

# Effects of Initiators on the Cure Kinetics and Mechanical Properties of Vinyl Ester Resins

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**ABSTRACT:** Initiators play an important role in the curing of vinyl ester resins. In this study, two kinds of initiators were used to investigate the effects of initiator systems on the cure kinetics, microstructure, and mechanical properties of vinyl ester resins. The reaction kinetics, investigated with isothermal differential scanning calorimetry (DSC), showed that the combination of different kinds of initiators could significantly decrease the induction times and exothermal peak times and increase the amount of isothermal reaction heat in comparison with a single-initiator system. The residual heat of the isothermal cure of vinyl ester resins, obtained by DSC, demonstrated the existence

of microheterogeneity in the cured resins. The DSC data also showed that the highly crosslinked phase (the microgel phase) was more perfect for the resins cured with an initiator-combination system. No significant difference was observed in the mechanical properties of resins cured under different conditions, whereas the cure temperature had a great effect on the mechanical properties of cured resins. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2539–2545, 2008

**Key words:** heterogeneous polymers; kinetics (polym.); mechanical properties

## INTRODUCTION

Vinyl ester resins are thermosets for which a thermally activated peroxide is usually used to initiate polymerization in some resin/fiber composite processing techniques, such as resin transfer molding and pultrusion, in which the resins need to be cured with a combination of several initiators as the initiator system. The initiator system plays an important role in the processing of composites and may affect the efficiency and final quality of products. Hence, it is important to investigate the effects of initiator systems on the cure kinetics and mechanical properties of vinyl ester resins.

The reaction between styrene and vinyl ester is a heterogeneous free-radical copolymerization. An important characteristic of this copolymerization is the formation of a biphasic structure, which may affect the cure behavior and mechanical properties of vinyl ester resins.<sup>1,2</sup> Many researchers have investigated microstructure formation in unsaturated polyester resins<sup>3,4</sup> and vinyl ester resins.<sup>1,5–8</sup> The widely accepted concept of microgel formation is that microgels are densely crosslinked structures that

form in the early stages of polymerization and result in the formation of a biphasic structure.

It is believed that initiator systems and cure temperatures may affect the mechanical properties of cured resins via microgel formation.<sup>1,9,10</sup> However, few detailed studies exist in the literature on the effects of the combination of initiators on the kinetics, microstructure, and mechanical properties. This study was designed to investigate the effect of a combination of initiators on the cure kinetics of vinyl ester resins by isothermal differential scanning calorimetry (DSC). The biphasic structures of the cured resins were studied with the residual reaction heat of isothermal DSC. The effect of the initiator system on the mechanical properties of cured resins was also evaluated. This work is part of a larger study of the use of vinyl ester resins in pultrusion techniques for manufacturing long fiber-composite suck rods used in oil wells, for which a thorough understanding of the cure behavior is critical.

## EXPERIMENTAL

### Materials

A vinyl ester resin, Hetron 922, containing a mixture of styrene and a dimethacrylated epoxy compound was obtained from Ashland Chemical Co. (Kunshan, China). The chemical structure of Hetron 922 is shown in Figure 1. The average molecular weight of

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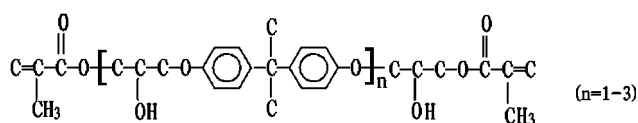


Figure 1 Chemical structure of vinyl ester.

the vinyl ester in Hetron 922 is 987 g/mol, and the concentration of styrene is 40.85 wt %, as determined by  $^1\text{H-NMR}$ .

Trigonox C (C) and Perkadox-16 (P16), purchased from Akzo Nobel Peroxides, Ltd. (Tianjin, China), were used as initiators. Their chemical structures and properties are shown in Figure 2 and Table I, respectively. All other materials were used as received without further purification.

## DSC

A differential scanning calorimeter (Pyris-1, Perkin Elmer, USA) was used to measure the overall reaction rate profiles. Isothermal kinetic experiments from 70 to 120°C were performed under a dry nitrogen atmosphere. Isothermally cured samples were again scanned from 50 to 250°C at a scanning speed of 10°C/min to determine the residual reaction heat of isothermal curing. The weigh ratios of resins to initiators and detailed experimental conditions are listed in Table II.

