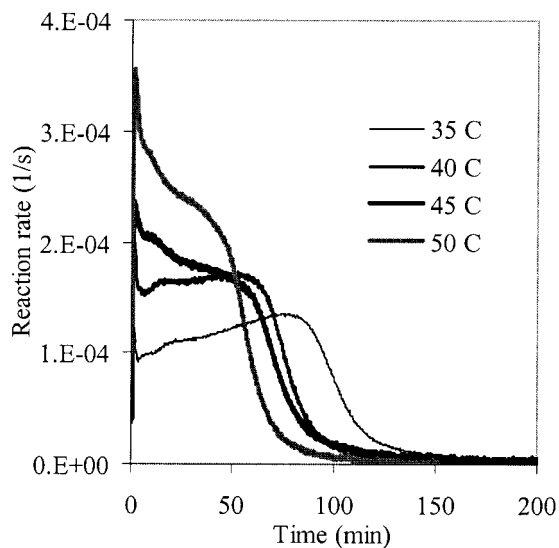
(b)

**Figure 2** (a) Isothermal reaction rate profiles and (b) conversion profiles of polyester resin measured by DSC at different temperatures (0.8 wt % MEKP, 0.1 wt % Co).

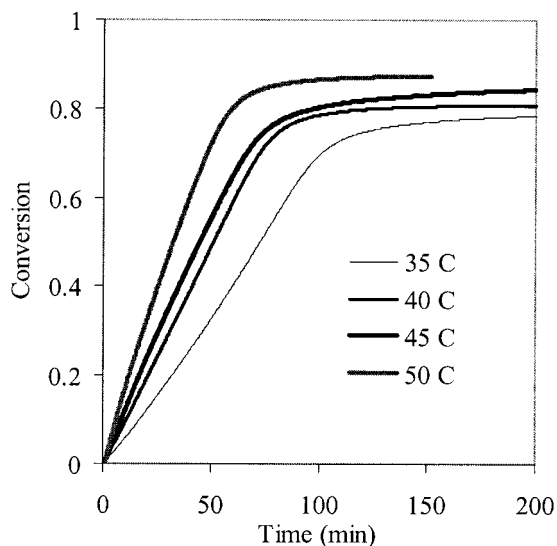
### Effect of Temperature

Isothermal reaction rates and conversion profiles of polyester and vinylester resins measured by DSC at different temperatures are shown in Figures 2 and 3. For both resins, the reaction rate increases accordingly as the temperature increases, and it takes a shorter amount of time for the reaction to reach the final conversion. For the polyester resin, the reaction rate increases rap-

idly from zero to a maximum value due to the Trommsdorf effect, then decreases with reaction time due to the consumption of C=C bonds. Finally, the reaction stopped before reaching complete reaction due to the diffusion limitations caused by vitrification. The entire reaction rate profile forms a bell shape, and the final conversion is 78.8, 82.2, 84.2, 86.4% at 35, 40, 45 and 50°C, respectively. For the vinylester resin, the



(a)



(b)

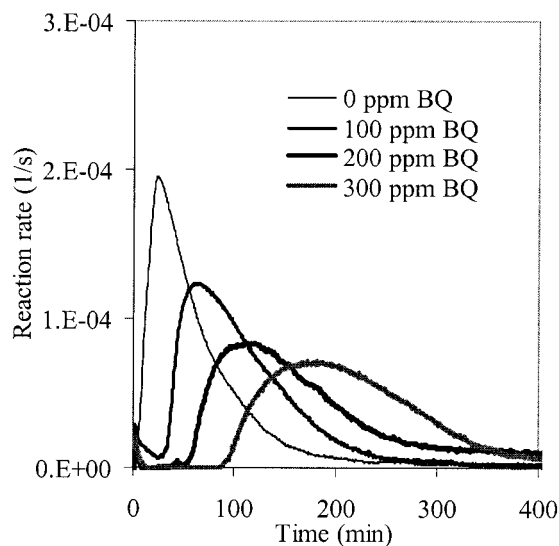
**Figure 3** (a) Isothermal reaction rate profiles and (b) conversion profiles of vinylester resin measured by DSC at different temperatures (1.6 wt % MEKP, 0.2 wt % Co).



