Research Article

Curing Kinetics of Hybrid Networks Composed of Benzoxazine and Multifunctional Novolac Epoxy

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A novel hybrid network composed of benzoxazines (BZ) and novolac epoxy resin (F-51) was prepared successfully. Thermal properties, curing kinetics, and decomposition process were studied using isothermal differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in this paper. The reactive mechanism of F-51/BZ mixture system is different from the BZ homopolymers at low temperatures; two resin systems follow the autocatalytic model mainly at high temperatures. Thermogravimetric analysis indicates that F-51 can have no significant effect on thermal degradation temperatures and on increasing char yield.

1. Introduction

Polybenzoxazines (PBZ) are a relatively new class of thermosetting addition-cure phenolic resins developed in the recent years [1–5]. These newly developed resins possess special features, such as near-zero shrinkage upon curing, low water absorption, high char yield, no strong acid catalysts required for curing, and release of no byproducts during curing [6]. Benzoxazines (BZ) can be prepared by the Mannich-like condensation of different types of phenol, formaldehyde, and an amine, by employing either solution or solventless methods, so the molecular structure of BZ offers enormous design flexibility. This allows the properties of the cured materials to be tailored for a wide range of applications. These resins have gained great interest because they have the capability to exhibit the thermal and flame retardance properties with molecular design flexibility. PBZ resins are widely used in various applications to the needs of the high-technology aerospace industry.

Though BZ has so many fascinating characteristics, some works show that the cross-linked structure of polybenzoxazines is quite loose. Blending has been attempted to improve the properties of benzoxazines, such as undergoing hybrid network formation with other polymers [7–9], rubbers [10–12], and inorganic materials [13–19]. Recently, many authors have investigated the copolymerization of benzoxazine resin with epoxy resin to increase the cross-linking density and glass-transition temperature and through this have gained plentiful and substantial achievements [8, 20–22]. The curing kinetic of benzoxazine-epoxy hybrid networks by non-isothermal differential scanning calorimetry was noted by Jubsilp et al. [23]. However, the curing kinetic of benzoxazine-novolac epoxy resin hybrid networks by isothermal differential scanning calorimetry is scarce.

In present works, the properties and processing of hybrid networks of BZ and novolac epoxy resin (F-51) are studied, using isothermal differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Experimental Section

2.1. Chemicals. BZ (solid state, gel time more than 40 min at 180°C, viscosity less than 500 mpa·s at 100°C) was purchased from Sichuan University; the structure of the BZ is shown in Scheme 1. All chemicals were used without further purification. Novolac epoxy resin (F-51, epoxy equivalent weight 155 g/equiv.~180 g/equiv.) was obtained from China National BlueStar (Group) Co., Ltd. The structure of the F-51 is shown in Scheme 2.
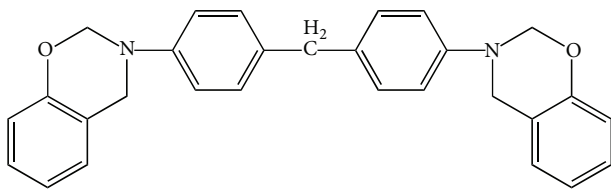
Scheme 1: Structure of benzoxazines.
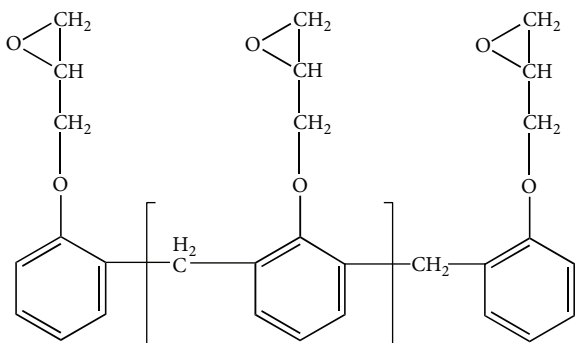
Scheme 2: Structure of novolac epoxy resin.