## Sample preparation

The casting mold consisted of two stainless steel plates with dimensions of 40 cm  $\times$  40 cm  $\times$  2 cm. A rubber belt (thickness  $\sim$  2 mm) covered with a poly(ethylene terephthalate) film was first placed between the plates to control the thickness of the sample and prevent the leakage of resins. The inside of the plate was coated with a thin layer of a release agent diluted with acetone. The mold was then clamped with six binder clips placed evenly on both sides.

The well-mixed resin was poured into the casting cell from the top through a poly(ethylene terephthalate) funnel and then placed vertically in a curing oven. The formulations of the initiator systems and cure temperatures are also shown in Table II.

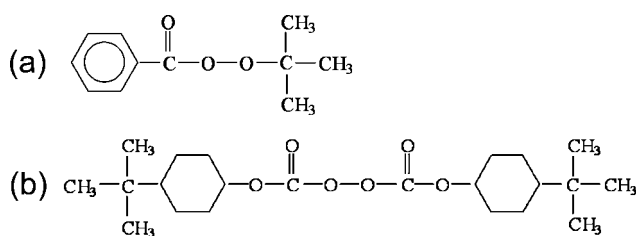


Figure 2 Chemical structures of (a) C and (b) P16.

TABLE I  
Properties of Two Peroxide Initiators

Initiator	10-h $t_{1/2}$ (°C)*	Molding temperature (°C)	Storage temperature (°C)
P16	48	70–120	<20
C	103	135–165	0–25

\* $t_{1/2}$ : Half-life of reaction.

The specimens (15 cm  $\times$  1 cm  $\times$  2 mm) were cut from the cast resins with a diamond saw and used for tensile and three-point-bending tests. The tensile and flexural tests were conducted on an Instron 1811 universal testing machine according to GB 2568-1995 and GB 2570-1995, respectively. All experiments were performed at 20  $\pm$  2°C.

## RESULTS AND DISCUSSION

### Curing kinetics

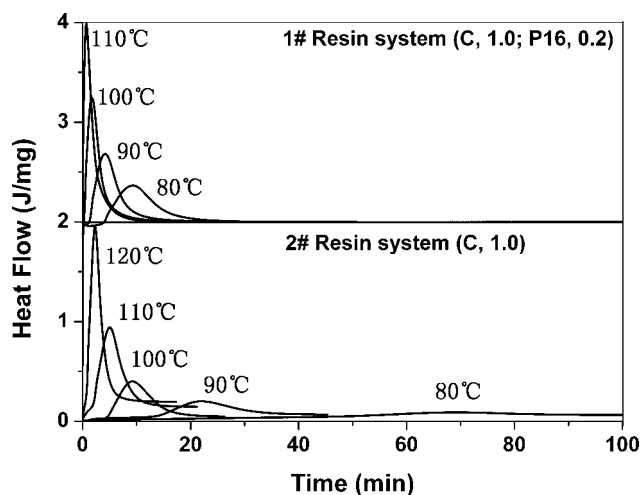
#### Induction time and exothermal peak time

In the pultrusion processing of vinyl ester resin/fiber composites, using one kind of initiator can have some disadvantages. For example, using only a high-temperature-decomposing initiator may result in lower production efficiency and quality because of the rapid decomposition of the initiator at a high reaction temperature. On the contrary, when a only low-temperature-decomposing initiator is used, the initiator will decompose in an early stage of polymerization, and this will result in a low degree of crosslinking in the cured resins. Thus, the obtained resins will have poor mechanical properties. Therefore, usually several kinds of initiators are employed as an initiator system for pultrusion processing. For example, a type of high-temperature-decomposing initiator is incorporated with a type of lower temperature decomposing initiator, and sometimes a type of middle-temperature-decomposing initiator is further added. In this study, two kinds of initiators were combined as the initiator system: one initiator was P16, a low-temperature-decomposing initiator, and the other initiator was C, a high-temperature-decomposing initiator.

