# Cure Kinetics, Microheterogeneity, and Mechanical Properties of the High-Temperature Cure of Vinyl Ester Resins

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**ABSTRACT:** A kinetic model has been developed that is based on the irreversible thermodynamic fluctuation theory, in which the conversion of comonomers is a function of the curing relaxation time, reaction time, and reaction temperature. This modified model permits a better prediction of the course of the high-temperature cure reaction of vinyl ester (VE) resins under isothermal conditions. The microheterogeneity in cured resins was investigated through the measurement of the residual heat of isothermally cured samples with differential scanning calorimetry and through the observation of the fracture surfaces of samples under different cure conditions with scanning electron microscopy (SEM). The SEM photographs demonstrated the existence of clusters of microgels of about 20 $\mu$m in samples isothermally cured at 80°C for 3 h. The results of the dynamic mechanical thermal analysis of postcured samples verified the microheterogeneity in the cured samples and showed that the glass-transition temperatures were not affected by the curing conditions. The effect of postcuring on the conversions of VE and styrene varied with the different cure schedules. The postcure for a sample isothermally cured at 80°C increased the tensile strength and flexural strength. On the contrary, the postcure for samples isothermally cured at 120°C reduced the tensile strength and flexural strength. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1124–1133, 2004

**Key words:** modeling; microgels; mechanical properties

## INTRODUCTION

There is an important relationship between the cure behavior, microheterogeneity, and mechanical properties, which plays a vital role in high-speed and continuous pultrusion processing for manufacturing greater than 2500-m carbon fiber/vinyl ester (VE) resin composites used as sucker rods in petroleum exploitation. Therefore, it is important to understand this relationship to optimize the properties of composites. In general, studying the cure behavior begins with studying the cure kinetics of resins. It is difficult to model the cure kinetics of crosslinking free-radical polymerization[1] because of the competing reactions among the initiators, inhibitors, and comonomers, the heterogeneities during network formation, and diffusion limitations. At present, there are primarily two kinds of models used to simulate the reaction rate profiles of VE resins: autocatalytic models[2–5] and mechanistic models.[6–8] Mechanistic models have many parameters and are not easy to use in process simulations.[6] The autocatalytic model developed by Kamal and Sourour[9] has been used by many researchers to simulate the reaction rate profiles of VE resins. However, the kinetic exponents $m$ and $n$ are not constant and change with the cure temperature. It might be inappropriate to use these models to simulate the high-temperature cure rate profiles of VE resins.

The free-radical crosslinking copolymerization of a styrene-unsaturated polyester resin is characterized by the formation of microgels, which are followed by their growth and coagulation into clusters and the linking of the clusters into the final morphology of the cured resin, resulting in a heterogeneous structure.[10] The phase-separation process stops after the resin reaches its gel point, and the domain size of the separated phase remains the same throughout the rest of the reaction period. Yang and Lee[11] suggested that the network structure might be coral-like or flakelike and that the formation of microgels might enhance intraparticle crosslinking. Similar behavior may occur in VE resin systems, leading to microgel structures possessing more VE monomer content than the bulk. Atomic force microscopy (AFM) photographs of cured VE specimens showed that these systems were characterized by a nodular morphology[12] or closely packed microgels around 100 nm in diameter,[13] which resulted from the formation of microgels during the early curing stages. Therefore, the early curing stages
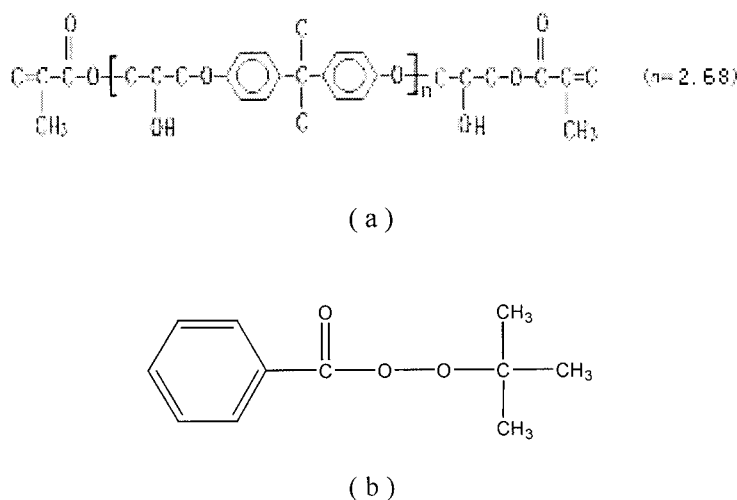
**Figure 1** Chemical structures of (a) VE and (b) *t*-butyl peroxybenzoate.

play a critical role in determining the morphology of the final cured resin. The reactive groups are within the repeated units for styrene-unsaturated polyester resins, whereas VE resins only have reactive groups at the ends of the polymer chains, there being no intramolecular crosslinking that can affect the microstructure of the initial polymer. In addition, the results of AFM may be affected by sample preparation, and so the same sample may have different fracture surfaces. To our knowledge, very few studies have shown the sizes and shapes of the clusters of microgels of a VE resin on a micrometer scale.

Postcuring plays an important role in composite processing. The effect of postcuring on the mechanical properties depends on the resin formulations, cure times and temperatures, postcure times and temperatures, and so forth, and this makes it difficult to draw identical conclusions. A few researchers have studied the effect of postcuring on the mechanical properties of VE resins.[12,14]

For this article, the effects of isothermal cure and postcure on the structures, phase separations, comonomer conversions, and mechanical properties of VE resins were comprehensively investigated with differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and dynamic mechanical thermal analysis (DMTA) to determine the relationships between the microstructures, conversions, and mechanical properties under the studied conditions.

