

# Effects of Processing Conditions on the Curing of a Vinyl Ester Resin

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**ABSTRACT:** The effects of temperature, initiator, and accelerator levels on the curing of an epoxy bisphenol-A vinyl ester resin Derakane<sup>®</sup> 411-45 (formulated with styrene) were investigated by gel-time and exotherm-peak measurements on bulk samples. It was observed that the gel time was reduced as the initiator or accelerator ratio increased. Except at higher contents of the accelerator, a small kinetic plateau was seen in the gel curve and a shift of the maximum exotherm toward high temperatures in the DSC curves. This was explained by the dual role played by the accelerator species. A regression analysis of all gel-time data showed a dependence of 3/2 order in the accelerator and first order in the initiator concentrations. Thus, for this polymerization initiation system, the gel time can be predicted for any initiator and cobalt levels and at any temperature within the ranges studied. The effect of the initiator on the unreacted styrene and vinyl ester was also examined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1146–1154, 2002; DOI 10.1002/app.10403

**Key words:** vinyl ester; radical polymerization; gel time; DSC; curing of polymers; gelation; polyesters

## INTRODUCTION

The need for composite materials destined for chemical engineering or for marine applications is increasingly evident, in particular, for corrosive environments. In recent years, numerous attempts have been made to obtain a suitable matrix for these materials. Initial work concerned the most classic and economic matrices such as unsaturated polyesters denoted “standard” polyesters, epoxies, and bisphenol-A fumarate-type polyesters. In the case of all these matrices, the results showed low stability of these materials

after cure toward aging. Standard cured polyesters are well known for their weak chemical resistance, in particular, toward hydrolysis, and the epoxies by the processing difficulty caused by the high viscosity, long cure cycle, and the toxicity of some hardeners.<sup>1</sup> On the other hand, cured polyesters of the bisphenol A-fumarate type have been accepted for a long time for their good chemical resistance, but their mechanical performance is insufficient, being similar to that of standard polyesters, thus limiting their use.<sup>2</sup>

Vinyl ester resins have been found to overcome many of these drawbacks and can be fabricated with the same processes as used with conventional polyesters. Recent reviews reveal that they are becoming very important in new industrial applications such as in coating, printed circuit

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**Table I** Derakane® 411–45 Characteristics at 25°C

Properties	Derakane® 411–45
Viscosity (mPa s)	440
Ratio of styrene (wt %)	45
Density	1.04
Shelf life (in months)	6

boards, metal foil laminates, building materials, automotive parts, and fiber-reinforced composites.<sup>3</sup> Such developments are not only due to the good chemical properties of the cured resins but also to the opportunities offered to the fabricator to combine the mechanical properties of epoxies with easy processing of unsaturated polyesters. Furthermore, their low molecular weight, in comparison with that of unsaturated polyesters, allows them to incorporate a high ratio of fillers (60–70% by weight)<sup>4</sup> and also good wetting of the fiber. If the problem of chemical stability under humid and corrosive conditions does not intervene, then these cured resins must be favored provided that further specific problems of the processing in use can be resolved.

The aim of this work was to contribute toward a knowledge of the factors which influence the processing of these resins. Recently, the kinetics of the polymerization of various vinyl ester resins was published.<sup>5</sup>

## EXPERIMENTAL

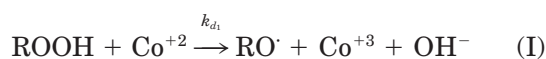
### Materials

Epoxy vinyl ester resin (Derakane® 411-45, Dow Chemical Co.) diluted with styrene (Table I) was used in this study. The chemical structure of the epoxy vinyl ester monomer is presented in Figure 1. The catalytic system was composed of a methyl ethyl ketone peroxide (MEKP) initiator—50% of peroxide and 8.5% of active oxygen—supplied as Butanox LPT (Akzo) activated by a solution of 6

wt % of cobalt octoate in dibutyl phthalate supplied as NL51P (Akzo, France). In the text,  $x\%$  of the initiator (or catalyst Co) means  $x$  wt % of the commercial solution of MEKP (or Co octoate). The reactive formulation is prepared by first mixing the resin with the accelerator, followed by the addition of the initiator (MEKP).