Inhibitors were introduced into the resins to prevent the commercial resins from reacting during the storage periods. These inhibitors needed to be

TABLE II  
Initiator Contents and Cure Temperatures for Different Initiator Systems

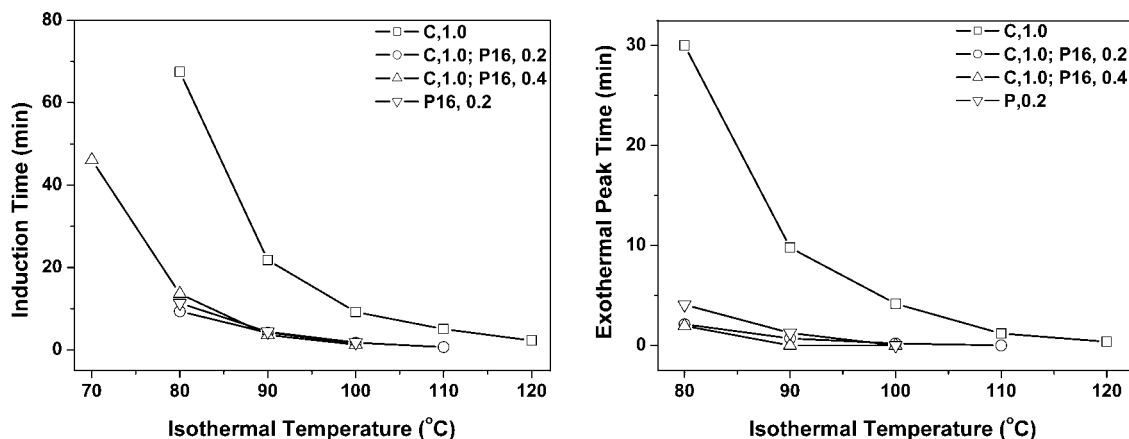
Code	Initiator content (wt %)	Temperature range (°C)
1	C, 1.0	80–120
2	C, 1.0; P16, 0.2	80–110
3	C, 1.0; P16, 0.4	70–110
4	P16, 0.2	80–110



**Figure 3** DSC isothermal curing thermographs for vinyl ester resins (systems 1 and 2) at different temperatures.

depleted by the system before the reaction could begin.<sup>11</sup> Therefore, during the curing of the vinyl ester resins, there was an induction time, which can be seen from the DSC isothermal curing thermographs shown in Figure 3. The induction time and the exothermal peak time in the isothermal DSC thermograms could be used to evaluate the cure speed of the resin systems and provide instruction for molding processing. Figure 4 shows that the induction time did not change linearly with the cure temperature for the cure systems studied, and neither did the exothermal peak time.

Figure 4 also shows that the combination of the two initiators greatly decreased the induction time and exothermal peak time, especially when the resins were cured at the lower temperature. When they were cured at 80°C, the induction time for system 1 (C, 1.0) was 67.5 min, whereas for system 2 (C, 1.0; P16, 0.2), it was only 9.367 min. With the cure temperature increasing, the induction time and peak time of different initiator systems were approached.



**Figure 4** Effect of the combination of initiators on the induction times (left) and peak times (right).

For example, when the resins were cured at 100°C, the induction time for system 1 was 9.2 min, and for system 2, it was 1.74 min, as also shown in Figure 3.

An interesting result shown in Figure 4 is that the two cured resin systems, one containing 0.2 wt % P16 (system 2) and the other containing 0.4 wt % P16 (system 3), showed no differences in the induction time or peak time.

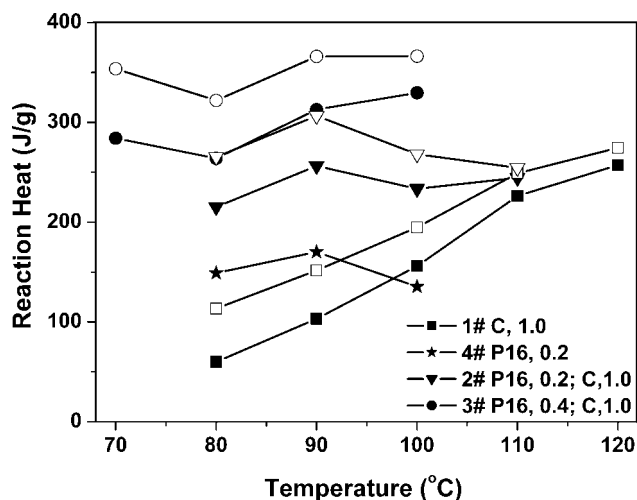
Initiator P16 can decompose at a lower temperature than initiator C because of its low activation energy. When it is combined with initiator C and initiates the polymerization of the resin system, it decomposes first and releases reaction heat, which results in the decomposition of nearby high-temperature initiator molecules, and then it initiates the system to polymerize at the lower temperature.