## EXPERIMENTAL

### Materials

A VE resin (Hetron 922, Ashland Chemical Co.), containing a mixture of styrene and a dimethacrylated epoxy compound, was used. The chemical structure of

Hetron 922 is shown in Figure 1(a). The average molecular weight of VE in Hetron 922 was 987 g/mol, and the styrene monomer concentration, determined by $^{1}$H-NMR, was 40.85 wt %. This molecular weight of VE corresponded to a value of 2.68 for $n$. The molar ratio of styrene to VE was 6.568. The heat of polymerization was determined to be 67.4 kJ/mol for styrene and 57.8 kJ/mol for methyl methacrylate.[7] Thus, the heat of reaction for the VE resin was 334.1 J/g, and this value was used as the total amount of reaction heat throughout the analysis.

Trigonox C was used as the initiator at a concentration of 1 wt % with respect to the resin; it was purchased from Tianjin Akzo Nobel Peroxides, Ltd. (China). Trignox C contained 98 wt % *t*-butyl peroxybenzoate, and its chemical structure is shown in Figure 1(b). All the materials were used as received without further purification.

### Characterization

DSC (Pyris-1, PerkinElmer) was used to measure the overall reaction rate profiles. Isothermal kinetic experiments were performed at five different temperatures (80, 90, 100, 110, and 120°C) 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.

The conversions of VE and styrene double bonds for cured samples were obtained from FTIR spectra (model 750, Nicolet). A milled sample was mixed with KBr and then pressed into a solid disk with a diameter of 1 cm before the measurement. The peaks at 945 and 910 cm$^{-1}$ represent the bending of the carbon–hydrogen bonds of the vinyl groups in VE and styrene, respectively. The peaks at 830 and 700 cm$^{-1}$ represent the bending of the aromatic carbon–hydrogen bonds

**TABLE I**
**Cure Conditions for the Samples**

| Sample | Cure | | Postcure | |
|---|---|---|---|---|
| | Temperature (°C) | Time (h) | Temperature (°C) | Time (h) |
| 1 | 80 | 3 | — | — |
| 2 | 80 | 3 | 135 | 1 |
| 3 | 120 | 2 | — | — |
| 4 | 120 | 2 | 135 | 1 |

in VE and styrene, respectively, and were used to normalize the conversion values for the changes in the thickness or evaporation of styrene during the cure.[5,12,15] The normalized fractional conversions of VE and styrene double bonds were calculated with eqs. (1) and (2), respectively:

$$\alpha_{\text{vinyl}} = 1 - \frac{A_{t(945)}}{A_{0(945)}} \times \frac{A_{0(830)}}{A_{t(830)}} \tag{1}$$

$$\alpha_{\text{st}} = 1 - \frac{A_{t(910)}}{A_{0(910)}} \times \frac{A_{0(700)}}{A_{t(700)}} \tag{2}$$

where $\alpha_{\text{vinyl}}$ is the conversion of VE, $\alpha_{\text{st}}$ is the conversion of styrene, $A_t$ is the absorption intensity of the peaks for the cured samples, and $A_0$ is the absorption intensity of the peaks for the pure resin.

The dynamic mechanical characterization of the specimens was conducted on a Rheometric Scientific DMTA instrument with a double-cantilever geometry at 1 Hz with a scanning speed of 2.5°C/min. The specimens used in the dynamic testing were 5 cm $\times$ 0.5 cm $\times$ 1.75 cm.

### Sample preparation

The casting equipment consisted of two stainless steel plates (40 cm $\times$ 40 cm $\times$ 2 cm). An approximately 2-cm-thick rubber belt, covered with a poly(ethylene terephthalate) (PET) film, was first placed between the plates to control the thickness of the sample and to prevent leakage of the resin from the mold. The inside of the plate was coated with a thin layer of a release agent diluted with 95 wt % acetone. The mold was then clamped with six binder clips placed on three of its sides.

The well-mixed resins were poured into the casting cell from the top through a PET funnel. After being filled, the mold was placed vertically in a curing oven. There were four different curing conditions, as shown in Table I.

The specimens (15 cm $\times$ 1 cm) were cut from the cast resin with a diamond saw and used for tensile and three-point bending test. The tensile and flexural tests were conducted on an Instron 1811 universal

testing machine according to GB2568-1995 and GB 2570-1995, respectively. All experiments were performed at 20 $\pm$ 2°C.

### Microstructure study

For the microstructure study, the investigated specimens were cooled in liquid nitrogen and then fractured. A Cambridge Stereo-scan 250 MK3 was used to observe the fracture surfaces.

## RESULTS AND DISCUSSION

### Cure reaction kinetics

It has been reported that the isothermal heat released before resin vitrification increases with the isothermal cure temperature,[4,16] as does the final extent of reaction.[3,13] Some researchers have found that the glass-transition temperature ($T_g$) increases with the isothermal cure temperature and that the difference between $T_g$ and the isothermal cure temperature is constant at a certain temperature.[7] $T_g$ of a partially cured sample at different cure temperatures is nearly a linear function of the final conversion ($\alpha_f$) at the cure temperature: $T_g = a + b\alpha_f$.[6,7] Because $T_g$ is related to the molecular relaxation process, the chemical reaction can be explained with the irreversible thermodynamic fluctuation theory, as discussed by Hsich.[17] Therefore, the irreversible thermodynamic fluctuation theory has been applied to simulate the changes in the conversion with time in the isothermal cure of VE resins but not to elucidate the kinetic mechanisms of the reaction.