2.2. Preparation of Samples.

A blend of BZ and F-51 resin with equal mass composition was prepared by solution blending. The mixtures were stirred and dissolved in acetone and allowed to evaporate slowly at 50°C under a vacuum for 20 hours. The samples were used for isothermal and thermogravimetric analyzing. Mixtures were polymerized according to the following profiles: 180°C for 1 h, 200°C for 2 h, and 220°C for 2 h in an air-circulating oven. The pure BZ resin was cured according to the following profiles: 180°C for 1 h, 220°C for 2 h, and 240°C for 5 h in an air-circulating oven. Phenolic hydroxyl groups and F-51 were polymerized as shown in Scheme 3.

2.3. Thermal Characterization.

The curing behaviors of BZ and mixtures were evaluated by using Perkin-Elmer Thermal Analysis DSC7. The DSC instrument was calibrated by indium standards and α-Al$_2$O$_3$ was used as the reference material. The isothermal analysis was performed at temperatures ranging from 205°C to 245°C in 20°C increments in nitrogen atmosphere and a sample mass of 5 mg ~6 mg in aluminum pans was used. The blends were dried under vacuum at 323 K for 1 h before DSC analysis.

2.4. Thermogravimetric Analysis.

A thermogravimetric analyzer (TGA) from TA Instruments, High Res Q600, was used for thermogravimetric analysis. Thermal degradation experiments were done under purged nitrogen. The gas flowing rate used for all experiments was 90 mL/min. A heating rate of 10°C/min from 50°C~900°C was used.

3. Results and Discussions

3.1. The Isothermal Curing Kinetics of BZ Monomer and F-51/BZ Mixture by DSC.

DSC is a powerful tool to trace the progress of curing process in order to obtain cure process parameters such as the extent and rate of chemical conversion. Thermal curing of the benzoxazine monomers forms the corresponding polymer PBZ with ring-opening of the oxazine of the two monomers. The curing behaviors of BZ monomer and F-51/BZ mixture were monitored by DSC. Figures 1 and 2 are isothermal DSC curves plotted of BZ and F-51/BZ mixture as heat flow versus time at 205°C, 225°C, and 245°C curing temperatures, respectively. The heat flow at 245°C is seen to increase rapidly with time and reach a maximum and then rapidly decrease, finally tending to zero. However, when the heat temperatures are 205°C and 225°C, the heat flow increases relatively slowly. Compared with the F-51/BZ mixture, the time for BZ to reach the heat flow maximum is shorter, which means that the reactive rate of BZ is faster than that of the F-51/mixture.

As for thermosetting resin cure kinetics, it is generally assumed that the rate of reaction can be described as follows:

$$\frac{d\alpha}{dt} = \frac{(dH/dt)}{\Delta H_0}, \tag{1}$$

where $d\alpha/dt$ is the rate of reaction, α is the degree of curing reaction, ΔH_0 is total reaction enthalpy, and dH/dt is the rate of reaction enthalpy.

The kinetic model may represent all processes if the chemical reactions occur simultaneously. For thermosetting materials that follow nth-order kinetics, the rate of conversion is proportional to the concentration of unreacted material, as in the following:

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n, \tag{2}$$

where $k(T)$ is the reaction rate constant and n is the reaction order.

The $k(T)$ is the temperature-dependent rate constant given by the Arrhenius relationship, which can be expressed as the following:

$$k(T) = A\exp\left(-\frac{E}{RT}\right), \tag{3}$$

where E is the activation energy, R is the gas constant, T is the absolute temperature, and A is the preexponential factor.

We can obtain the curve plot of $d\alpha/dt$ versus *time* at different temperature from the DSC data and (1), (2), and (3), which is shown in Figures 3 and 4.