#### Heat of reaction

The isothermal heat ( $Q_I$ ) and total heat ( $Q_T$ ) of DSC were calculated from the area under the heat flow curve obtained in the DSC thermograph and are shown in Figure 5. Figure 5 shows that for system 1 (C, 1.0),  $Q_I$  increased with increasing temperature, and so did  $Q_T$ . For the systems containing C and P16,  $Q_I$  and  $Q_T$  were almost independent of the curing temperatures. For the same curing temperature,  $Q_I$  had the following tendency:

$$Q_I(\text{C}, 1.0; \text{P16}, 0.4) > Q_I(\text{C}, 1.0; \text{P16}, 0.2) > Q_I(\text{C}, 1.0)$$

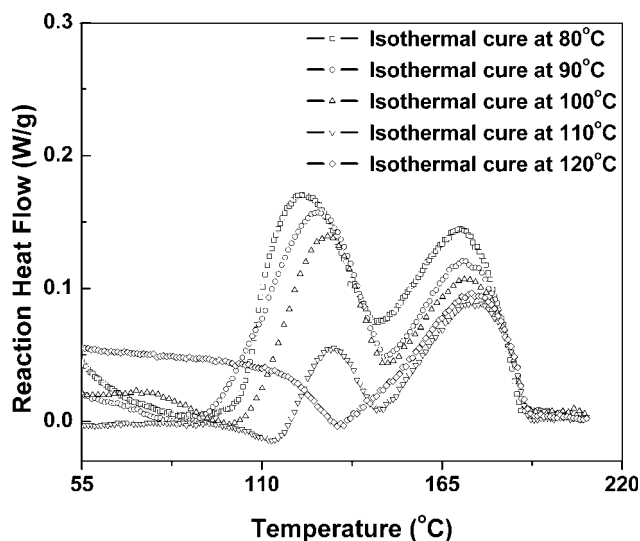
As for system 4 (P16, 0.2),  $Q_I$  changed little with the curing temperature, and the residual heat did not exist when it was measured with DSC (the residual heat is discussed in the next section). Obviously, the initiator had decomposed completely within the cure time at the temperatures at which the isothermal DSC runs were performed. Therefore, the reaction heat was almost unchanged within the temperature range investigated. When the isothermal DSC



**Figure 5** Reaction heat under different conditions from isothermal DSC. The full symbols represent the isothermal curing heat, and the empty symbols represent the total heat, which includes the isothermal curing heat and residual heat.

samples were reheated, no residual heat was observed because no initiator remained to initiate the polymerization of unreacted double bonds.

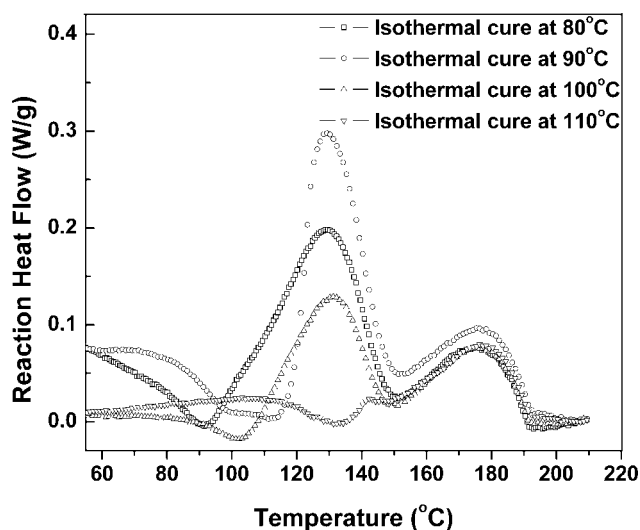
There are some articles reporting the reaction heat of vinyl ester resins.<sup>11–15</sup> In most of them, the same conclusion has been drawn: with increasing temperature,  $Q_I$  increases, whereas the residual heat decreases, and  $Q_T$  is nearly constant within the temperature range studied. However, this is not the case for the reaction heats studied here. The initiator system affects the reaction heat measured from DSC thermographs. A possible explanation can be provided as follows.