### Reaction Mechanism

The reaction mechanism of MEKP with cobalt octoate is the well-known alternating reduction–oxidation (redox) reaction that is shown by the following scheme:



where  $k_{d1}$  and  $k_{d2}$  are the rate constants for the formation of the alkoxy (RO·) and peroxy (ROO·) radicals, respectively.

Beaunez et al.<sup>6</sup> noted that the alkoxy radical is much more reactive to ethylenic monomers than is the peroxy radical and, therefore, (I) can determine the rate of initiation described by

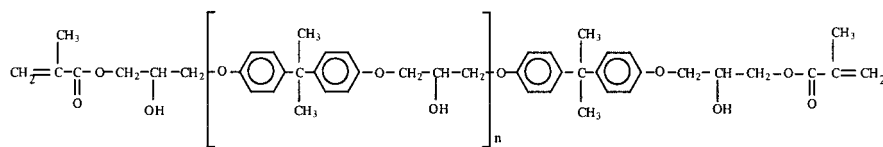
$$d[\text{RO}\cdot]/dt = k_{d1}[\text{Co}^{+2}] [\text{ROOH}] \quad (1)$$

Assuming, through the consumption and regeneration of the  $\text{Co}^{+2}$  species, that a steady state is achieved, the equilibrium concentration of  $\text{Co}^{+2}$  attained can be given by

$$[\text{Co}^{+2}]_{\text{equiv}} = k_{d2}[\text{Co}^{+2}]_0 / (k_{d1} + k_{d2}) \quad (2)$$

The substitution of the term  $[\text{Co}^{+2}]_{\text{equiv}}$  in eq. (2) by that given in eq. (1) gives

$$d[\text{RO}\cdot]/dt = k_{d1}k_{d2}[\text{Co}^{+2}]_0[\text{ROOH}] / (k_{d1} + k_{d2}) \quad (3)$$



**Figure 1** Chemical structure of the epoxy vinyl ester monomer.

Alternatively, the rate of polymerization of the monomer is given by the relation<sup>7</sup>

$$-d[M]/dt = k_p[M][M_n] = k_p[M](fR_i/k_t)^{1/2} \quad (4)$$

where  $[M]$  and  $[M_n]$  are the monomer and radical concentrations;  $f$ , the initiation efficiency;  $R_i$ , the rate of initiation which was shown in eq. (1), and  $k_p$  and  $k_t$ , the propagation and termination rate constants, respectively.

The combination of eqs. (3) and (4) indicates that the rate of polymerization should increase with increased cobalt and MEKP levels:

$$-d[M]/dt = k_p[M] \times (fk_{d_1}k_{d_2}[\text{Co}^{+2}]_0[\text{ROOH}]/k_t(k_{d_1} + k_{d_2}))^{1/2} \quad (5)$$

Commercial resins are supplied containing a phenolic stabilizer, which, while present only in small amounts, leads to an observable induction period before polymerization. This inhibitor,  $Z$ , is added to scavenge adventitious peroxy and alkoxy radicals  $R^*$  and, therefore, will not promote polymerization:



The relationship among the induction period, inhibitor concentration, and rate of initiation can be derived as follows<sup>8</sup>: The radical concentration during the induction period is given by

$$d[R^*]/dt = R_i - k_z[Z][R^*] \quad (7)$$

and assuming steady-state radical concentration, then

$$[R^*] = R_i/k_z[Z] \quad (8)$$

Hence, the rate of inhibitor consumption can be expressed as

$$d[Z]/dt = -k_z[Z][R^*] = R_i = k_d[\text{Co}^{+2}]_0[\text{ROOH}] \quad (9)$$

from which an induction time can be derived in which  $Z_0$  is the initial inhibitor concentration:

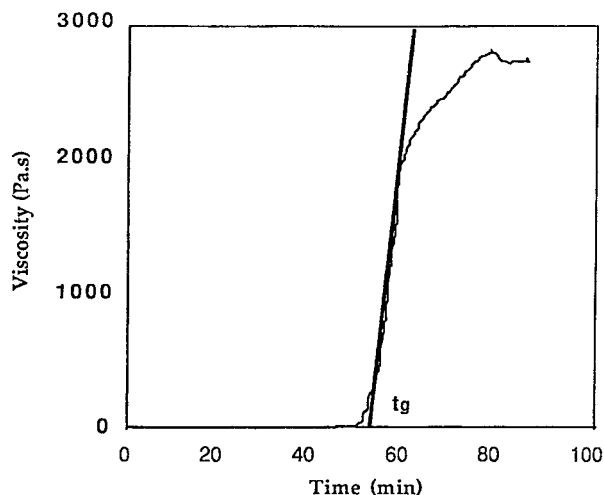


Figure 2 Curve of viscosity versus time.

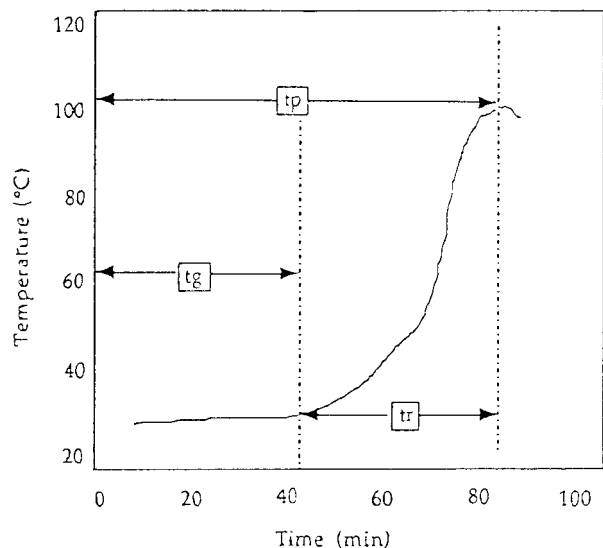
$$t = \frac{Z_0}{k_d[\text{Co}^{+2}]_0[\text{ROOH}]} \quad (10)$$

## Methodogy

### Measurement of Gel Times

The technique of studying the kinetics of polymerization and the crosslinking reaction, using the Trombomat apparatus, was described in detail in a previous article.<sup>9</sup> A mobile, constituted by a bar terminated by a calibrated ball ( $\theta = 16$  mm), is immersed into the resin and vibrated by a pendular movement. As the reaction system proceeds, the viscosity increases as a consequence of the increase in molecular weight and the amplitude of the pendulum decreases. Forces on the ball are proportional to the viscosity of the medium. This technique shows the sharp increase of the viscosity (Fig. 2), which may correspond to gelation when vitrification of the medium occurs after gelation. On the other hand, one can follow, simultaneously, the state change of a reaction medium from a liquid state to a gel state and thereafter to an infusible and insoluble solid. The second phenomenon is the exotherm engendered by the crosslinking reaction and measured by a thermocouple and given by the Trombomat. The progress of the reaction can be evaluated by the quantification of parameters such as

- Gel time ( $t_g$ ), determined by the curve of viscosity versus time (Fig. 2),
- Reactivity time ( $t_r$ ), determined by the curve of temperature versus time (Fig. 3),



**Figure 3** Curve of temperature versus time (temperature of the system during the crosslinking reaction—hypothetical curve generated by Trombomat thanks to the thermocouple).

