Curing Behavior Study of Polydimethylsiloxane-Modified Allylated Novolac/4,4′-Bismaleimidodiphenylmethane Resin

Wanwan Li,[1,2] Feng Liu,[1,2] Liuhe Wei,[1] Tong Zhao[1]

[1]*Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China*

ABSTRACT: The curing behavior of polydimethylsiloxane-modified allylated novolac/4,4′-bismaleimidodiphenylmethane resin (PDMS-modified AN/BDM) was investigated by using Fourier transform infrared spectrometry (FTIR) and differential scanning calorimetry. The results of FTIR confirmed that the curing reactions of the PDMS-modified AN/BDM resins, including ''Ene'' reaction and Diels–Alder reaction between allyl groups and maleimide groups, should be similar to those of the parent allylated novolac/4,4′-bismaleimidodiphenylmethane (AN/BDM) resin. The results of dynamic DSC showed that the total curing enthalpy of the PDMS-modified AN/BDM resins was lower than that of the parent resin. Incorporation of polydimethylsiloxane (PDMS) into the backbone of the allylated novolac (AN) resin favored the Claisen rearrangement reaction of allyl groups. The isothermal DSC method was used to study the kinetics of the curing process. The experimental data for the parent AN/BDM resin and the PDMS-modified AN/BDM resins exhibited an nth-order behavior. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 554–561, 2008

Key words: allylated novolac resin; polysiloxane; kinetics (polym.); infrared spectroscopy; differential scanning calorimetry (DSC)

INTRODUCTION

Phenolic resins possess many desirable properties, such as excellent ablative property, dimensional stability, thermal stability, and solvent resistance.[1,2] These characteristics make them ideal candidates as matrices for thermostructural application in the aerospace industry.[3] However, the high viscosity, the limited shelf life, and the volatiles upon curing make them unsuitable for advanced processing technology (such as resin transfer molding, i.e., RTM) and high quality materials (such as void-free component).[3,4]

Efforts have been made to overcome the shortcomings of phenolic resins mentioned earlier. Addition-cure type phenolic resins have been developed to meet the requirement of high quality material and advanced-processing technology.[3] Several thermally stable addition-curable functional groups have been incorporated into the backbone of phenolic resins.[5–7] In our group, allyl groups have been introduced onto the backbone of novolac resin and the viscosity of the allylated novolac (AN) resins are reduced.[8] Furthermore, the allylated novolac resins can undergo cocuring reaction with 4,4′-bism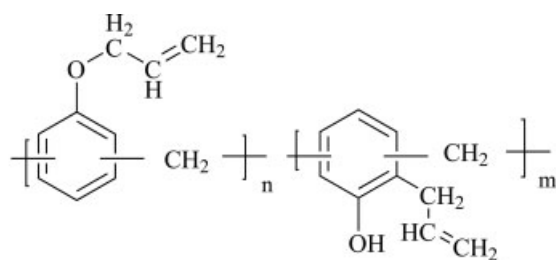aleimidodiphenylmethane (BDM) through ''Ene'' reaction and Diels-Alder reaction.[8,9] The cured resins (AN/BDM) exhibit better thermal resistance and flexural properties.[8] However, because of the high curing density and high content of aromatic structure, AN/BDM resins still suffer from brittleness.[10,11] Efforts to render the resins more flexible are desirable.

Polydimethylsiloxane (PDMS) displays high degree of chain flexibility[12] and excellent thermal stability,[13] and is a good toughening agent for thermosetting resins. In our previous work, PDMS had been incorporated into the backbone of the allylated novolac resin through hydrosilylation reaction between allyl groups of AN resin and Si—H groups of hydrogen functional dimethylsiloxane oligomer.[14] The toughness of the PDMS-modified AN/BDM resins could be enhanced without considerably affecting the thermal stability.[14] At the same time, phase separation was confirmed by dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM).[14]
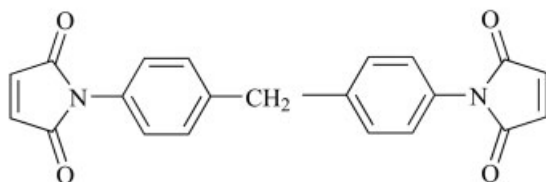
To optimize the curing process and to define carefully the property-structure relation, a clear understanding of the curing mechanism and the ability to develop suitable kinetic model to simulate the curing reaction are essential.[15,16]