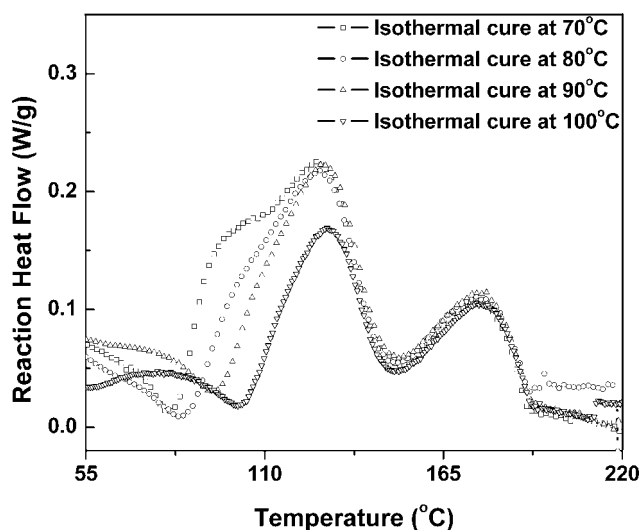
**Figure 6** Rescanned DSC thermographs for measuring the residual heat of reaction (system 1: C 1.0).

First, the heat of cure cannot be easily measured by a single isothermal run because the reaction becomes highly diffusion-controlled during the last stage of cure and requires a very long time to reach completion under the isothermal conditions. At a low temperature (80°C), at the start and end of the reaction, the heat cannot be detected by DSC if the sensitivity of the apparatus is not sufficient.<sup>16</sup> Initiator C is a high-temperature-decomposing initiator. It needs a longer time to finish the reaction than initiator P16 at a low temperature. Therefore, for the resin system containing initiator C without P16, it reacts slowly, and so it is difficult to determine the baseline of the DSC thermograph, which can be seen clearly in Figure 3 (system 1, 80°C), coupled with the sensitivity of the apparatus. Therefore, there undoubtedly is some heat lost in the beginning and at the end of the reaction. On the contrary, when the resin system contains two kinds of initiators, the system reacts quickly, and the reaction heat is released in a short time, so the apparatus will detect more reaction heat. This may be the reason that the cure reaction heat was lower for resin system 1, especially when it was cured at 80°C.

Second, the combination of initiators will release more reaction heat and increase the conversion of double bonds. Figure 5 shows that for resin systems 2 and 3, the cure reaction heat changed little with the cure temperatures, and the isothermal cure reaction heat for system 2 was always lower than that for system 3. Figure 4 shows that at the same cure temperature, the two cure systems had almost the same induction time and peak time, which were shorter than those for resin system 1. Therefore, the differences between the two resin systems may have resulted from the differences in the initiator systems.



**Figure 7** Rescanned DSC thermographs for measuring the residual heat of reaction (system 2: P16, 0.2; C, 1.0).



**Figure 8** Rescanned DSC thermographs for measuring the residual heat of reaction (system 3: P16, 0.4; C, 1.0).

#### Residual heat of isothermal curing DSC and network microstructures

There have been some articles on the biphasic structures formed in the curing of vinyl ester resins.<sup>1,6,7</sup> It has been reported that nodular microstructures, or so-called microgels, can be observed in cured vinyl ester resins. However, very few researchers have used isothermal DSC thermographs to demonstrate the biphasic structures in vinyl ester resins. Because in the isothermal curing process the two exothermic peaks superpose together, it is difficult to distinguish the biphasic structures formed in the cure process by isothermal DSC. However, the biphasic structures can be distinguished by a rescanned DSC thermograph of isothermal DSC.