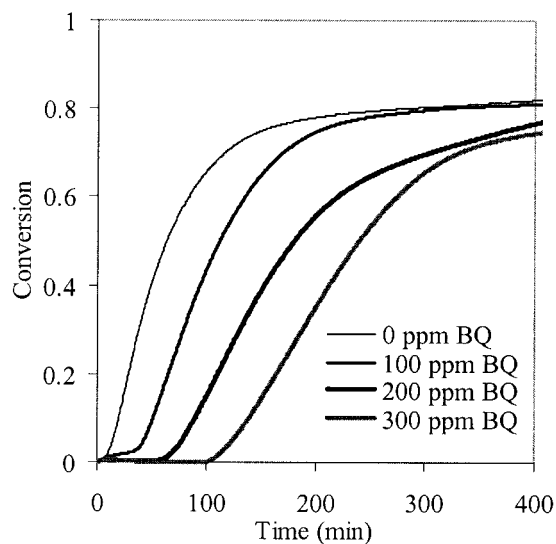
initial reaction rate is not zero (i.e.,  $9 \times 10^{-5} \text{ s}^{-1}$  at  $35^\circ\text{C}$ ) as shown in Figure 3(a). The reaction rate profile showed multiple peaks during the reaction time. The first reaction peak is due to the copolymerization between styrene and vinyl ester double-double bonds. The second reaction peak is caused by the homopolymerization of styrene monomers, because the styrene content in the vinyl ester resin is very high (e.g., the molar ratio of styrene to unsaturated vinylene C=C bond is 3.8). The final conversion for the vinyl ester resin is very close to that of the polyester resin, i.e., 78.5, 80.6, 84.2, 87.3% at 35, 40, 45 and  $50^\circ\text{C}$ , respectively.

### Effect of BQ

The effects of inhibitor (BQ) on the reaction rate and conversion profiles of the two resins are shown in Figures 4 and 5. The addition of BQ in both resins reduces the reaction rate significantly. For the polyester resin, as shown in Figure 4, when BQ is added, the reaction rate at the beginning is approximately zero for a certain time, and then starts to increase. The period during which there is no reaction is called the induction time. As shown in Figure 4, the addition of BQ in the polyester resin not only reduces the rate of polymerization but also delays the onset of the polymerization, resulting in a clear induction time. For instance, when 300 ppm BQ is added into the polyester resin, the induction time is about 90 min. The final conversion, however, is not substantially affected by the addition of BQ. For the vinyl ester resin (as shown in Fig. 5), although the total reaction rate decreases with the addition of BQ, there is no clear induction period observed. When BQ is added into the vinyl ester resin, the initial stage of the reaction shows a clear trend of exponential decay, which becomes more profound with an increase of BQ concentration. With the addition of 300 ppm BQ, only a small peak in the reaction rate profile is observed, which indicates that not enough initiator is left to start the polymerization. As a result, the final conversion is less than 10% as shown in Figure 5(b). In room temperature molding processes, BQ is used to increase the gel time to allow the mold to be fully filled, and after that, it is desirable for the reaction to resume rapidly and reach a high conversion. Based on the experimental results in this study, it was found that the addition of BQ



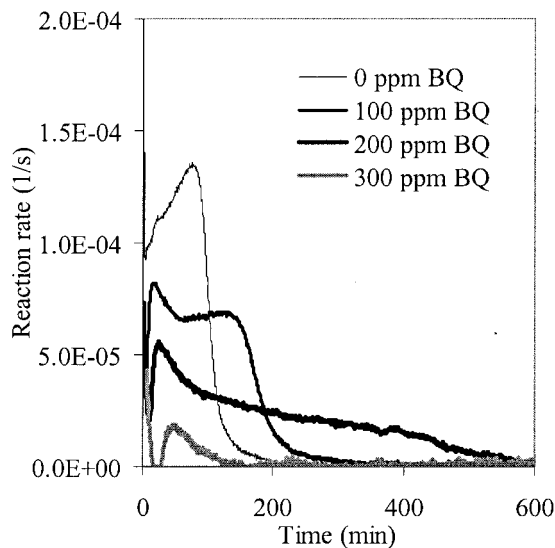
(a)



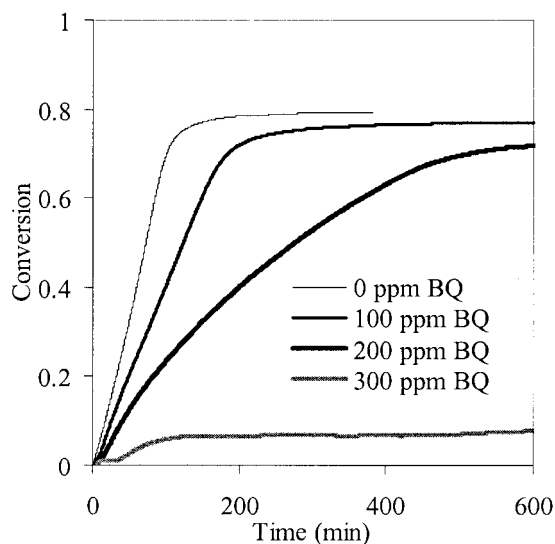
(b)

**Figure 4** (a) Isothermal reaction rate profiles and (b) conversion profiles of polyester resin with different amounts of inhibitor (BQ) measured by DSC at  $35^\circ\text{C}$  (0.8 wt % MEKP, 0.1 wt % Co).

induces a long induction time for the polyester resin but not for the vinyl ester resin. Also, it was found that after 7 h the conversion for the polyester resin with 300 ppm BQ is about 75%, while for the vinyl ester resin it is less than 10%. These facts indicate that BQ is a good low temperature inhibitor for polyester resins, but should not be used in vinyl ester resins.