With the nonequilibrium thermodynamic fluctuation theory, Hsich[17] developed a kinetic model to explain the cure kinetics of polymer–filler systems, in which the physical or mechanical properties of polymer systems during isothermal cure can be expressed as follows:

$$\frac{P_\infty - P(t)}{P_\infty - P(0)} = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \tag{3}$$

where $P(t)$, $P_\infty$, and $P(0)$ are the physical or mechanical properties during the cure at times $t$, $\infty$, and zero, respectively. $\beta$ is a constant. $\tau$ is the curing relaxation time:

$$\tau = \tau_0 \exp\left(\frac{H}{RT}\right) \tag{4}$$

where $\tau_0$ is a constant, $R$ is the gas constant, $T$ is the absolute cure temperature, and $H$ is the activation energy of the cure reaction.

Taking into account certain correlations between the conversion of comonomers ($\alpha$) and the physical or mechanical properties of cured resin systems ($P$), we
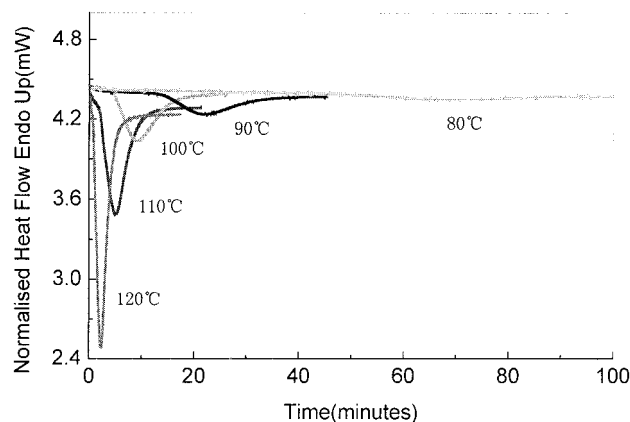
**Figure 2** DSC isothermal cure thermographs for the Hetron 922 VE resin at different temperatures.



**Figure 3** Final conversion as a function of the curing temperature.

can substitute $\alpha$ for $P$. The conversion at $t = 0$ is zero; the conversion is designated 1 when there is no change in the isothermal DSC thermograph. Therefore, the following conversion expression, modified from eq. (3), is used in this work:

$$1 - \alpha = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \quad (5)$$

where $\alpha$ is the conversion at time $t$ in the isothermal cure reaction. $\tau$ is the time when $\alpha$ is 0.632 in the conversion–time curve obtained from the isothermal DSC thermograph.

Figure 2 gives plots of the rates of heat generated during the isothermal cure versus the cure times at 80, 90, 100, 110, and 120°C. The polymerization of the VE resin involves three stages:[2]

Inhibition zone. Radicals generated by initiator decomposition are consumed by the inhibitor. The heat of reaction in this zone is too small to be observed from DSC thermographs.

Propagation zone. After the inhibitor is consumed, the polymerization rate accelerates because of diffusional limitations on the bimolecular termination reactions, and this results in the seemingly autocatalytic behavior known as the gel or Tromsdorff effect.
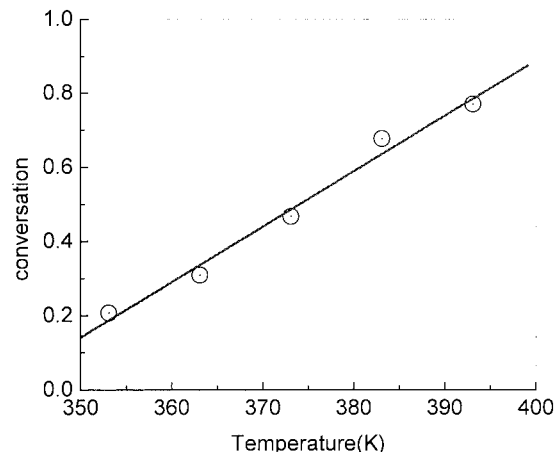
Diffusion zone. The polymerization rate decreases because of limitations in the mobility of large molecules.

Table II shows that the final conversion increases with the cure temperature. The resin is not completely cured at these temperatures because it vitrifies before the cure reaction is complete, and this leads to some double bonds remaining unreacted.[6] Within the temperature range studied, the final conversion ($\alpha_T$) can be described as a linear function of the temperature (Fig. 3):

$$\alpha_T = -5.0884 + 0.01494T \quad (6)$$

There is also a linear relationship between $\ln \tau$ and $1/T$ (Fig. 4):

$$\ln\tau = -26.965 + 11006.6/T \quad (7)$$

Once $\tau$ is obtained, the parameter ß can be obtained as follows:

$$\log[-\ln(1 - \alpha)] = \beta\log\left(\frac{t}{\tau}\right) \quad (8)$$

From the slope (Fig. 5), ß can be obtained for different temperatures. ß is not a constant within the tempera-

**TABLE II**
**Curing Characteristics of VE Resins Obtained from Isothermal DSC**

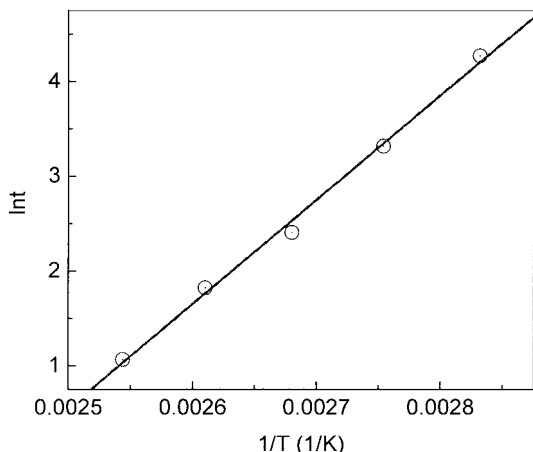| | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | 80 | 90 | 100 | 110 | 120 |
| Isothermal cure heat (J/g) | 69.03 | 103.23 | 155.94 | 226.21 | 257.23 |
| Isothermal cure conversion | 0.21 | 0.31 | 0.47 | 0.68 | 0.77 |