- Polymerization time ( $t_p$ ), related to the above times by the relation

$$t_p = t_g + t_r \text{ (Fig. 3)}$$

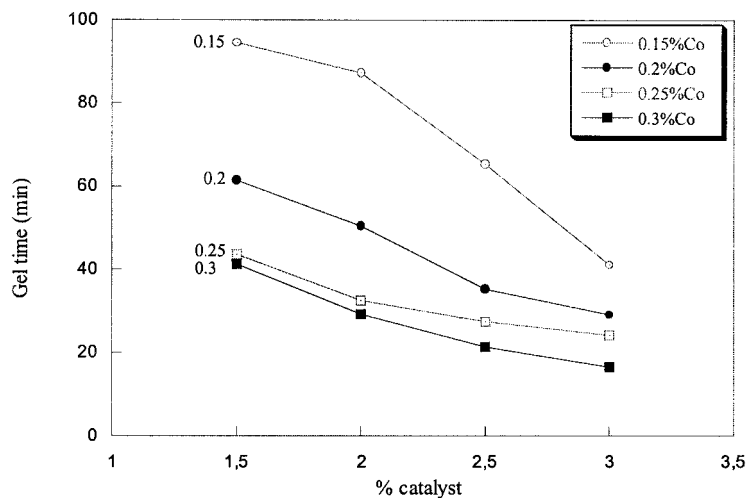
Peak of the exotherm temperature, which is the maximum temperature determined by the graph of temperature versus time (Fig. 3).

All these parameters are strongly influenced by the sample volume and surface area. The sys-

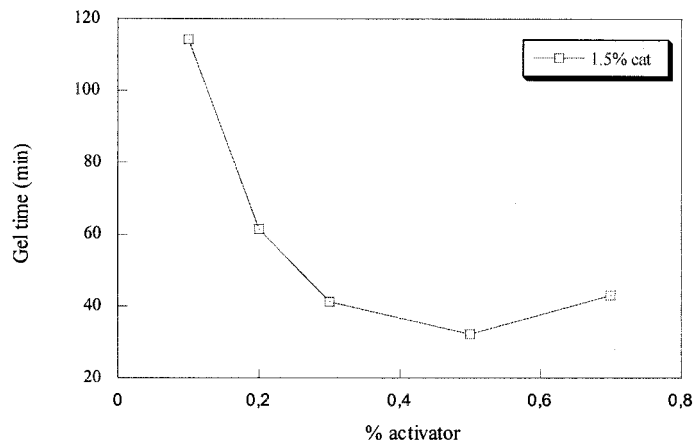
tem was optimized for 130 g and a density of resin of 1.3, and the optimal surface area is  $60 \text{ cm}^2$  ( $r = 4.38 \text{ cm}$ ).<sup>10</sup> All experiments were conducted in an air atmosphere. Data from this technique are shown in Figures 4–8.

**Residual Reactivity Measurements**

A differential scanning calorimeter (DSC, DuPont 912) was used to measure the exotherm rate during polymerization. A DSC was also used to obtain the total heat of reaction by heating to  $200^\circ\text{C}$ . Residual heats of reaction were obtained by heating the cured specimens to  $200^\circ\text{C}$ . All the reactions were conducted in aluminum pans under a static air atmosphere. The Al pans were carefully tightly closed to avoid styrene evaporation. Sample weights were 10–20 mg with an empty pan as a reference. Samples (resin in bulk) were heated from room temperature to  $200^\circ\text{C}$  in a dynamic mode with a heating rate of 10 K/min to detect the residual reactivity. Time  $t_0$  was defined as the time where, just after the last adjuvant (initiator) is added, the resin is put in the pan, sealed, and then heated. The average total heat of the reaction measured at this time and at different concentrations of the initiator was  $356.9 \pm 20.5 \text{ J/g}$ . This enthalpy was used as a reference and considered to correspond to 100% of polymerization (no residual reactivity). On the other hand, this value was approximately the same as that given by Suzuki et al.<sup>11</sup> for the copolymerization of the blend styrene/methyl methacrylate:  $67.3 \text{ kJ/mol}$



**Figure 4** Gel time versus weight percent of the catalyst (MEKP) measured at  $25^\circ\text{C}$  for different weight percents of the accelerator (cobalt salt).