(a)



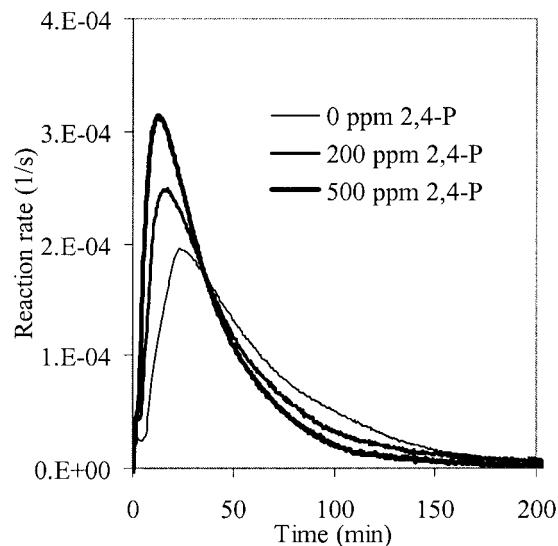
(b)

**Figure 5** (a) Reaction rate profiles and (b) conversion profiles of vinyl ester resin with different amounts of inhibitor (BQ) measured by DSC at 35°C (1.6 wt % MEKP, 0.2 wt % Co).

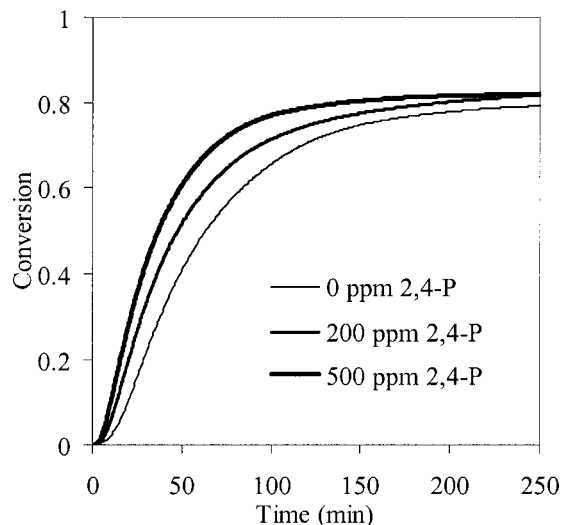
#### Effect of 2,4-P

2,4-P (acetylacetone) is an effective chelating agent, capable of interacting with metal chelates such as cobalt octoate to form complex cobalt ions. The formed chelates may have either decreased or enhanced catalytic effect on the decomposition of peroxides, depending on the resin type and the initiation system.<sup>10-12</sup>

The effect of 2,4-P on the reaction rate profiles of the polyester and vinyl ester resins is shown in Figures 6 and 7. For the polyester resin, with the addition of 2,4-P, the reaction rate increases from the very beginning and the reaction rate profiles remain bell-shaped. The final conversion of the polyester resin with the addition of 2,4-P is 81.7%, slightly higher than without 2,4-P as shown in Figure 6(b). For the vinyl ester resin, when 2,4-P is added ( $\geq 500$  ppm), the initial reaction rate

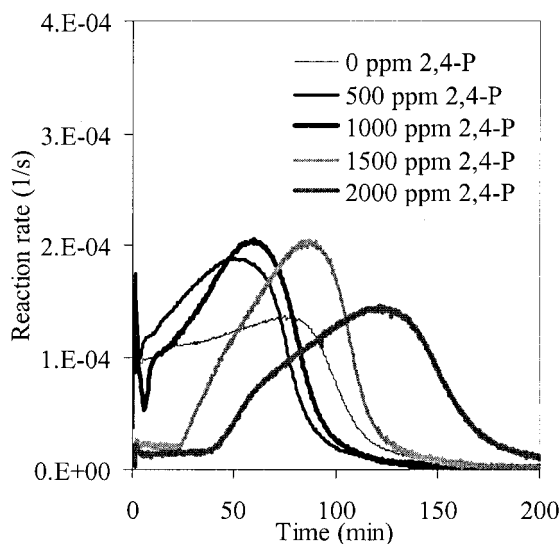


(a)