As the isothermal temperature of monomer increases, the maximum reaction rate of BZ monomer and the F-51/BZ mixture increases while the time required to reach the peak decreases. The time of the maximum reaction rate of F-51/BZ mixture is 97 s at 245°C heating temperature, which is higher than that of BZ homopolymer (45 s). The time of the maximum reaction rate of the F-51/BZ mixture is 320 s, 770 s at 225°C, and 205°C heating temperature, respectively, which is higher than that of BZ homopolymer (135 s and 435 s). Rimdusit and Ishida have observed two separate peaks for the epoxy-benzoxazine system depending on composition [24]. The study shows that a single peak was observed with the epoxy content lower, which means that two peaks had
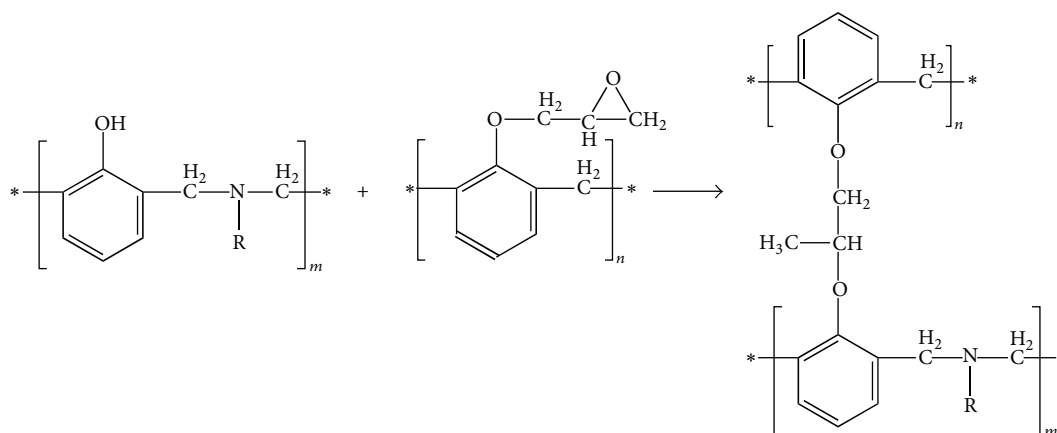
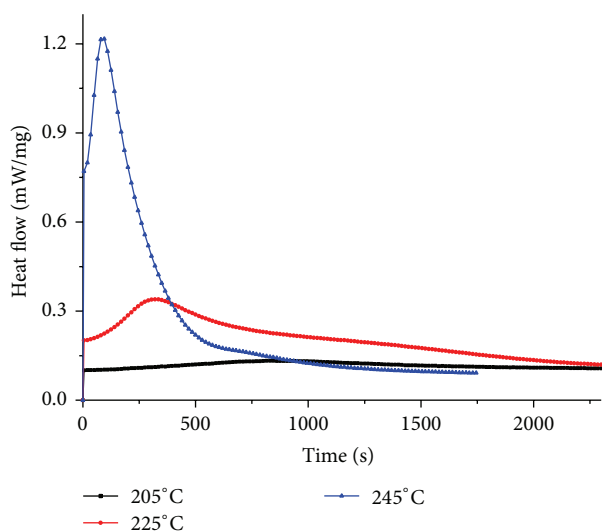SCHEME 3: The reaction between phenolic hydroxyl groups and F-51.

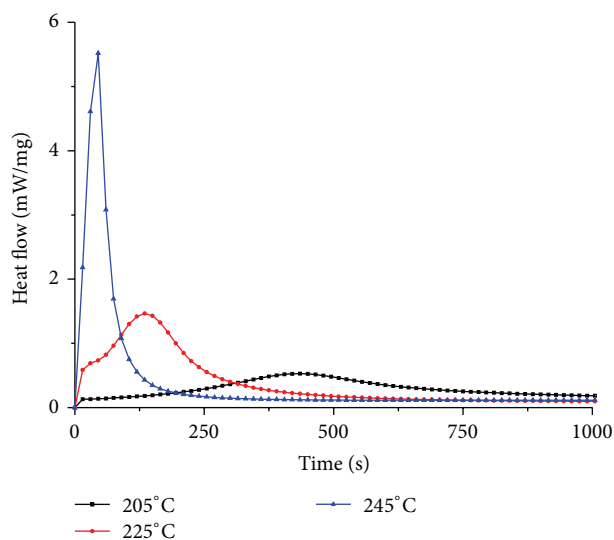FIGURE 1: Isothermal curing DSC curves of BZ/F-51 hybrid networks.

FIGURE 2: Isothermal curing DSC curves of BZ homopolymer.

merged at the same time, although two exothermic peaks begin to separate with increase of epoxy content. However, in our study, epoxy-benzoxazine system ratio is 1 : 1, and there was only one peak in the plot, which is attributed to the benzoxazine-benzoxazine reaction and epoxy-benzoxazine system reaction takes place at nearly the same time. On the other hand, the reaction time of epoxy-benzoxazine system is higher than that of benzoxazine homopolymer; the difference in time of reaction between epoxy-benzoxazine and benzoxazine homopolymer was attributed to the presence of epoxy resin diluting concentration of benzoxazine monomer.