**Figure 5** Gel time versus weight percent of the accelerator (cobalt salt) measured at 25°C for 1.5 wt % of the catalyst (MEKP).

(360 J/g). We should also note that it was independent of the added initiator level.

The amount of residual reactivity, mainly unreacted styrene, determined at time  $t$  is given by the relation

$$\% S = (\Delta H_t / \Delta H_0) 100$$

where  $\Delta H_t$  is the heat of reaction measured at time  $t$ , and  $\Delta H_0$ , the heat measured at time  $t_0$ . DSC results are shown in Figure 9.

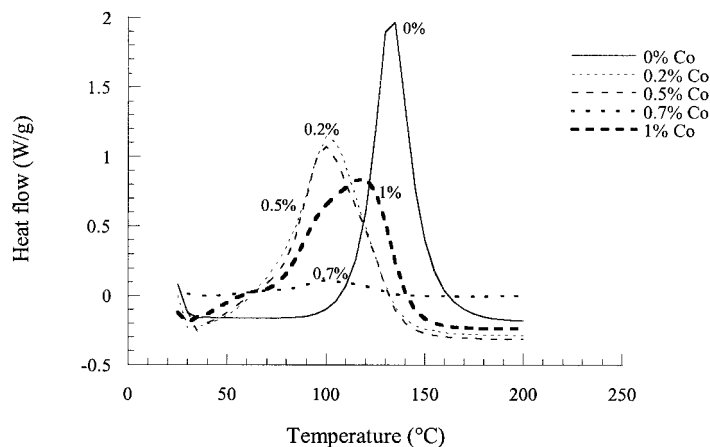
## RESULTS AND DISCUSSION

### Effect of Initiator (MEKP) Concentration

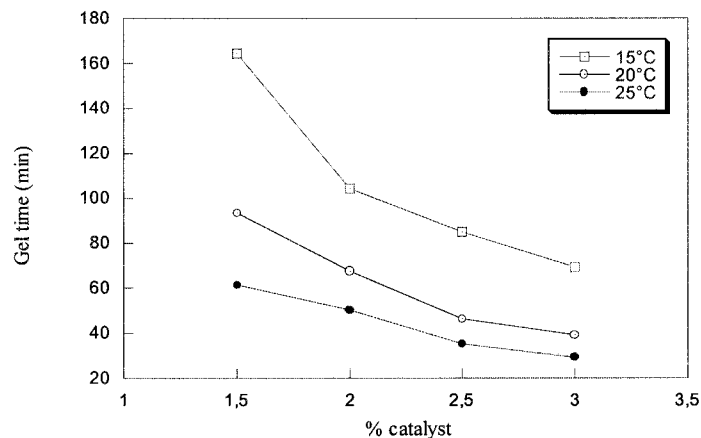
The Derakane® 411-45 was accelerated and catalyzed at different concentrations of cobalt salt

(NL51P) and organic peroxide (Butanox LPT) which varied for the accelerator from 0.15 to 0.30 wt % and for the initiator from 1.5 to 3.0 wt %. We represented in Figure 4 the variation of the gel time versus the initiator weight percentage for different cobalt levels. We observe that, for a given weight percent of the accelerator, the gel time decreases when the concentration of the initiator increases. This was in agreement with the prediction of eq. (5).

In fact, an increase in initiator level results in a faster polymerization rate and can give a network rich in residual double bonds, the initiator not being totally consumed. The presence of this unreacted initiator could have significant consequences for the final properties of the material.<sup>12</sup> On the other hand, a slow reaction rate, which corresponds to a low level of the initiator, would