Much attention has been focused on the curing mechanism and kinetics of bismaleimide (BMI) and allylphenol/allylphenyl system.[17–23] However, because of the complexity of the curing reaction, the current extent of understanding to the curing mechanism and
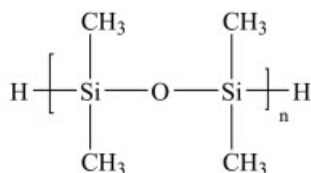
Correspondence to: T. Zhao (tzhao@iccas.ac.cn).

Scheme 1 The chemical structures of allylated novolac resin, 4,4′-bismaleimidodiphenylmethane and hydrogen functional polydimethylsiloxane oligomer.

kinetics is limited. To the best of our knowledge, study on the cure kinetic modeling of allylated novolac/4,4′-bismaleimidodiphenylmethane resin is paucity.

As a continuation of our comprehensive research program in the PDMS-modified AN/BDM resin system, the purpose of the present work was to analyze the curing behavior of the PDMS-modified AN/BDM resin and to study the effects of PDMS on the curing behavior. For comparison, the curing behavior of the AN/BDM resin was also investigated. The curing behavior studies were carried out by using Fourier transform infrared spectrometry (FTIR) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Allylated novolac resin (AN) was synthesized in our laboratory as described in our previous paper.[8] The number–average molecular weight was 420 and the allylation degree was 103% (O-allylation = 100% and C-allylation = 3%), which were calculated from ^{1}H-NMR. Hydrogen functional polydimethylsiloxane oligomer (PDMS) was synthesized according to the

literature procedure[24] and its number–average molecular weight was 1000 (obtained from ^{1}H-NMR). 4,4′-Bismaleimidodiphenylmethane (BDM) was purchased from Fengguang Chemical (Honghu, China). It was a crystalline substance with melting temperature of 156–158°C and molecular weight of 358. The chemical structures of AN, PDMS, and BDM were shown in Scheme 1. Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was from Beijing Organic Chemical Company (Beijing, China) and was dissolved in isopropyl alcohol prior to use. Toluene and isopropyl alcohol were commercially supplied and were used without further purification.

Sample preparation

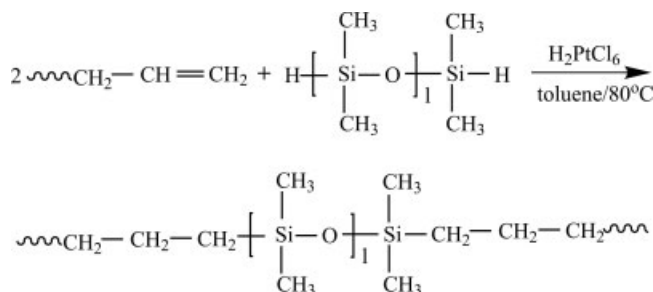#### Synthesis of polydimethylsiloxane-modified allylated novolac resin

The PDMS-modified AN resin was synthesized according to the procedure presented in Scheme 2, and the preparation was similar to the description in our previous work.[14]

Preparation of blends for cure

The molar ratio of allyl to maleimide groups in blend was 1 : 0.3 on the basis of our previous research.[25] The blends were prepared by dissolving BDM in the PDMS-modified AN resins or AN resin at 150°C with constant stirring for about 10 min until a homogeneous blend was obtained.

The thermal rearrangement reaction of the an resin

A typical procedure for the thermal rearrangement reaction of the AN resin was described as follows: a 100-mL three-necked round bottom flask, equipped with a mechanical stirrer, a thermometer, and a condenser, was charged with 30.00 × g AN resin. The resin was heated to 200°C and was maintained at this temperature for 4 h under nitrogen atmosphere. With the proceeding of the reaction, the color of the resin became dark and the viscosity of the resin

Scheme 2 Synthesis of the polydimethylsiloxane-modified allylated novolac resin (PDMD-modified AN/BDM).

became large. The as-prepared resin was characterized by ^{1}H-NMR.