**Figure 4**  Ln $\tau$ as a function of the inverse cure temperature $(1/T)$.

ture range studied: it decreases with increasing temperature. It can be approximately described as a linear function of $T$ with the temperature range studied (Fig. 6):

$$\beta = 44.53 - 0.11T \qquad (9)$$

This is contrary to the cure kinetics of rubber, for which ß is a constant at different cure temperatures.[17]

The conversion of the VE resin with the curing time at different temperatures was can be expressed as follows:

$$\alpha = \{1 - \exp[-(t/\tau)^{(44.53-0.11T)}]\}(0.01494T - 5.0884) \qquad (10)$$

Figure 7 presents the experimental and theoretical conversion as a function of the cure time at different isothermal temperatures. The theoretical predictions from the model agree well with the experimental data.
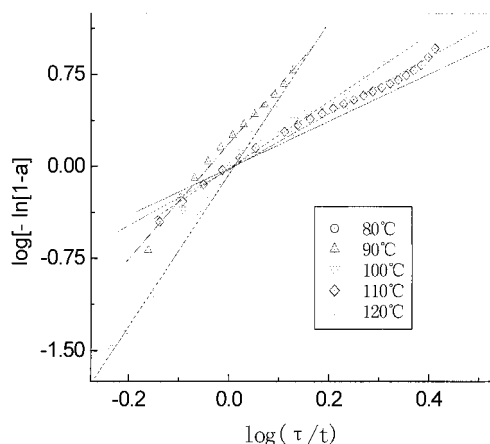


**Figure 5**  Log$\{-[\ln(1 - \alpha)]\}$ as a function of log$(t/\tau)$.
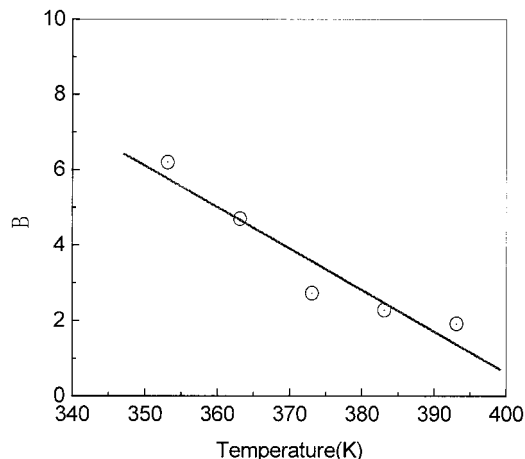


**Figure 6**  ß as a function of the curing temperature

## Biphase structures and the microgels

The residual heat of reaction for the isothermally cured resins was measured via rescanning from 50 to 250°C at 10°C/min with DSC. The rescanned DSC thermographs are shown in Figure 8, and the results obtained from the DSC thermographs are listed in Table III. The curves from 80 to 110°C show two exothermic peaks and one endothermic peak. The temperatures of the first exothermic peaks (lower $T_g$ peaks) increase with the isothermal cure temperatures, whereas the heat generated during the first peak ($Q_{r1}$) decreases significantly with the isothermal temperatures. The same tendency has been found for the second exothermic peaks, but the heat generated decreases more slowly than that of the first peaks. However, for the curve of the residual heat of the sample cured isothermally at 120°C, there is a superposition of the heat capacity step of $T_g$ (endothermic peak) with only one exothermic peak.

As mentioned previously, heterogeneous biphase networks develop during the cure of the resins. One phase with a higher crosslinking density is rich in VE, whereas another phase with a lower crosslinking density is rich in styrene. Because of the incompletion of the isothermal reaction, there are some monomers unreacted and trapped in the resins. After being reheated above $T_g$, the unreacted monomers will react. It is well known that $T_g$ is proportional to the crosslinking density.[18] Therefore, with reheating, the styrene-rich phase first reaches its $T_g$, and the monomers trapped in the styrene-rich phase react first. However, the VE-rich phase reaches its $T_g$ after the styrene phase, and this results in the monomers trapped in the VE phase reacting second. It is reasonable to assign the first exothermic peaks to the polystyrene-rich phase with a lower $T_g$ and the second exothermic peaks to the VE-rich phase with a high $T_g$.[18]

The decreases in the relative areas of the first exothermic peaks with the isothermal cure temperatures
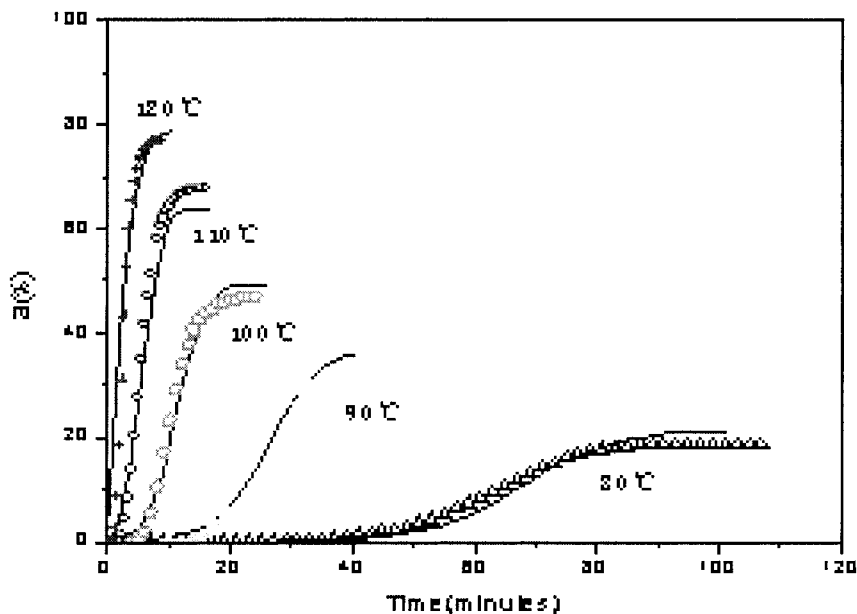
**Figure 7** Experimental and theoretical conversions versus the cure time at different isothermal temperatures. The solid curves represent the theoretical predictions.