**Figure 6** Heat flow versus weight percent of the accelerator (cobalt salt) using 1.5 wt % of the catalyst (MEKP).



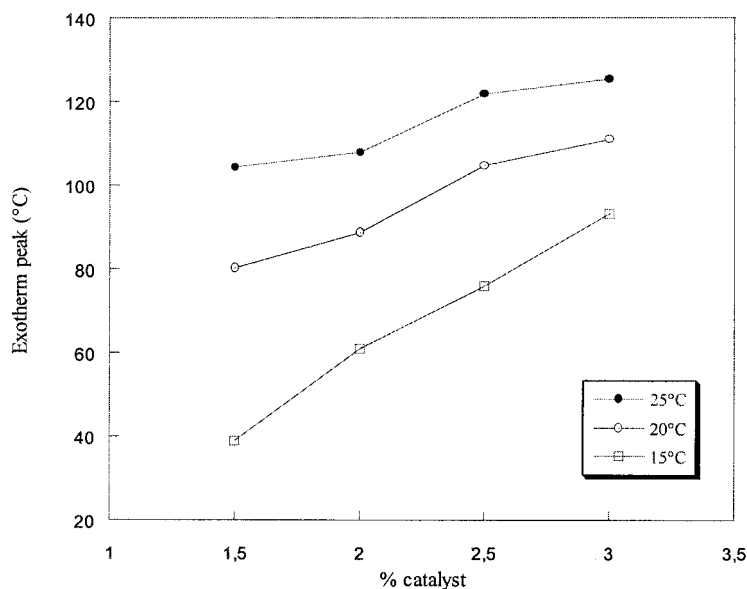
**Figure 7** Gel time measured at different temperatures and for 0.2 wt % of the accelerator (cobalt salt).

increase the role of the inhibition of oxygen and, therefore, affect the copolymerization reaction and ultimately modify the final structure of the network.

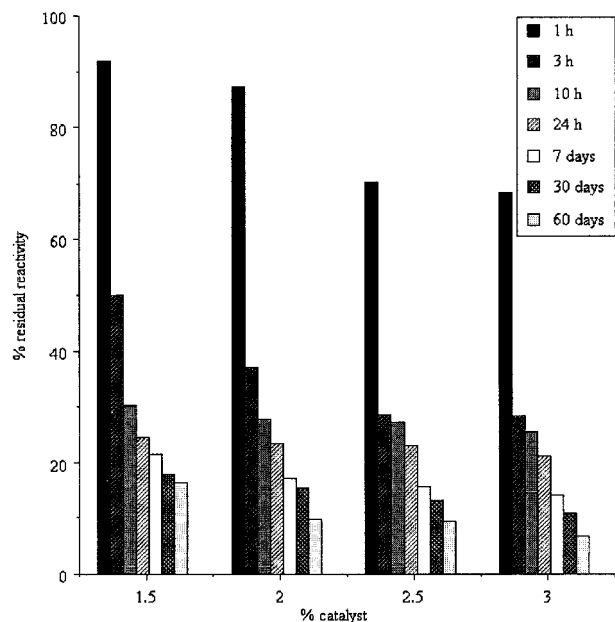
#### Effect of Accelerator (Cobalt Salt) Concentration

To investigate the effect of the accelerator level, the Derakane® 411-45 was cured at a range of cobalt concentrations varying from 0.1 to 0.9% by weight of the resin and at a constant concentration of the initiator of 1.5% by weight. Figure 5 shows that increasing the cobalt salt concentra-

tion in the range 0.2–0.5 wt % reduces the gel time. Above this range, and to 0.9 wt %, the gel time continues to increase, reaching a plateau. This was confirmed also by the DSC results (see Fig. 6), where the maximum in exotherm shifts to higher temperatures after the value of 0.5 is reached. However, it is clear, through these results, that the cobalt species play a double role. They accelerate the reaction in its initial stages encompassing the gelation process, which is in agreement with our results in the range 0.1–0.5 wt % and which is also in accord with eq. (5), but

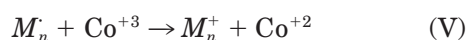
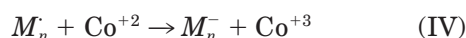
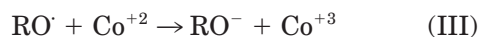


**Figure 8** Exotherm peak versus weight percent of the catalyst (MEKP) determined at different temperatures for 0.2 wt % of the accelerator (cobalt salt).