The ^{1}H-NMR spectrum (dimethyl sulfoxide) showed major chemical shifts (δ, in ppm from TMS = 0) at: 7.1, 7.0, 6.9, 6.8(phenyl), 5.9, 5.8 ($\Phi—CH_2CH{=}CH_2$), 5.0, 4.8 ($\Phi—CH_2CH{=}CH_2$), 3.8, 3.7, 3.6($\Phi—CH_2—\Phi$), 3.3, 3.2($\Phi—CH_2CH{=}CH_2$).

Fourier transform infrared spectrometry

Fourier transform infrared spectra (FTIR) were recorded in the transmission mode on a Perkin–Elmer System 2000 Fourier transform infrared spectrometer. The as-prepared blends, cast on KBr plate, were placed in an oven at 210°C and were withdrawn from the oven at different time intervals.

Nuclear magnetic resonance

^{1}H-NMR spectra were obtained in deuterated dimethyl sulfoxide (DMSO) as solvent on a Bruker DMX-300 NMR instrument.

Differential scanning calorimetry

A heat-flux type differential scanning calorimetry (Mettler Toledo DSC 822[e]) was used for dynamic and isothermal curing experiments. The temperature scale of the calorimeter was calibrated using the melting pointing of high purity indium. Dry nitrogen was used as purge gas at a flow rate of 50 mL/min.

Isothermal curing reaction was performed between 190 and 230°C at an interval of 10°C. The as-prepared blend, weighing about 7–10 mg, was placed in an aluminum crucible with a sealed lid. The calorimeter was preheated to the desired reaction temperature, and then the sample in the aluminum crucible was placed opposite the empty reference pan in the oven chamber. Thermal equilibrium was regained within 30 s after sample insertion. The reaction was considered complete when the isothermal DSC thermogram leveled off to the baseline.

To calculate the conversion, α, it is necessary to know the total curing enthalpy, ΔH_{RXN}. In this work, the total curing enthalpy was obtained by a dynamic scan, which was performed at a heating rate of 10°C/min from 25 to 400°C.

RESULTS AND DISCUSSION

FTIR analysis

It has been suggested that allyl groups of the AN resin can undergo ''Ene'' reaction and Diels–Alder reaction with maleimide groups of BDM at elevated temperatures.[26,27] FTIR spectrum could provide some information on the curing reaction. The profiles of FTIR spectra for the parent AN/BDM resin with different curing time at 210°C were depicted in Figure 1.

The FTIR spectrum of the uncured AN/BDM resin showed the characteristic bands of maleimide group towards 3075, 1150, 826, and 690 cm^{-1} and the characteristic band of allyl group towards 923 cm^{-1}.[26,28] It was remarkable that the intensity of the above-mentioned bands decreased to a considerable extent with the proceeding of the curing reaction. Furthermore, upon curing, the intensity of maleimide carbonyl (stretching C=O) at 1717 cm^{-1} was found to decrease. It has been reported that owing to transforming maleimide groups to succinimide groups during polymerization, the absorption of —C=O peak in IR spectrum generally decreases by about 50% without any significant change in the frequency of absorption.[26] At the same time, a broad band towards 1185–1190 cm^{-1}, characteristic band of the succinimide functional groups formed as the curing reaction progressed.[29] These indicated that the reaction between allyl groups and maleimide groups occurred. It should also be noted that the characteristic band of $\Phi—O—C$ toward 1243 cm^{-1} decreased and the characteristic band of hydroxyl groups toward 3470 cm^{-1} increased. This implied that some of O-allyl groups were converted into C-allyl groups in the curing process, and more explicit elucidation would be given in ''Dynamic DSC analysis'' section.