may result from the isothermal cure temperatures: the higher the isothermal cure temperature is, the more reaction heat is released, and so less reaction heat is released during the postcure. However, for the second exothermic peaks, because it is related to the VE-rich phase with a higher density, the effect of the isothermal cure temperature on the structures of the VE-rich phase is less than on that for the styrene-rich phase, so the changes in the relative areas with the isothermal temperatures for the second exothermic peaks are slower than for the first peaks.

Figures 9–12 show SEM micrographs of fracture surfaces of the samples cured under different conditions. There are distinct differences in the fracture surfaces of the samples. As shown in Figure 9, the
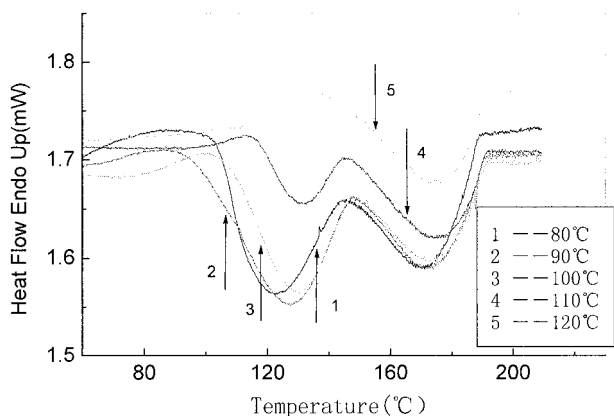
clusters of the microgels disperse throughout the entire fractured surface, each cluster of microgels containing many microgels with coral-like structures. The biggest cluster is about 20 $\mu$m, whereas the biggest microgel is about 4 $\mu$m. It is possible for the clusters of microgels to form instantly because of the difficulty in releasing reaction heat; otherwise, some individual microgels should form. However, if these clusters form instantly, they should form after the gel time because so many clusters forming at the same time would undoubtedly bring about changes in the resin properties.

We can see by comparing Figures 9 and 10 that the fracture surface of a sample postcured at 135°C for 1 h is rougher, whereas the fracture surface of a sample without postcuring is smoother, except for the clusters of microgels. Thus, it may be inferred that the mechanical properties of the two samples are different. No microgel can be discovered from the SEM micrograph in Figure 10. This may be due to the disappearance of the biphase structure.

The regional clusters of microgels shown in Figure 11 have been compared with those in Figure 9. The influence of the temperature on the cluster size could not be determined. However, the clusters are clearly fewer in number for the sample isothermally cured at 120°C (Fig. 11). Also, after the postcuring of sample 3, regional clusters cannot be seen with SEM (Fig. 12).

## Properties of the cured VE resin

It is believed that the curing conditions (temperature, curing time, postcuring, etc.) of the VE resin affect the



**Figure 8** Rescanned DSC thermographs for resins cured isothermally at the indicated temperatures.

**TABLE III**
**Results from Rescanned DSC Thermographs**

| | Isothermal temperature (°C) | | | | |
| --- | --- | --- | --- | --- | --- |
| | 80 | 90 | 100 | 110 | 120 |
| Temperatures (first exo peak, °C) | 122.59 | 127.26 | 129.77 | 130.56 | — |
| Temperatures (second exo peak, °C) | 172.67 | 173.88 | 173.85 | 175.36 | 174.14 |
| $Q_{r1}$ (J/mg)[a] | 18.96 | 21.78 | 15.44 | 5.49 | — |
| $Q_{r2}$ (J/mg)[a] | 15.68 | 14.18 | 11.78 | 13.52 | 17.27 |