Figures 5 and 6 show DSC data on the F-51/BZ mixture system and BZ homopolymer plotted as $d\alpha/dt$ versus α at different isothermal temperatures. The conversion of maximum reaction rate of BZ homopolymer is 19%, 28%, and 36% at 205°C, 225°C, and 245°C, respectively. And the conversion of maximum reaction rate of the F-51/BZ mixture system is 4%, 13%, and 25%. The conversion of maximum

reaction rate gradually increases with the increase of heating temperature, and, at the same temperature, the conversion of maximum reaction rate of BZ homopolymer is higher than that of the F-51/BZ mixture system. The accelerating isothermal conversion rate typically reaches its maximum between 20% and 40% conversion [25]. In this case, BZ homopolymer, by principles, is unsuitable to follow nth-order kinetics, while the F-51/BZ mixture system does not abide by this rule at low temperatures. According to the autocatalytic model, the rate of reaction is zero or very tiny initially and obtains a maximum value at some conversion. Figure 5 shows that the F-51/BZ mixture system follows the autocatalytic model mainly at high temperature. Meanwhile, the whole conversion of BZ homopolymer exceeds the conversion of the F-51/BZ mixture system at 205°C and 225°C, which means BZ homopolymer has more cross-linking density at the same temperature, when the rate of reaction obtains a maximum value.
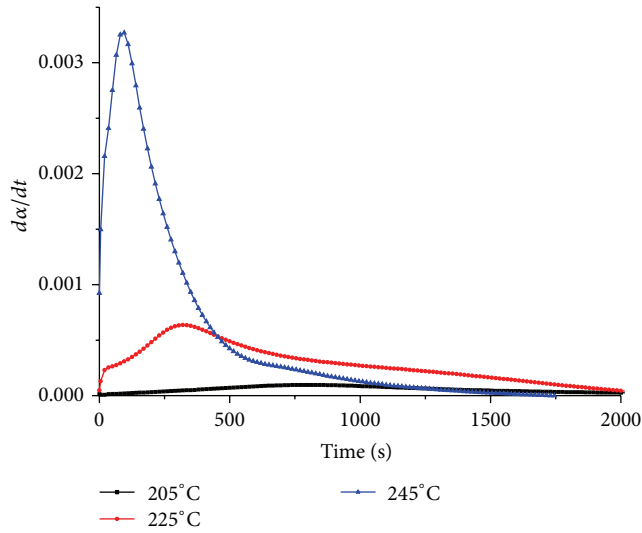
FIGURE 3: $d\alpha/dt$ versus time of BZ/F-51 hybrid networks in isothermal DSC.
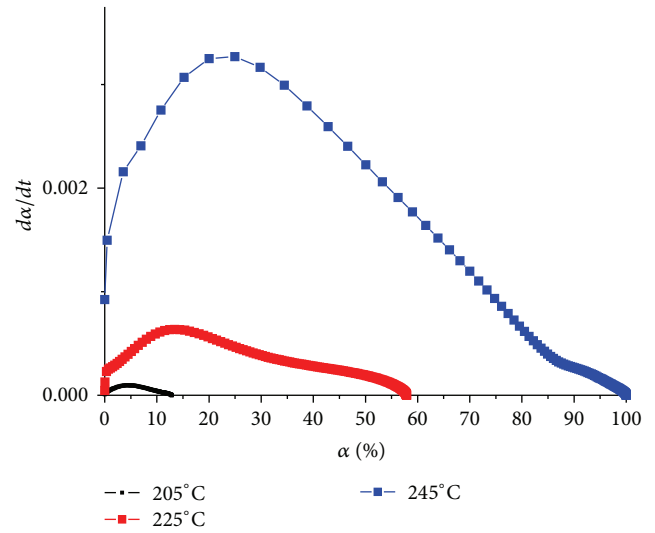