To study the effect of PDMS on the curing reaction, it was necessary to identify several bands clearly. Shown in Figure 2 were the FTIR spectra of the uncured 10 wt % PDMS-modified AN/BDM resin and PDMS from 2000 to 650 cm^{-1}. The band at 800 cm^{-1} was attributed to the Si-Me$_2$ and the band
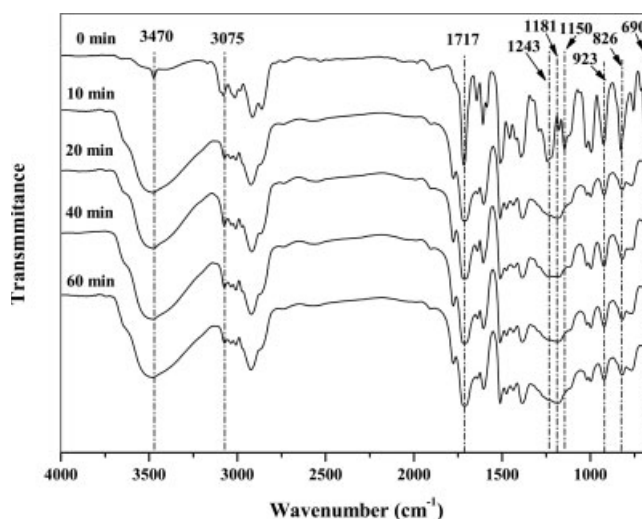

Figure 1 FTIR spectra of the parent AN/BDM resin at 210°C with the increase in curing time.
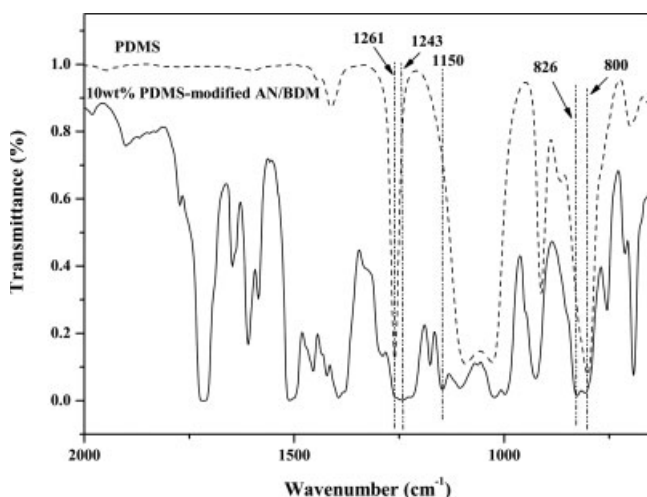
Figure 2 FTIR spectra of the uncured 10 wt % PDMS-modified AN/BDM resin and PDMS.

at 1261 cm^{-1} was resulted from CH$_3$ attached to Si atom. In the curing process, the abovementioned bands maintained, however, the intensity of the adjacent bands (826 and 1243 cm^{-1}) would change.

The FTIR spectra for the 10 wt % PDMS-modified AN/BDM resin with different curing time at 210°C were depicted in Figure 3. Compared with the parent AN/BDM resin, the FTIR spectra of 10 wt % PDMS-modified AN/BDM resin with the increase in curing time exhibited similar change tendency. Therefore, it could be concluded that incorporation of PDMS into the backbone of the AN resin did not change the curing pathway. The cocuring reaction between allyl groups and maleimide groups in the PDMS-modified AN/BDM resins proceeded via the ''Ene'' reaction and the Diels–Alder reaction.
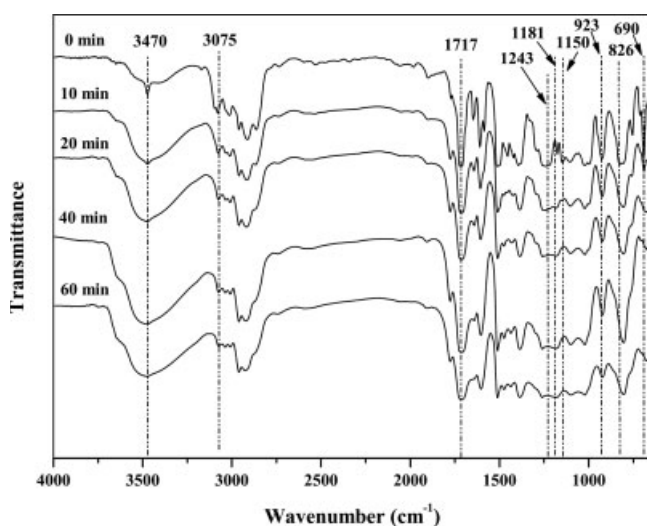