Figures 6–8 show the rescanned DSC thermographs for different curing systems. These figures clearly show that the exothermic peaks can be divided into two peaks at lower isothermal curing temperatures. Only one exothermic peak existed at a higher isothermal temperature, which was 120°C in Figure 6 and 110°C in Figure 7. It is well known that the glass-transition temperature is proportional to the crosslink density. Thus, it is reasonable to assign the higher temperature peak to the microgel phase with a higher glass-transition temperature and the lower temperature peak to the nonmicrogel phase with a lower glass-transition temperature.<sup>17</sup>

Figures 6–8 also shows that the areas for the first peaks (lower temperature peaks) obviously decreased with increasing isothermal temperatures until the first peaks disappeared. However, for the second peaks (higher temperature peaks), the areas were almost unchanged, especially in Figures 7 and 8. Table III shows the residual heats from Figures 6–8. Because of the superposition of the two exothermic peaks, the absolute heat of each peak was not easy to calculate. Therefore, only the total residual heat could be calculated. The total residual heat, as shown in Table III, decreased with the isothermal cure temperatures and was almost independent of the initiator systems.

It is well known that in the isothermal curing process, the conversion of double bonds generally is not 100%. There are always some double bonds remaining in the reaction system. Therefore, after a sample previously isothermally cured is rescanned, the unreacted double bonds will react again. With the isothermal curing temperature increasing, the number of unreacted double bonds decreases. As a result, in the next rescanning step, the residual heat decreases correspondingly. Combining Figures 6–8 and Table III, we can see that for initiator system 1 (Fig. 6), the decrease in the residual heat with increasing temperature came from the first and second peaks, which corresponded to the microgel phase and nonmicrogel phase structures, respectively. For the combined initiator systems with two kinds of initiators (Figs. 7 and 8), although the residual heat decreased with the isothermal temperature increasing, the decrease in the residual heat mainly resulted from the first peak, that is, from the nonmicrogel phase. Therefore, the conclusion can be drawn that for the combined initiator systems, a more consistent microgel phase may be constructed within the investigated temperature range. This is because in the isothermal cure of vinyl ester resins, the double bonds in the microgel phase react first before the gel point, and subsequently, the double bonds in the nonmicrogel phase react.

#### Effects of resin systems on the mechanical properties of cured resins

The tensile and flexural properties of different samples are shown in Figures 9 and 10. The samples cured isothermally at a low temperature (80°C) or at

**TABLE III**  
Residual Heats (J/g) for Different Initiator Systems

Initiator content (wt %)	70°C	80°C	90°C	100°C	110°C	120°C
P16, 0.2; C, 1.0	—	50.143	50.230	34.654	10.045	—
P16, 0.4; C, 1.0	69.560	57.934	52.230	36.648	—	—
C, 1.0	—	53.370	48.406	38.856	22.745	17.274

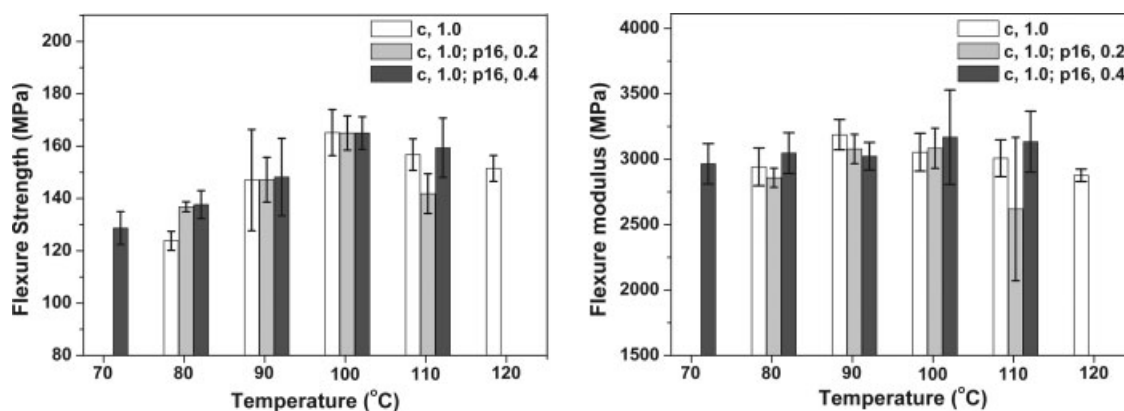


Figure 9 Flexural properties of different samples (error bars represent one standard deviation).

a high temperature (120°C) had poor mechanical properties for all resin systems investigated. The samples cured at 100°C had the best properties. It is clear that the cure temperature affects the mechanical properties of the cured vinyl ester resins, rather than the initiator system or resin formulation.