FIGURE 5: $d\alpha/dt$ versus conversion of BZ/F-51 hybrid networks in isothermal DSC.
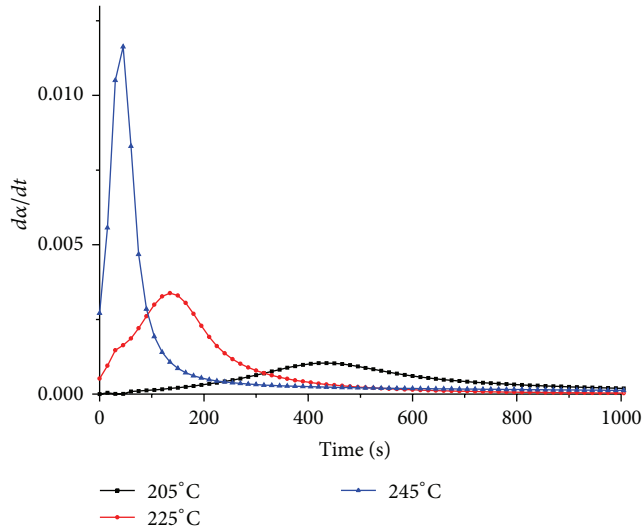

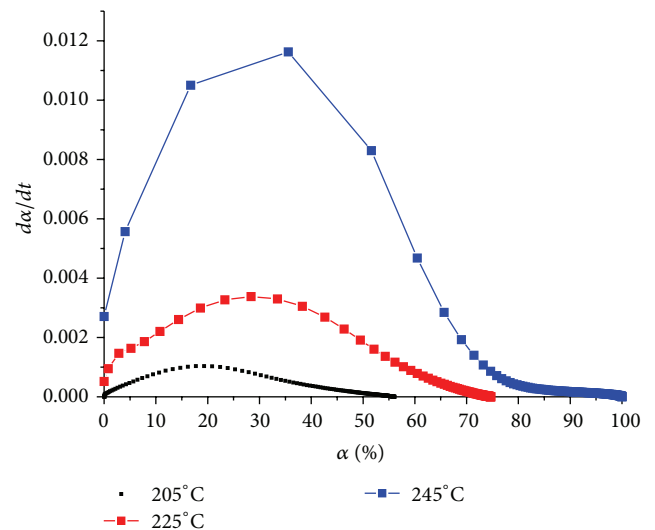FIGURE 4: $d\alpha/dt$ versus time of BZ homopolymer in isothermal DSC.

FIGURE 6: $d\alpha/dt$ versus conversion of BZ homopolymer in isothermal DSC.

We take natural logarithms on (2) and get

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[k\left(T\right)\right] + n\ln\left(1-\alpha\right). \qquad (4)$$

Equation (4) shows that $\ln(d\alpha/dt)$ had a liner relation with $\ln(1-\alpha)$, if the curing process follows the nth-order reaction.

Figures 7 and 8 show DSC data on the F-51/BZ mixture system and BZ homopolymer plotted as $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ at different isothermal temperatures. From these figures, $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ curves of F-51/BZ mixture system and $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ curves of BZ homopolymers show that a nonlinear relationship between them can be obtained. Particularly, $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ curves of BZ homopolymers at some conversion generate an

obvious inflection point in 205°C, 225°C, and 245°C plots, respectively. The reaction of BZ homopolymers is not a single reactive mechanism; there are probably two reactive stages: one process is controlled by the chemical reaction and the other process is controlled by diffusion. The reactive mechanism of the F-51/BZ mixture system is different from the BZ homopolymers. In the reactive process, $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ curves of F-51/BZ mixture system does not generate an inflection point at low temperature, which means the reactive mechanism has changed with the increase of epoxy.