[a] Because of the superposition of two exothermic peaks and one endothermic peak, it was difficult to obtain the correct peak area of residual heat. Therefore, the peak area was defined as the area between the DSC curve and the line from the point deviating from the baseline to the connection point of two peaks. The exothermic area of 120°C was the area under the baseline.
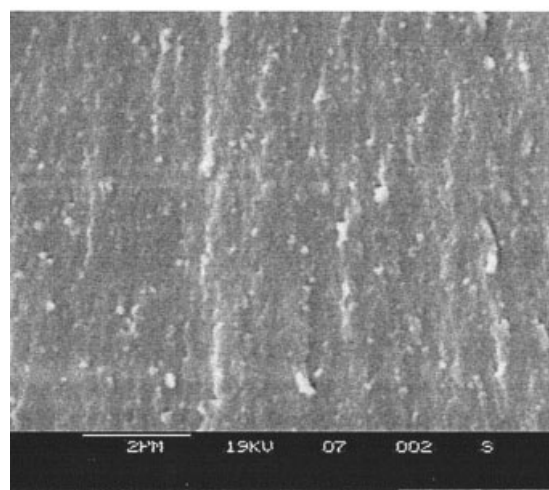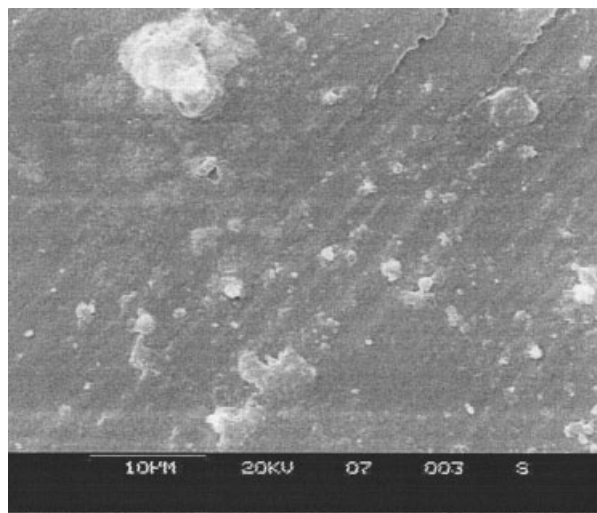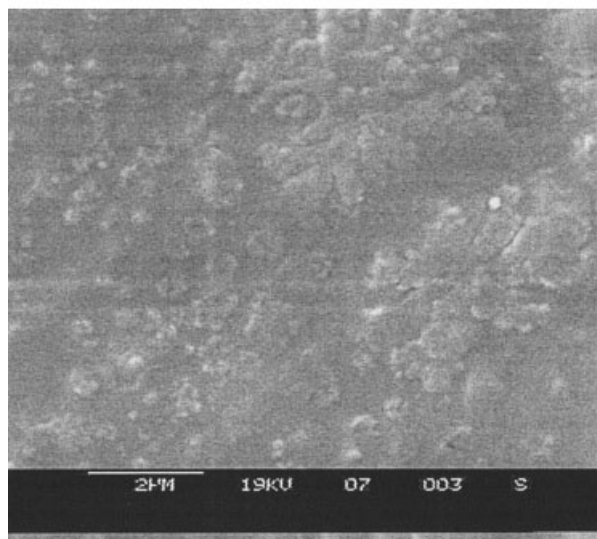


(a)
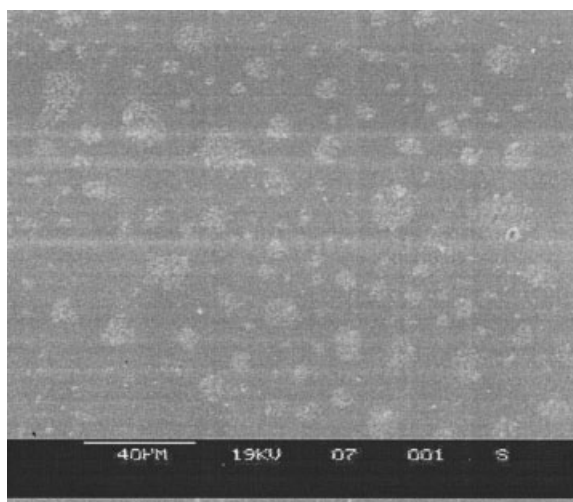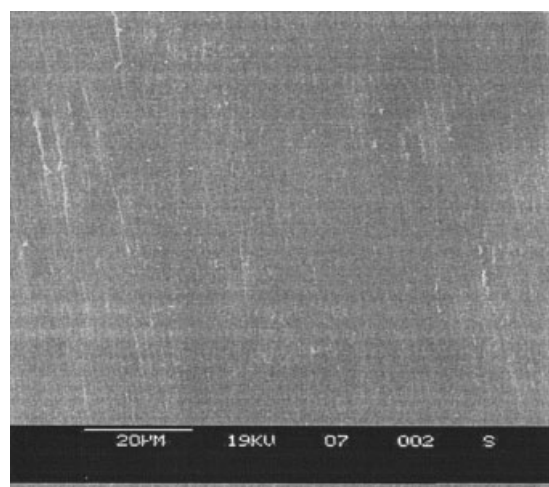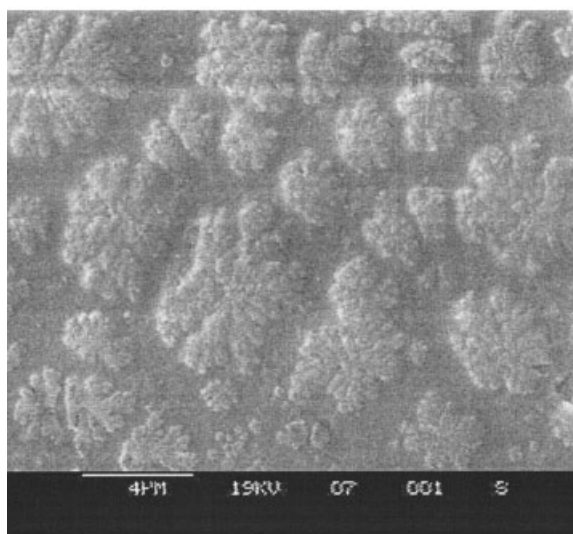


(b)

**Figure 9** SEM micrographs of the fracture surface of a VE resin isothermally cured at 80°C for 3 h (sample 1).



(a)



(b)

**Figure 10** SEM micrographs of the fracture surface of a VE resin isothermally cured at 80°C for 3 h and then postcured at 135°C for 1 h (sample 2).