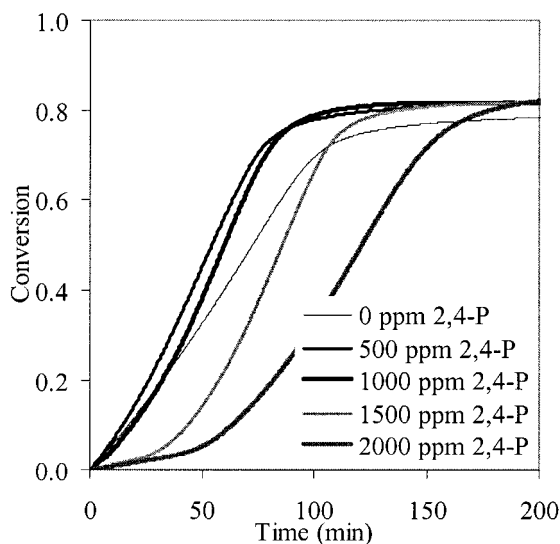


(b)

**Figure 6** (a) Isothermal reaction rate profiles and (b) conversion profiles of polyester resin with different amounts of 2,4-P measured by DSC at 35°C (0.8 wt % MEKP, 0.1 wt % Co).



(a)



(b)

**Figure 7** (a) Isothermal reaction rate profiles and (b) conversion profiles of vinyl ester resin with different amounts of 2,4-P measured by DSC at 35°C (1.6 wt % MEKP, 0.2 wt % Co).

experiences an exponential decay, then the reaction rate increases to a maximum point. The maximum reaction rate with 2,4-P is much higher than without 2,4-P. When more 2,4-P is added (e.g.,  $\geq 1500$  ppm), the initial reaction rate is further depressed, and the reaction rate remains low for a certain time (e.g., about 30 min for 1500 ppm). After that, the reaction resumes. For the vinyl ester resin, the addition of 2,4-P slightly in-

creases the final conversion as shown in Figure 7(b). Without 2,4-P, the final conversion is about 78.5%, and with the addition of 2,4-P, the final conversion is increased to 82%.

The literature study showed that the initiation of free-radical polymerization could be delayed when excess  $\beta$ -dicarbonyl compounds with an enol content of at least 4% and a dicarbonyl angle of less than 120° (e.g., 2,4-P) are present.<sup>10</sup> It was also reported that the initiation reaction of unsaturated polyester resins by redox decomposition involving peroxides (e.g., methyl ethyl ketone peroxide) and soluble salts of redox active metals (e.g., cobalt octoate) is significantly accelerated in the presence of enolizable ketones (e.g., 2,4-P).<sup>11</sup> The exact acceleration/retardation mechanism of 2,4-P is not well understood, and further investigation is needed.

## RHEOLOGICAL BEHAVIORS

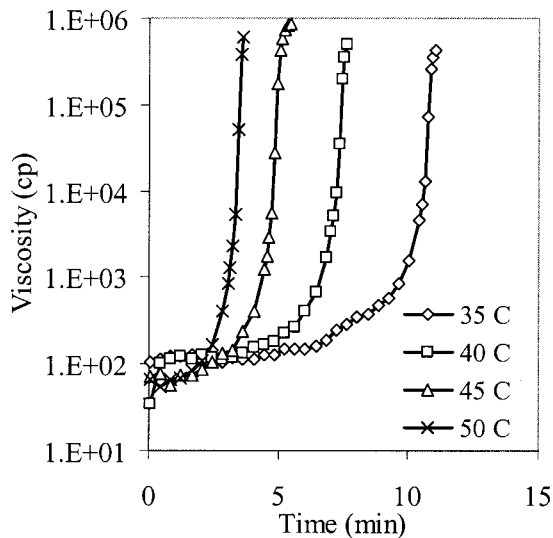
### Effect of Temperature, BQ, and 2,4-P

The viscosity changes of polyester and vinyl ester resins at different temperatures obtained by the steady shear test are shown in Figure 8. The concentrations of MEKP and Co were fixed at 0.8 and 0.1 wt % for the polyester resin, and 1.6 and 0.2 wt % for the vinyl ester resin, to achieve a similar range of gel time for both resins. As expected, with increasing reaction temperature, the resin viscosity starts to increase earlier due to the increased reaction rate. Therefore, the gel time of both resins decreases with increasing temperature.