3.2. Thermal Degradation of BZ Monomer and F-51/BZ Mixture System. Figure 9 shows the TG and the corresponding derivative thermogravimetry (DTG) curves (Figure 10) of the
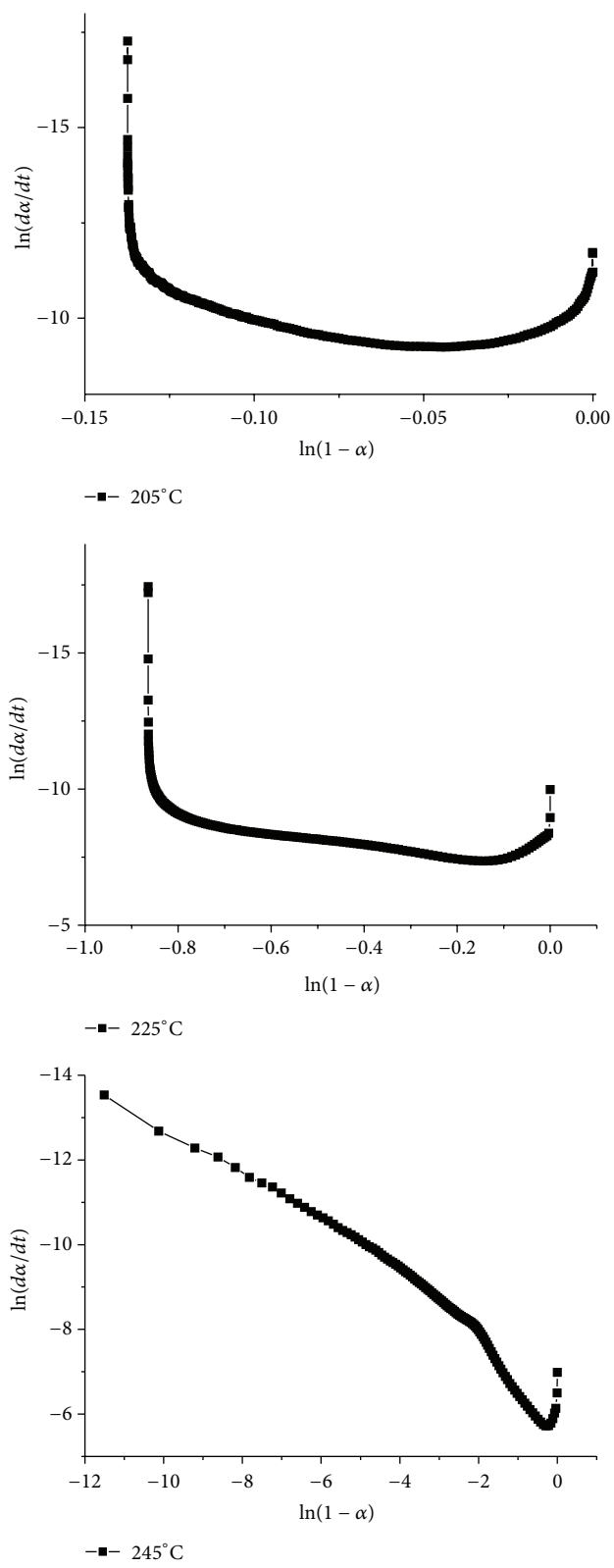
FIGURE 7: $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ curves of F-51/BZ hybrid networks.
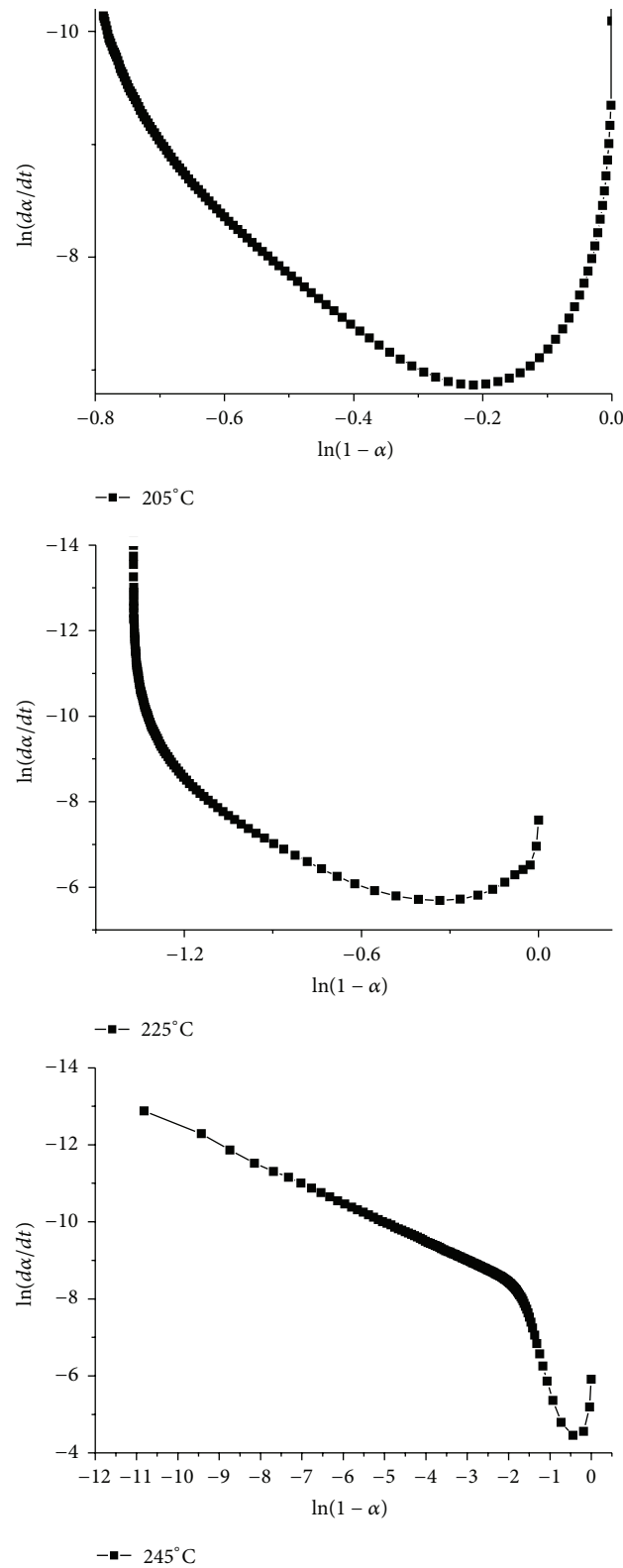
Figure 8: $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ curves of BZ homopolymers.