Figure 3 FTIR spectra of the 10 wt % PDMS-modified AN/BDM resin at 210°C with the increase in curing time.
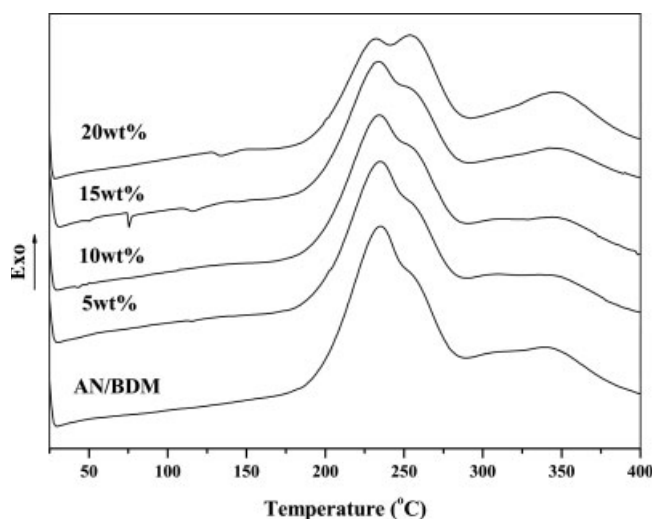

Figure 4 Dynamic DSC thermograms of the PDMS-modified AN/BDM resins and the parent AN/BDM resin (N$_2$ atmosphere: 50 mL/min; heating rate: 10°C/min).

Dynamic DSC analysis

Dynamic DSC experiment was performed from 25 to 400°C at a heating rate of 10°C/min. Shown in Figure 4 was the dynamic thermograms for the PDMS-modified AN/BDM resins together with the parent AN/BDM resin.

The integrated area under the exothermic curve was used to calculate the total enthalpy of the curing reaction, ΔH_{RXN}.[30,31] These values along with the peak temperatures of exothermic polymerization, T_p, were listed in Table I for every PDMS-modified AN/BDM resin and the parent AN/BDM resin.

Compared with the parent AN/BDM resin, the T_p of the modified resins was almost unchanged, but ΔH_{RXN} of the PDMS-modified AN/BDM resins were lower than that of the parent AN/BDM resin. In this work, the allylation degree for the unmodified AN resin was 103%. It had been confirmed that incorporation of PDMS into the AN resin led to the decrease in the allylation degree.[14] As the PDMS content increased from 5, 10, 15 to 20 wt %, the allylation degree was 96.7, 93.0, 91.5, and 91.1%, respectively.[14]

TABLE I
The Peak Temperature (T_p) and the Total Enthalpy of the Curing Reaction (ΔH_{RXN}) for the PDMS-Modified AN/BDM Resins with Different PDMS Content and the Parent AN/BDM Resin (Heating Rate: 10°C/min; Nitrogen Flow: 50 mL/min)

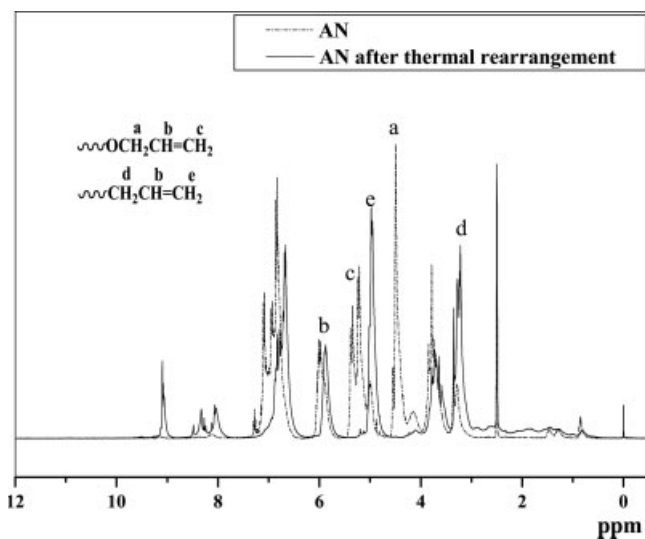| Samples	PDMS Content (wt %)	T_p (°C)	ΔH_{RXN} (J/g)
AN/BDM	0	234.73	392.25
PDMS-AN/BDM	5	234.18	357.28
PDMS-AN/BDM	10	233.67	354.40
PDMS-AN/BDM	15	233.37	334.50
PDMS-AN/BDM	20	231.59	312.16

Figure 5 ^{1}H-NMR spectra of the neat AN resin and the AN resin after thermal rearrangement reaction (solvent: DMSO).