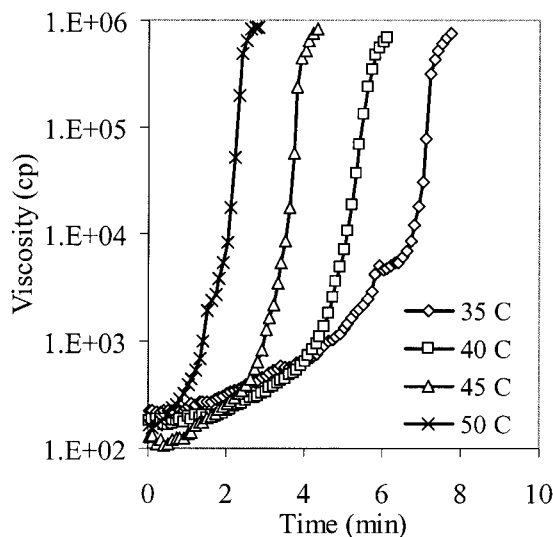
The effect of inhibitor (BQ) on the rheological changes of these two resins at 35°C is shown in Figure 9. Increasing the BQ concentration leads to a lower reaction rate and slower viscosity rise, delaying gelation. With the addition of BQ, while both resins have a longer gel time, the effect of BQ on the gel time of the polyester resin is much stronger than for the vinyl ester resin (similar to the DSC results).

The effect of 2,4-P on the rheological changes of the two resins is shown in Figure 10. The addition of 2,4-P decreases the gel time for the polyester resin, but increases the gel time for the vinyl ester resin when the 2,4-P concentration is higher than 500 ppm. This phenomenon can be explained by the change of the initial reaction rate with the addition of 2,4-P. The initial reaction rate is im-





(a)



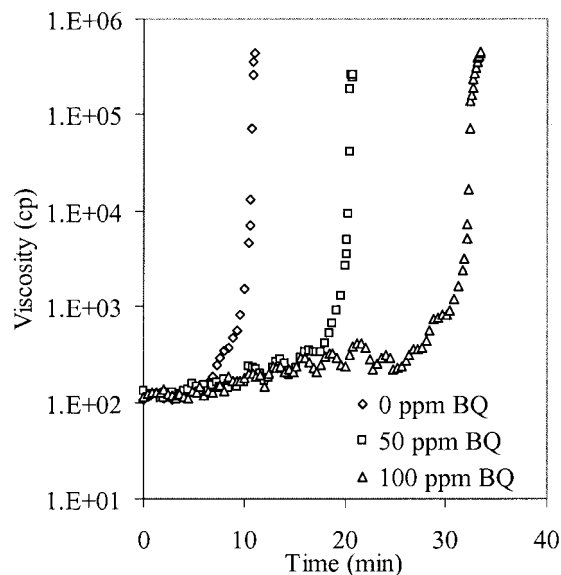
(b)

**Figure 8** Viscosity rises during isothermal cure of (a) polyester resin (0.8 wt % MEKP, 0.1 wt % Co), and vinylester resin (1.6 wt % MEKP, 0.2 wt % Co) at different curing temperatures.

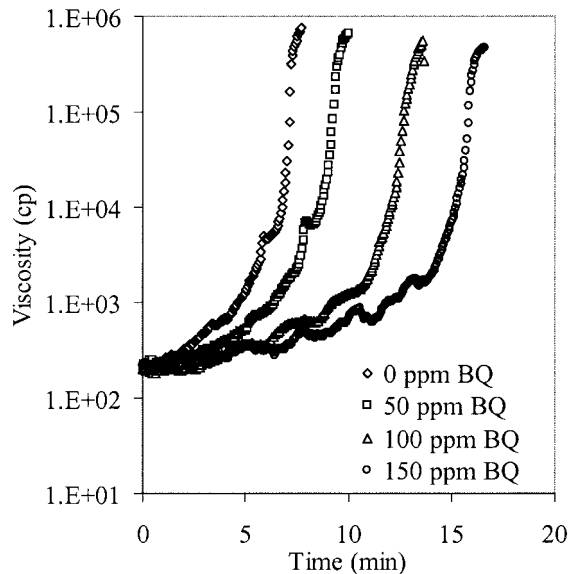
portant for polymerization, because gelation occurs when the conversion is very low, usually less than 5%.<sup>13</sup>

Because the gel conversion is very low for these resins, it is not easy to compare viscosity changes as a function of resin conversion. On the other hand, viscosity changes can be rearranged in the form of  $\ln(\eta/\eta_0)$  vs.  $t/t_{gel}$ , as shown in Figure 11. For the polyester resin, a master curve of the

relative viscosity with respect to the reduced reaction time ( $t/t_{gel}$ ) is obtained. This relation is independent of temperature, BQ concentration, and 2,4-P concentration, as shown in Figure 11(a). This implies that the gelation mechanism in the polyester resin does not change within the