**Figure 9** Actual and calculated gel times at 25°C for various catalyst concentrations and at accelerator concentrations a, b, c, and d of 0.15, 0.2, 0.25, and 0.3 wt %, respectively.

at higher extents of conversion, they act as a retarder. High concentrations of transition element initiators are well known to inhibit free-radical reactions. This could be explained by reactions such as



where initiating and propagating radical chains can be consumed by such a reaction with  $\text{Co}^{+2}$  (ref. 13).

#### Effect of Cure Temperature

The Derakane® 411-45/styrene system accelerated by 0.2 wt % of the commercial solution of cobalt salt and catalyzed at different ratios of MEKP was studied at different initial temperatures: 15, 20, and 25°C. Figure 7 shows that the gel time of the resin depends strongly on the initial temperature at which it is used. The increase in temperature has the effect of decreasing the gel time.

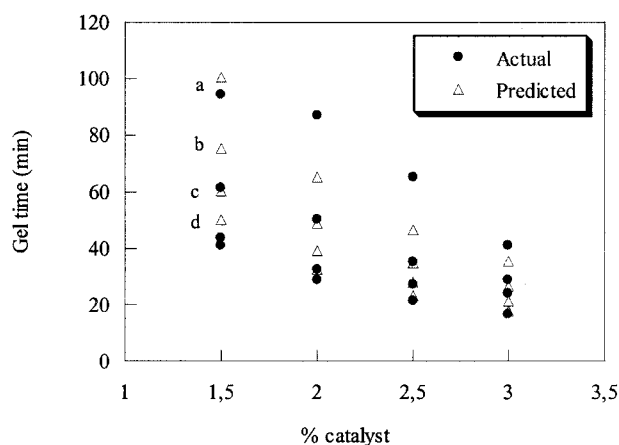
**Table II** Variation of Polymerization Time  $tp$  versus Temperature (2.5% of Catalyst and 0.2% of Accelerator)

Temperature (°C)	$tp$ (min)
15	111
20	63
25	45

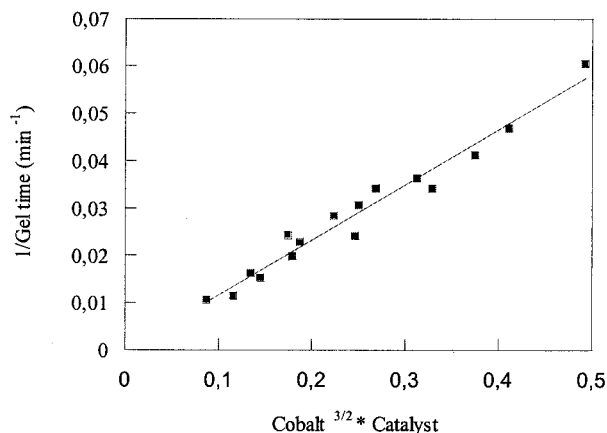
On the other hand, for a given increase in temperature, the exotherm peak increases (Fig. 8), whereas the polymerization time ( $tp$ ) decreases (Table II), that is, the reaction is more exothermic. Therefore, for 3% of peroxide and 0.2% of cobalt salt, the temperature achieved is 85°C for a reaction starting at 15°C, whereas it increases to 120°C when used at 25°C. These results are similar to those obtained for unsaturated polyester.<sup>9,10</sup>

#### Gel Time Results: Data Analysis

A regression analysis of the gel time data was performed and a comparison of actual and predicted times for 25°C is given in Figure 10. This analysis shows that the dependencies approximate a 3/2 order in the accelerator and first order in the initiator concentrations. The experimental error in the gel time is about 15%. For each temperature, a proportionality constant (equivalent to a rate constant) can be determined. Figure 11 gives a fit of the reciprocal of the gel time with the product  $[\text{ROOH}]^*[\text{Co}]^{3/2}$  at 25°C. Similar fits at 15