The decrease in the allylation degree accounted for the decrease in the total enthalpy of the curing reaction. This might also imply that the presence of PDMS did not apparently change the reaction pathway.[32,33]

A shoulder at 254°C appeared for all the thermograms. Upon heating, the Claisen rearrangement reaction of allyl groups occurred.[3,25,26] This meant that the O-allylation derivations would rearrange to the C-allylation derivations. Shown in Figure 5 was the ^{1}H-NMR spectra of the AN resin and the AN resin after thermal rearrangement reaction. Compared with the ^{1}H-NMR spectrum of the neat AN resin, it could be found that because of the Claisen rearrangement reaction, the resonances corresponding to the protons of the O-allylation derivations disappeared from the ^{1}H-NMR spectrum of the AN resin after thermal rearrangement reaction. At the same time, the resonances corresponding to the protons of the C-allylation derivations considerably enhanced in the spectrum of the AN resin after thermal rearrangement reaction. This implied that the Claisen rearrangement reaction proceeded completely. The curing thermograms of the AN/BDM resin, the neat AN resin and the AN resin after thermal rearrangement reaction were shown in Figure 6. The exothermal peak observed at 254°C in the thermograms of the AN/BDM resin and the neat AN resin, disappeared from the thermogram of the AN resin after thermal rearrangement reaction. Therefore, it was believed that the shoulder at 254°C should be attributed to the Claisen rearrangement reaction of the allyl groups. In addition, the exothermal peaks centered at 354°C were attributed to self-polymerization reaction of allyl groups.

However, as the PDMS content increased, the shoulder was more evident. This might arise from two possible reasons: phase separation and the decreased reaction probability between the reactive groups. Firstly, as the curing reaction proceeded, because of the thermodynamic immiscibility between PDMS and the matrix, phase separation might occur. With the increase in PDMS content, it should be reasonable that more AN resin would be miscible in the PDMS-rich phase. The reaction between allyl groups in the PDMS-rich phase and maleimide groups was hampered. Secondly, because of incorporation of PDMS into the curing system, the concentration of functional groups was diluted and the effective impact between allyl groups and maleimide groups reduced, which resulted in the decrease in the reaction probability between the reactive groups. Therefore the Claisen rearrangement reaction of the allyl groups was enhanced in the PDMS-modified AN/BDM resins.

According to the results of FTIR and dynamic DSC, it could be believed that the principle curing reactions of the PDMS-modified AN/BDM resins consisted of ''Ene'' reaction and Diels–Alder reaction between allyl groups and maleimide groups as well as the enhanced Claisen rearrangement reaction of allyl groups. The proposed curing reactions were depicted in Scheme 3.