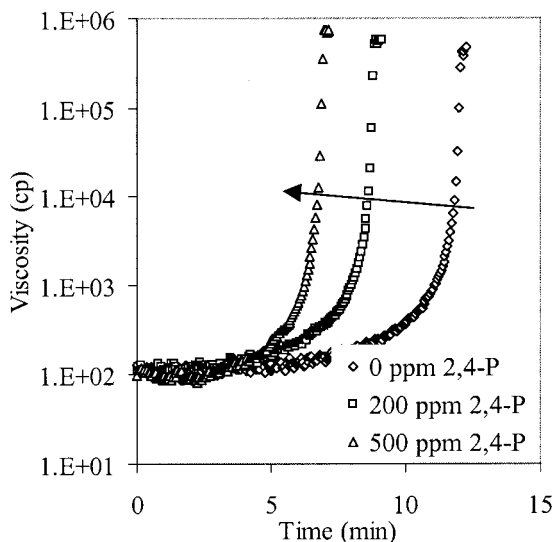


(a)

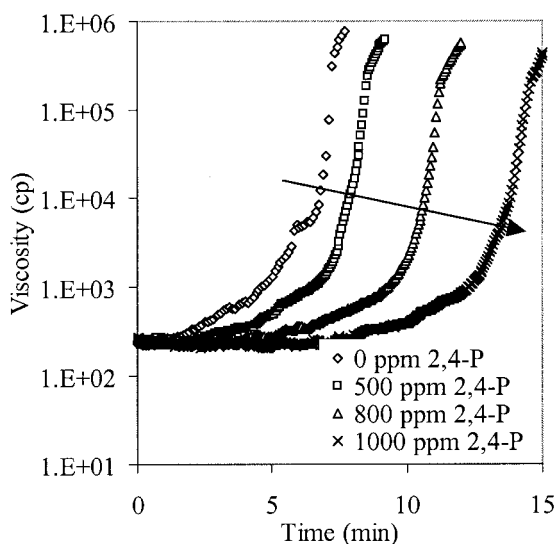


(b)

**Figure 9** Viscosity rises during isothermal cure of (a) polyester resin (0.8 wt % MEKP, 0.1 wt % Co, temp = 35°C), and (b) vinylester resin (1.6 wt % MEKP, 0.2 wt % Co, temp = 35°C) with different amounts of inhibitor (BQ).



(a)



(b)

**Figure 10** Viscosity rises during isothermal cure of (a) polyester resin (0.8 wt % MEKP, 0.1 wt % Co, temp = 35°C), and (b) vinylester resin (1.6 wt % MEKP, 0.2 wt % Co, temp = 35°C) with different amounts of 2,4-P.

ranges of temperature, BQ concentration, and 2,4-P concentration studied. Therefore, the relative viscosity is simply a function of reduced time ( $t/t_{\text{gel}}$ ) for the polyester resin. For the vinylester resin, a master curve can still be obtained under different temperatures and BQ concentration, as shown in Figure 11(b). However, no master curve is found when different amounts of 2,4-P are added in the vinylester resin, as shown in Figure

11(c). It can be seen that at the same dimensionless time ( $t/t_{\text{gel}} < 1$ ), the relative viscosity is lower when more 2,4-P is added. The detailed mechanism needs to be further investigated.

### A Gel Time Model

The relation of gel time with temperature can be expressed by the following Arrhenius-type equation proposed by Yang and Suspene<sup>14</sup>