BZ monomer and the F-51/BZ mixture system in nitrogen. Table 1 summarizes values of temperature of 5% weight loss ($T_d{}^5$) and temperature of 30% weight loss ($T_d{}^{30}$), the maximum weight loss temperature (T_{max}), the maximum weight loss rate (R_{max}), and the char yields at 900°C (W_{900}) of cured polymers. Figure 9 shows the temperature affects weight loss for cured F-51/BZ mixture (BZ/F-51 mass ratio 4:1 for BZ41, 2:1 for BZ21, 1:1 for BZ11, and 1:0 for BZ)

TABLE 1: Parameters of TGA and TG curves for BOZ-M/F-51 system.

Resin system	T_d^{5}/°C	T_d^{30}/°C	T_{max}/°C	R_{max}/%·min^{-1}	W_{900}/wt%
BZ41	298	417	397	3.1	40.5
BZ21	325	410	405	4.6	35.0
BZ11	298	402	393	3.9	35.6
BZ	323	403	398	4.6	34.7

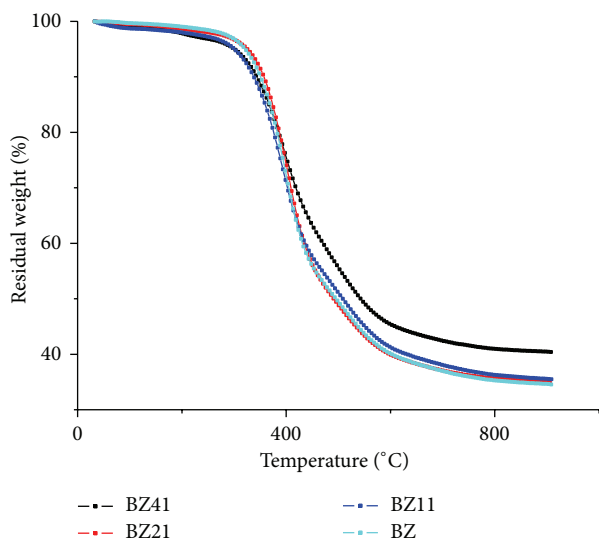FIGURE 9: TGA curves of BOZ-M/F-51 hybrid networks.