Isothermal DSC analysis

The curing kinetic study of thermosetting resin by DSC is based on the assumption that the rate of conversion is proportional to the measured heat flow, and this assumption is always valid when the curing reaction is the only thermal behavior.[34] Therefore,
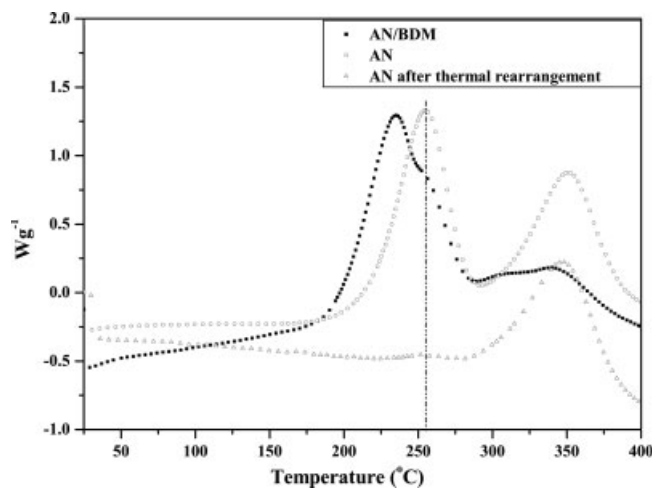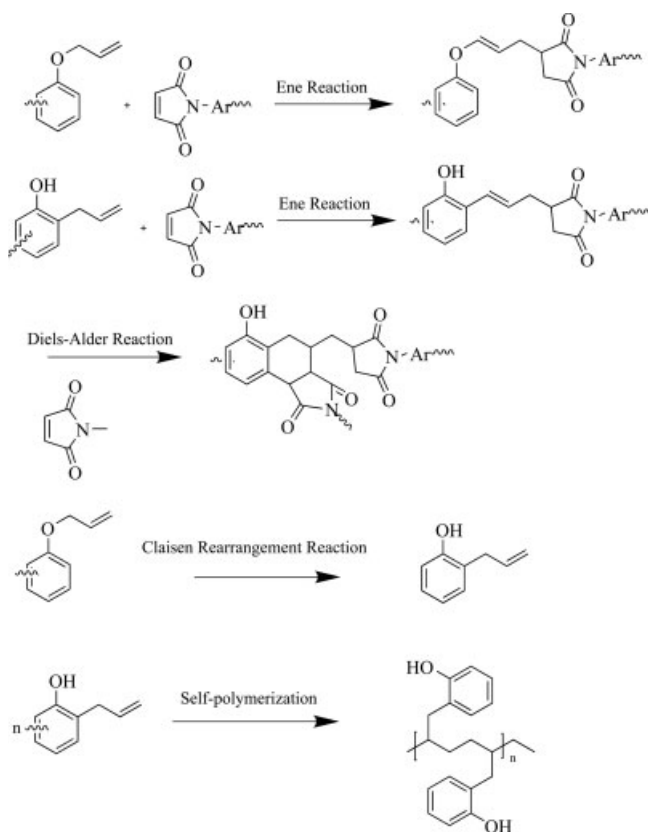

Figure 6 Dynamic DSC thermograms of the AN/BDM resin, the neat AN resin and the AN resin after thermal rearrangement reaction (N$_2$ atmosphere: 50 mL/min; heating rate: 10°C/min).

Scheme 3 The proposed curing reactions of the PDMS-modified AN/BDM resins and the parent AN/BDM resin.

the rate of conversion, $d\alpha/dt$, can be defined as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{RXN}} \quad (1)$$

where dH/dt is the measured heat flow and ΔH_{RXN} is the total enthalpy of curing reaction. In the present work, ΔH_{RXN} was determined by dynamic DSC as shown in Table I.

The conversion at any time, α_t, can be defined as follows:

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{RXN}} \quad (2)$$

where ΔH_t is the enthalpy at a specific time and can be determined by integrating the corresponding heat flow curve $\Phi(t)$:

$$\Delta H_t = \int_0^t \Phi(t)dt \quad (3)$$

Shown in Figure 7 was the conversion versus time for the 10 wt % PDMS-modified AN/BDM resin and for the parent AN/BDM resin.

In all cases, the conversion increased rapidly with the increase in curing time at the initial stage but subsequently reached a limiting value asymptotically. This typical profile might imply that the change of the curing reaction from a chemically controlled process to a diffusion controlled process.[34] It was also noticed that a higher isothermal cure temperature led to a shorter cure time to reach a given conversion. This meant that at higher temperatures the mobility of the segment increased and the chemical interaction between reactive groups was favored; therefore, the curing reaction proceeded rapidly.

Modeling of the curing process can be approached in both mechanistic and phenomenological ways.[32] In the present work, phenomenological approach was used.