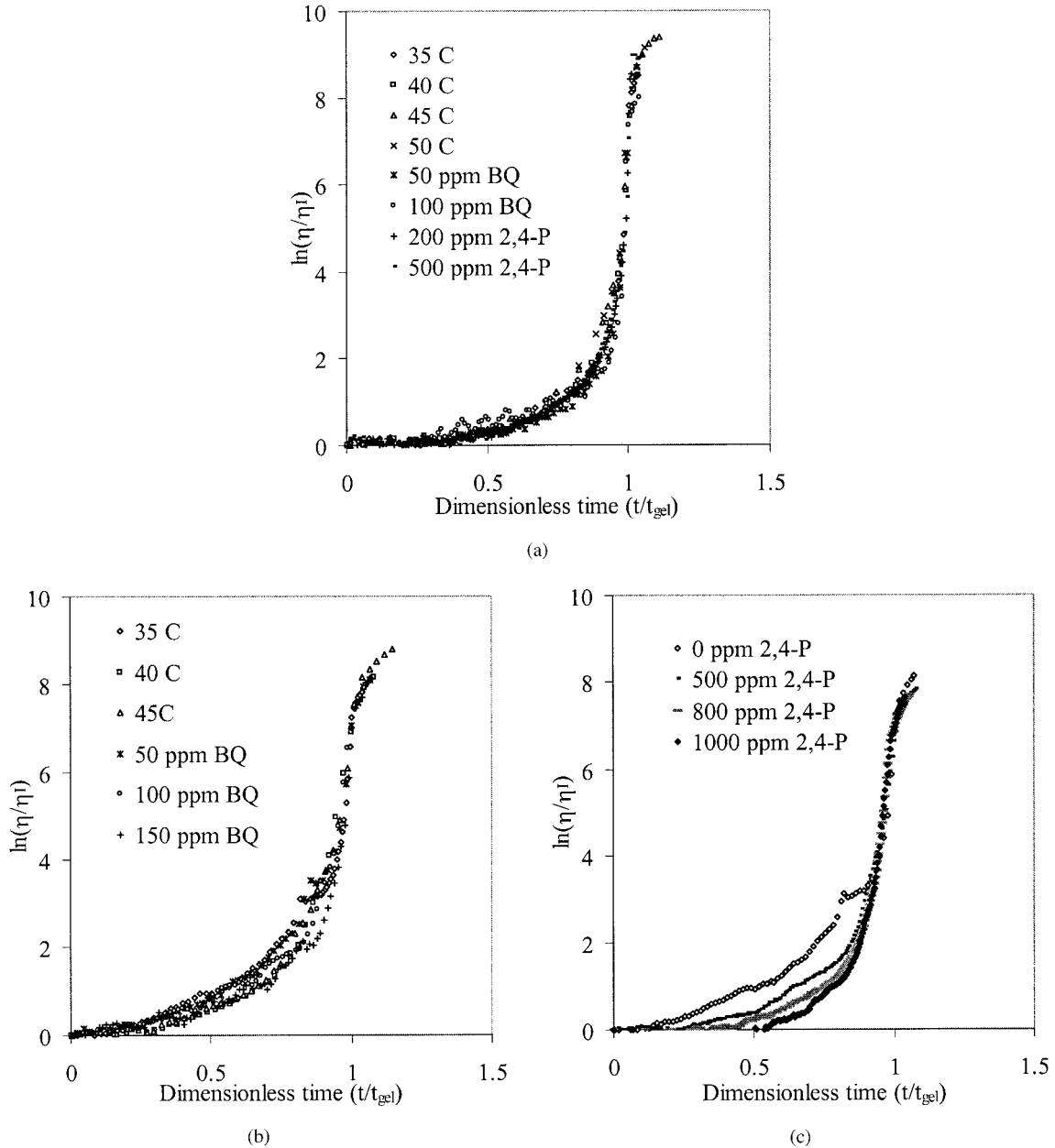
$$\ln(t_{\text{gel}}) = A + \frac{E_d}{R} \left( \frac{1}{T} \right). \quad (3)$$

The units for gel time and temperature are in minutes and Kelvin (°K). Figure 12(a) shows the logarithmic gel time vs. the reciprocal of reaction temperature for both resins. The points are experimental results, and the straight lines are the regression results. It was found that the change of gel time with temperature follows an Arrhenius-type relation for both resins. The parameter  $E_d/R$  represents the sensitivity of the resins to the temperature; values for the two resins are shown in Table II. For the polyester resin,  $E_d/R$  is slightly higher than for the vinylester resin, which implies that the gelation of the polyester resin is slightly more sensitive to the change of temperature.

Assuming that the parameter A in Eq. (3) is a linear function of the inhibitor and 2,4-P content, the effect of BQ and 2,4-P on the gel time can be incorporated into the gel time model by

$$\ln(t_{\text{gel}}) = A + \frac{E_d}{R} \left( \frac{1}{T} \right) = A_1 + B_1(C_{\text{BQ}}) + C_1(C_{2,4-P}) + \frac{E_d}{R} \left( \frac{1}{T} \right). \quad (4)$$

the unit for BQ and 2,4-P concentration is in ppm. The new parameters  $B_1$  and  $C_1$  indicate the sensitivity of the resin gelation to BQ and 2,4-P, respectively. The value of  $B_1$  is the slope of the straight line of  $\ln(t_{\text{gel}}) - \ln(t_{\text{gel}})_0$  vs.  $C_{\text{BQ}}$  as shown in Figure 12(b). The value of  $C_1$  is the slope of the straight line of  $\ln(t_{\text{gel}}) - \ln(t_{\text{gel}})_0$  vs.  $C_{2,4-P}$  as shown in Figure 12(c). Where  $(t_{\text{gel}})_0$  is the gel time of the resin when no BQ or 2,4-P is added. The values of  $B_1$  and  $C_1$  for the two resins are also shown in Table II. For the polyester resin,  $B_1$  is about twice as that of the vinylester resin (i.e.,  $9.7 \times 10^{-3}$  vs.  $5.3 \times 10^{-3}$ ), indicating that BQ is a more efficient