(a)



(b)

**Figure 11** SEM micrographs of the fracture surface of a VE resin isothermally cured at 120°C for 2 h (sample 3).



(a)



(b)

**Figure 12** SEM micrographs of the fracture surface of a VE resin isothermally cured at 120°C for 2 h and then postcured at 135°C for 1 h (sample 4).
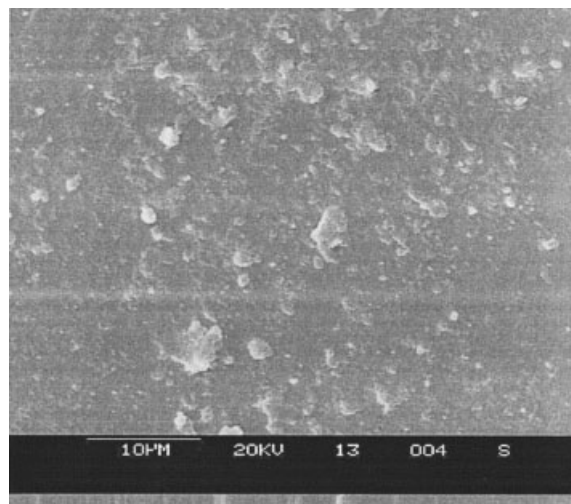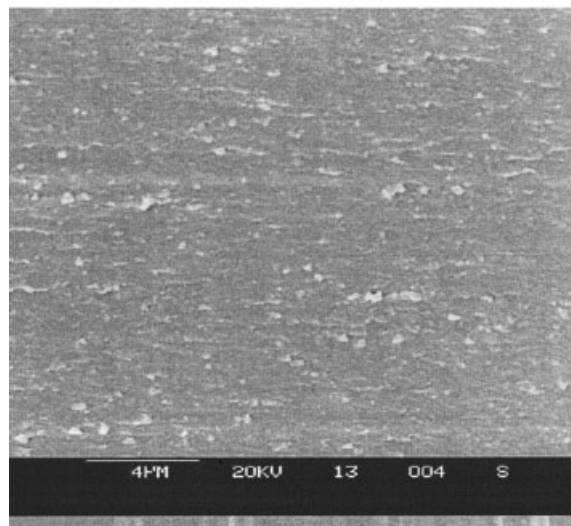
development of the resultant microstructures and properties. The previous results have proved that the cure temperatures and postcure have significant effects on the structures and conversion of C=C double bonds.

### Conversions under different curing conditions

The conversions of VE and styrene double bonds, calculated from FTIR spectroscopy data, are shown in Table IV. For sample 1, the conversion of the styrene double bonds increases from 88.3 to 93.8%, whereas the conversion of the VE double bonds decreases slightly after postcuring at 135°C for 1 h. This may be due to

1. Partial degradation of the network caused by depolymerization of the dimethacrylate.[1]
2. The insensitivity of FTIR for determining the conversion of methacrylate and styrene double bonds after postcure due to the fact that the

**TABLE IV**
**Conversions of VE and Styrene Double Bonds Obtained from the FTIR Data with Eqs. (1) and (2)**

|  | Sample | | | |
|---|---|---|---|---|
|  | 1 | 2 | 3 | 4 |
| $\alpha_{vinyl}$ (%) | 56.25 | 54.34 | 55.6 | 57.8 |
| $\alpha_{st}$ (%) | 88.3 | 93.8 | 94.0 | 94.8 |

infrared absorption bands were too small to be accurately measured.[2]

By comparing the conversions of double bonds for samples 3 and 4, we can that postcuring increases the conversion of VE double bonds for a sample isothermally cured at 120°C from 55.6 to 57.8%. Only a small increase in the conversion of styrene double bonds can be observed.

**Effect of the curing conditions on the mechanical properties**

As shown by the SEM micrographs (Figs. 9–12), the cure processes affect the fracture morphologies, which are related to the network structures. Therefore, the cure conditions also affect the mechanical properties of the cured samples.

The tensile strengths and flexural strengths of different samples are shown in Figure 13. The sample cured isothermally at 80°C without postcuring (sample 1) has the lowest tensile strength. After the postcure at 135°C for 1 h, its tensile strength increases by about 83% from 40.5 to 74 MPa, whereas the flexural strength increases by about 11.8% from 173.6 to 206 MPa. This agrees with the previous results observed in SEM micrographs: the fracture surface of sample 1 is smoother except for the clusters of microgels, whereas the fracture surface of sample 2 is rougher. As discussed in the previous section, the postcure can significantly increase the conversion of styrene double bonds for sample 1. The reaction of styrene mainly occurs between the clusters, leading to an increase in useful network crosslinks.

However, postcuring causes reductions in both the tensile strength and flexural strength of sample 3, especially the flexural strength. On the contrary, as mentioned previously, the conversions of VE and styrene double bonds of sample 3 increase slightly after postcuring. Therefore, it can be inferred that higher conversions of the monomers do not necessarily indicate greater strength.

The term *postcure* used here refers to *aging* in the contextual meaning. Pure postcuring is a chemical process and, therefore, chemical aging. The postcure processing that we have already discussed should involve chemical aging and physical aging. For sample 1 (isothermally cured at 80°C), the effect of chemical aging is greater than that of physical aging in the postcure process. On the contrary, for sample 3 (cured at 120°C), physical aging plays a greater role than chemical aging during postcuring. As a result, the effects of the postcure on the mechanical properties of samples 1 and 3 are different.

At high temperatures, the reactions take place very rapidly. Thus, polymer chains have less opportunity to achieve a relaxed conformation and maximize stress
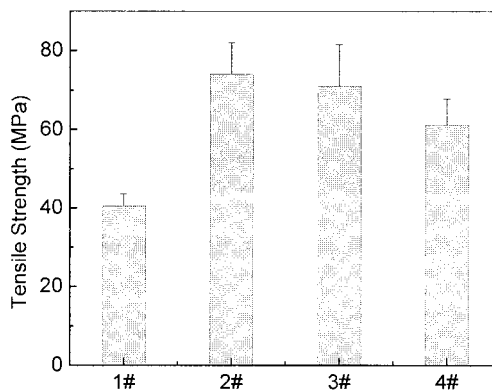


(a)
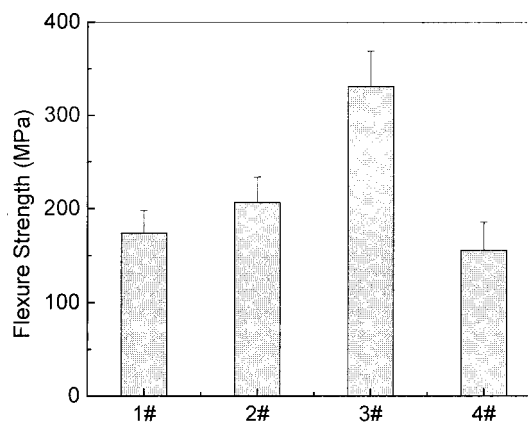


(b)

**Figure 13** (a) Tensile strength and (b) flexural strength of different samples. The error bars represent the standard deviation.

at high temperatures. Hence, when a sample isothermally cured at high temperatures is postcured, with the polymer chain relaxing, the tensile strength and flexural strength may decrease.