**Figure 10** Rate constant determination from the fit of the gel time to the product of the catalyst and accelerator.



**Figure 11** Arrhenius plot of rate constant and temperature.

and 20°C allow the estimation of the activation energy from the slope of the Arrhenius plot shown in Figure 12. This analysis gave an activation energy of  $64 \text{ kJ K}^{-1} \text{ mol}^{-1}$ , which is similar to that expected for catalyzed decomposition of the peroxide initiator.<sup>8</sup> A statistical analysis of all the data fitted to the three variables, initiator, cobalt, and temperature, gave a correlation of 0.96.

### Residual Reactivity Measurements

An example of the effect of the initiator concentration on the residual reactivity after cure is shown in Figure 9. It can be seen that the amount of residual reactivity decreased with an increasing amount of the initiator to 2.5–3% by weight of the resin. Within the concentration range of 2.5–3%, the residual reactivity level after 2 months at room temperature lay in the range 8.5–6.4%. However, 2.5% of the initiator should permit a reasonable cure.

### CONCLUSIONS

The catalytic system and cure conditions used for fabrication of reinforced resin equipment are very important factors to control. Measurement of the gel time, exotherm, and residual reactivity are useful techniques for optimizing process conditions and for quality control.

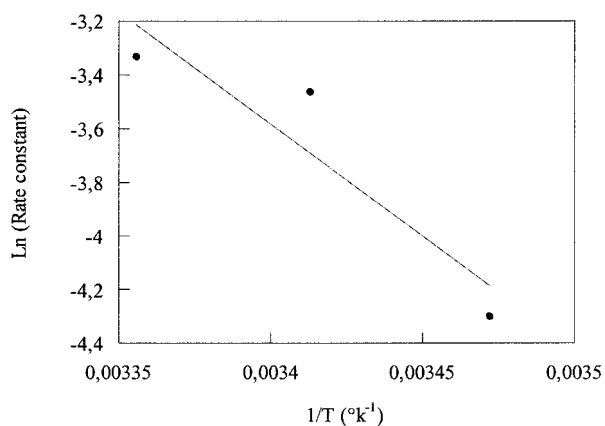
The advantage of a given system may be exploited for specific fabrication techniques and circumstances for obtaining chemically resistant and handling applications of reinforced plastics.

With commonly used methyl ethyl ketone peroxide and cobalt octoate systems, the level of peroxide has a great influence on the gel time, exotherm peak, and residual reactivity—mainly styrene—more so than does the level of the accelerator, for the investigated narrow range of MEKP and Co octoate concentrations.

Although the gel time is an important factor, which should be known by the industrialist, its measurement is not easy. It depends essentially on three parameters: initiator, temperature, and accelerator levels to which should be added the hygrometry of the medium (not discussed in this article). Thus, at 25°C, for a level of the accelerator between 0.2 and 0.3% and with 2% of the initiator, the average gel time is between 30 and 50 min.

Finally, and from an industrial point of view, it is preferable to obtain a long gel time by reducing the level of the accelerator rather than by reducing the level of the initiator; the temperature can be also reduced. In reality, it is the temperature which governs these two parameters. Generally, in winter, resins are accelerated at 0.3% to allow use in the temperature range  $15 \pm 4^\circ\text{C}$ , whereas, in summer, they are activated at 0.2% for use at  $25 \pm 4^\circ\text{C}$ .<sup>14</sup>

It is very important to indicate that the exothermic nature of the crosslinking reaction intervenes as a postcured process, relaxing residual strains. However, the long-term aim of this work not only concerns the behavior of materials. The matrix is only one element in the problem: The role played by residual chemical functions and



**Figure 12** Residual chemical functions (styrene) as function of the weight percent of the catalyst (MEKP) for 0.2 wt % of the accelerator (cobalt salt). Reaction conducted at an initial temperature of 20°C (DSC data).



microcracks within the fiber and interfacial area also have to be considered.

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