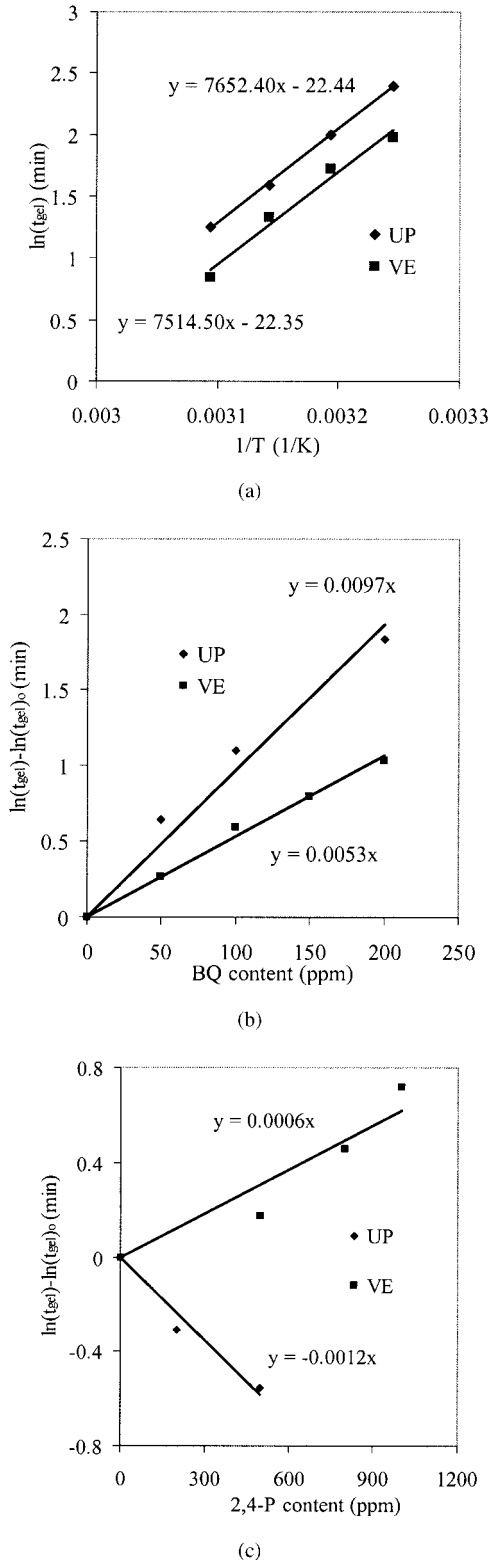


**Figure 11** Relative viscosity ( $\ln(\eta/\eta_I)$ ) vs. dimensionless time ( $t/t_{gel}$ ) under various conditions for (a) polyester resin (0.8 wt % MEKP, 0.1 wt % Co), (b) and (c) vinyl ester resin (1.6 wt % MEKP, 0.2 wt % Co).

inhibitor in polyester resins. For the polyester resin, 2,4-P is an accelerator, as shown by the negative value of  $C_1$ ; while for the vinyl ester resin, 2,4-P is a retarder, indicated by the positive value of  $C_1$ .

The gel time with different amounts of BQ and 2,4-P can be predicted by using eq. (4). This is

confirmed by conducting experiments with different amounts of BQ and 2,4-P in the two resins. For example, when 100 ppm BQ and 200 ppm 2,4-P were added in the polyester resin with 0.8 wt % MEKP and 0.1 wt % Co at 35°C, the measured gel time is 23.9 min, while the model prediction is 22.7 min. When 50 ppm BQ and 800



**Figure 12** Correlation results for the polyester and vinyl ester resins based on the gel time model: (a)  $\ln(t_{gel})$  vs.  $1/T$ , (b)  $\ln(t_{gel}) - \ln(t_{gel})_0$  vs. BQ content, and (c)  $\ln(t_{gel}) - \ln(t_{gel})_0$  vs. 2,4-P content.

**Table II** The Values of Parameters in the Gel Time Model

Resin Type	$A_1$	$B_1$	$C_1$	$E_d/R$
Polyester	-22.44	0.0097	-0.0012	7652.4
Vinylester	-22.35	0.0053	0.0006	7514.5

ppm 2,4-P were added in the vinyl ester resin with 1.6 wt % MEKP and 0.2 wt % Co at 35°C, the measured gel time is 14.5 min, while the model prediction is 16.1 min.

## CONCLUSIONS

The reaction kinetics and rheological behaviors of two widely used SCRIMP resins cured at low temperature, an unsaturated polyester and a vinyl ester resin, were studied. When using MEKP as the initiator, BQ provides a longer induction period and a higher final conversion for the polyester resin compared to the vinyl ester resin. Therefore, BQ is a better inhibitor for polyester resins. It was also found that 2,4-P is a good retarder for vinyl ester resins, but is an accelerator for polyester resins.

A gel time model was developed to quantify the effects of temperature, BQ, and 2,4-P on the gel time for both polyester and vinyl ester resins cured at low temperatures. It was found that the polyester reaction is slightly more sensitive to temperature change than the vinyl ester reaction. The effects of temperature, inhibitor and retarder (copromoter) on the gel time can be reasonably predicted using the proposed model.

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