FIGURE 10: DTG curves of BOZ-M/F-51 hybrid networks.

system, as well as the derivative curves. T_d^{30} of the cured BZ resin is 403°C, and its values decrease a little as F-51 contents increase, which is probably due to the decomposition of C–O bonds that are less thermally stable than C–C bonds. The char yield of BZ41 at 900°C in nitrogen is maximum (40.5%), and the shapes of the TGA curves of BZ21, BZ11, and BZ do not show significant differences. The char yield of them at 900°C in nitrogen is around 35%, probably contributing to the BZ41 resin system having more cross-linking density and possessing more Mannich bridges. In this sense, the ablative performance of BZ41 mixture system is enhanced from the pure BZ polymer.

Figure 10 shows that the onset temperatures of degradation of BZ41, BZ21, BZ11, and BZ are found at about 240°C; there are two stages of the weight loss process in high temperatures: the first one is at 400°C, while the second one is at 540°C. The reason for this is that the simultaneous degradation of Mannich bases in polybenzoxazines [26] and the first weight loss event in the TGA thermogram is due to the cleavage of C–C and C–N bonds occurring simultaneously, resulting in the degassing of amines from benzoxazine. The second weight loss is assigned to the phenolic degradation [27]. The thermal stability of hybrid networks is not dramatically enhanced with increase of F-51 content; two degradation peaks observed in TGA derivative thermograms of the F-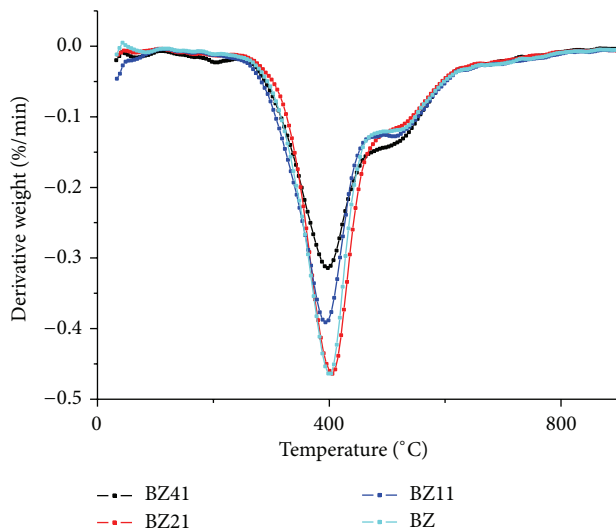51/BZ mixture system do not merge into a single peak for BZ41, BZ21, and BZ11 with increasing percentage of F-51 polymer content.

In order to characterize the cured thermosetting resin, we introduce the equation as follows [28]:

$$T_c = 0.49 \times \left[T_5 + 0.6 \left(T_{30} - T_5 \right) \right], \tag{5}$$

where T_c is heat resistance index.

The T_c of BZ41, BZ21, BZ11, and BZ resin system is 181°C, 184°C, 177°C, and 182°C, respectively. In this sense, there is no significant difference among them in regard to heat resistance.

4. Conclusions

The curing reaction of multifunctional novolac epoxy by benzoxazine resin was studied. The curing of hybrid networks consisted of only one dominant reaction, as evidenced by the presence of one peak on the DSC thermograms. Epoxy-benzoxazine system ratio is 1 : 1, and there was only one peak in the plot. The reactive mechanism of the F-51/BZ mixture system is different from the BZ homopolymers. In the reactive process, $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ curves of F-51/BZ mixture system did not generate inflection point, which means that the reactive mechanism had changed with the increase of epoxy. The autocatalytic models were found to describe the curing kinetics of both reactions of BZ homopolymers and the F-51/BZ mixture system. The reactive mechanism has changed with the increase of epoxy at high temperatures. The thermal degradation of BZ homopolymers and F-51/BZ mixture system proceeds through a two-step mass loss process in nitrogen, and the char yield is about 34.7%, 35.6%, 35.0%, and 40.5% at 900°C.
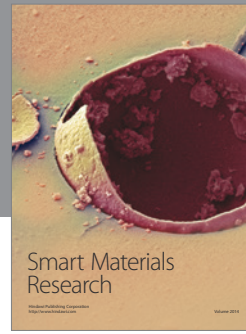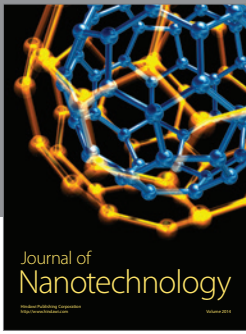
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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