As discussed in a previous section, biphasic structures form during the cure of vinyl ester resins. Microgels are domains with a high crosslinking density dispersed in a pool of a low-crosslinking-density material. Therefore, it is reasonable to compare the microgel phases to certain rigid particles filled in a nonmicrogel phase, which can be regarded as a certain polymer matrix. Therefore, the mechanical properties of the cured resins mainly depend on those of the nonmicrogel phases.

Rey et al.<sup>1</sup> divided the cure process of vinyl ester resins into four steps: the induction period, microgel formation and agglomeration, gelation, and postgelation. Before gelation, the resin molecules that are polymerized mainly grow and become connected into clusters of microgels; that is, they form into microgel phases. At this stage, termination reactions

are more and more diffusion-controlled, but the mobility of double bonds and radicals decreases little, so the polymerization rate increases. Therefore, at this stage, both the temperature and the initiator system determine the structure of the microgels. After gelation, no new microgels form, and the rest of the polymerization mainly occurs in the nonmicrogel phases. Then, this part of the polymerization determines the mechanical properties of the cured resins. However, in this part of polymerization, because residual monomers and radicals gradually stay trapped in the network, their mobility depends only on the cure temperature, and then the radical concentration is not a major factor; meanwhile, because it is a low-temperature initiator, the residual amount of initiator P16 is very low. Therefore, the mechanical properties of the cured resins studied here mainly depend on the cure temperature.

When the resins are cured at a low temperature, because the mobility of the network increases with the cure temperature, the mobility of the network is lower. Meanwhile, the number of radicals is lower. Therefore, a large number of double bonds are

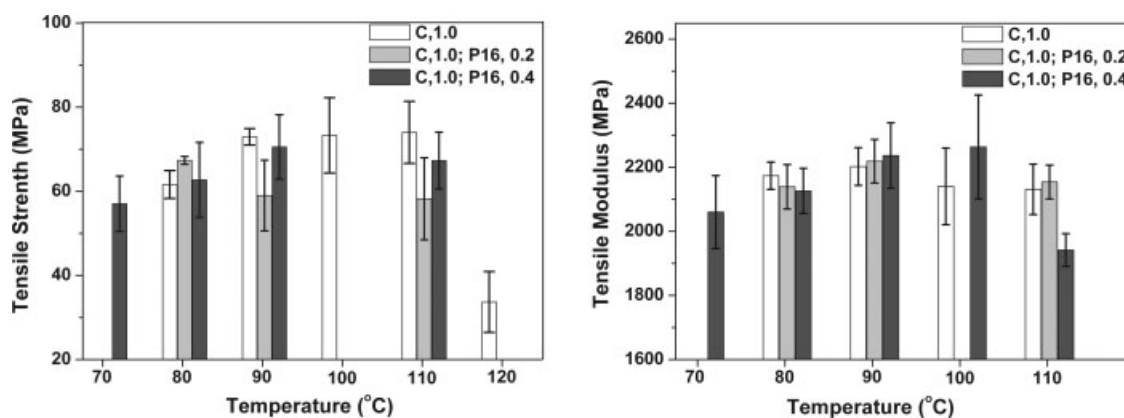


Figure 10 Tensile properties of different samples (error bars represent one standard deviation).

trapped in the network and unreacted. With the cure temperature increasing, the number of trapped double bonds becomes lower and lower. Therefore, the mechanical properties tend to increase with the cure temperature increasing. However, when the cure temperature is high enough, this makes the mobility of the radicals and monomer high, so the polymerization rate is too fast to make the polymer chain relax, and higher residual thermal stress builds up in the cured resins. Therefore, the mechanical properties decrease.

### CONCLUSIONS

A combination of initiators affected the cure kinetics of vinyl ester resins strongly. A 0.2 wt % concentration of P16 in the combination system reduced the induction time and the peak time obviously. However, there was no difference in the induction time and the peak time when the amount of P16 in the combination system was increased from 0.2 to 0.4 wt %. At the same time, the combination of initiators could increase the cure reaction heat.

The biphasic structures that formed during the cure of vinyl ester resins had no significant relationship with the formulation of the resin system. The combination of initiators could result in a more consistent microgel phase structure.

The initiator systems had little effect on the mechanical properties of the cured vinyl ester resins, which mainly depended on the cure temperature.

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