**Effect of the curing conditions on DMTA**

Figure 14(a,b) shows the effects of the cure conditions (temperature and postcure) on the dynamic mechanical properties of the cured samples. Sample 1 has three $T_g$'s at 105.6, 120, and 135°C, as shown in Figure 14(a). Its log $E'$–temperature curve [where $E'$ is the storage modulus; Fig. 14(b)] shows a decreasing–increasing–decreasing trend. In contrast, there is only one $T_g$ (133.95°C) for sample 2. However, the final $T_g$'s for the aforementioned samples are nearly identical. The
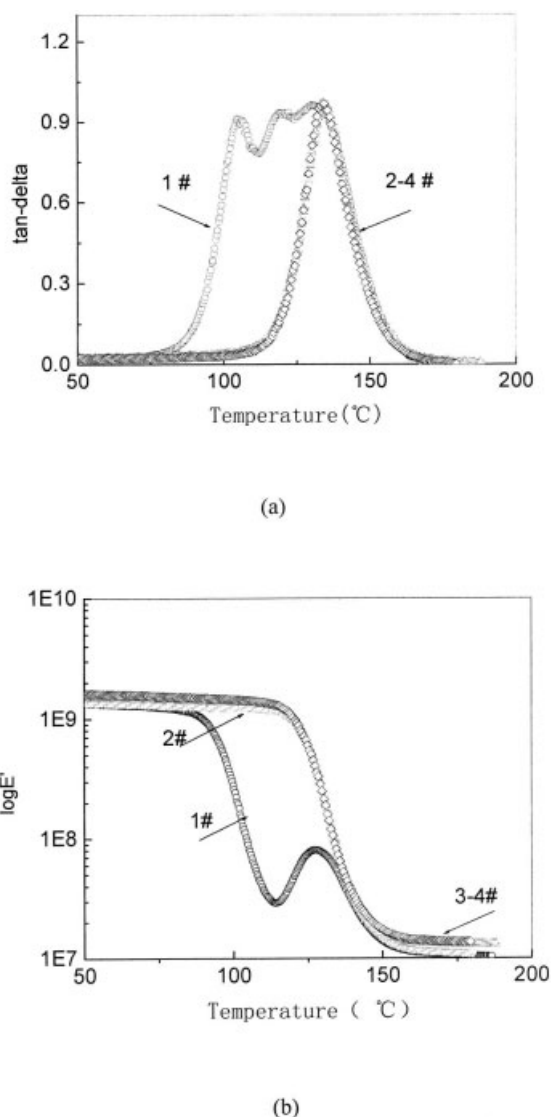
(a)



(b)

**Figure 14**   Figure. 14 (a) Tan $\delta$ and (b) $E'$ versus the temperature for VE resins under different cure conditions.

curves of the rubbery modulus for all the samples merge nicely into a single curve.

Similar behavior has been reported by some researchers[1] for an analogous resin cured at 23°C and postcured at 90°C with MEKP as the initiator and cobalt(II) octoate as the promoter. However, only two $T_g$'s, at approximately 65 and 115°C, were observed for the resin cured at 23°C without postcuring. The final tan $\delta$ maxima of the samples that they studied were obviously different. It has been proposed that the cure temperature and initiation system alter the heterogeneity in the network structure via microgel formation.[2] Therefore, the differences between the reported results and ours may be due to the different cure temperatures and initiation systems.

As discussed previously, clusters of microgels and biphase structure have formed in sample 1. Obviously,

$T_{g1}$ (105.6°C) at the tan $\delta$/temperature curves for the sample is caused by the styrene-rich phase, whereas $T_{g2}$ (120°C) is caused by the VE-rich phase. Therefore, it can be inferred that it is the structure of the styrene-rich phase, rather than the VE-rich phase, that determines the mechanical properties of sample 1.

Figure 14(a) illustrates that the curves of the four samples merge nicely into one another after the final tan $\delta$ maxima. The rubbery modulus of sample 2 is slightly higher than that of sample 1 [Fig. 14(b)]. There is no difference observed by DMTA between samples 3 and sample 4.

## CONCLUSIONS

A modified kinetic model based on the irreversible thermodynamic fluctuation theory can predict the conversion profiles of VE resins isothermally cured at 80–120°C and matches the experimental data quite well. Clusters of coral-like microgels with a maximum size of 20 $\mu$m can be clearly observed by SEM on the fracture surface of a sample cured at 80°C. Microgel formation with a maximum size of 4 $\mu$m possibly results from the difficulty of releasing the reaction heat. Postcuring can possibly cause the disappearance of biphase structures, with no clusters observed.

Postcuring can increase the conversion of comonomers for partially cured resins, thus affecting their mechanical properties. However, the mechanical properties have no direct relationship with the conversions of comonomers. A higher conversion does not necessarily mean higher mechanical properties. The DMTA results for postcured samples show that $T_g$ is not affected by the cure conditions.

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