For thermosetting resins those follow nth-order kinetics, the rate of conversion is proportional to the concentration of the unreacted material,[34] that is:
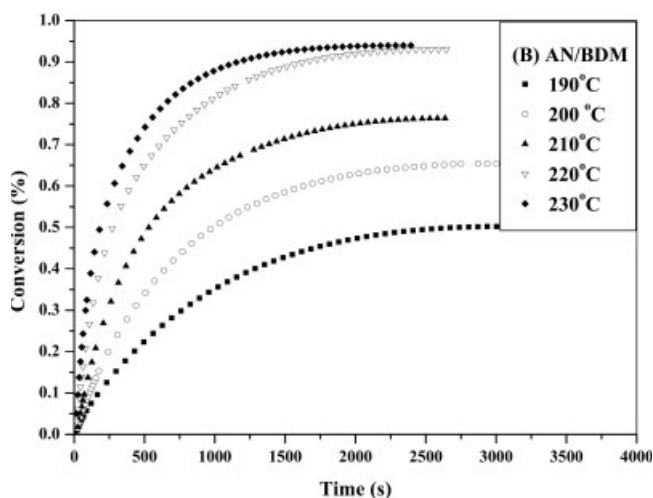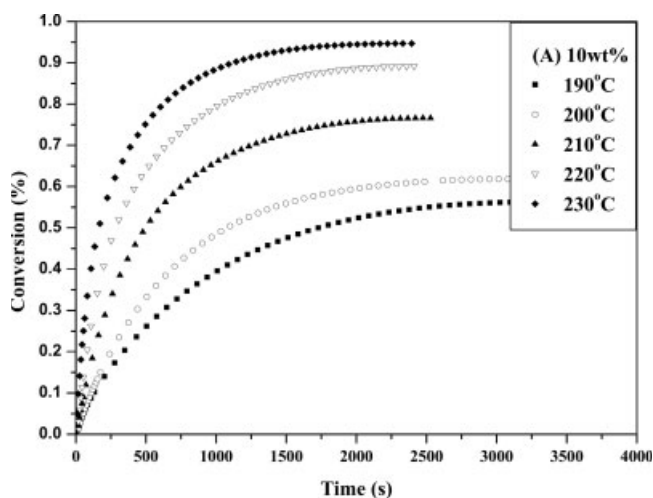

Figure 7 Plots of conversion versus time at each isothermal curing temperature: (A) the 10 wt % PDMS-modified AN/BDM resin (B) the parent AN/BDM resin.
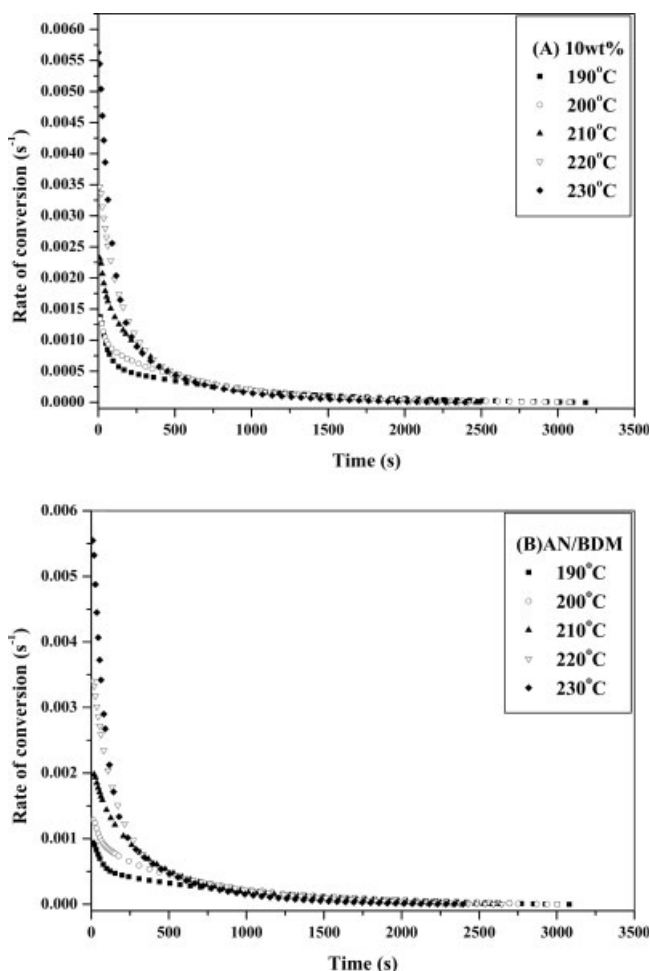
Figure 8 Plots of $d\alpha/dt$ versus time at each isothermal curing temperature: (A) the 10 wt % PDMS-modified AN/BDM resin (B) the parent AN/BDM resin.

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \qquad (4)$$

where n is the reaction order and k is the rate constant. Equation (4) indicates that the rate of conversion is dependent only on the amount of unreacted materials and the maximum rate of conversion occurs at $t = 0$.

Autocatalyzed curing reactions are characterized by an accelerating isothermal conversion rate, which typically reaches its maximum between 20 and 40%

conversion.[34] The kinetics of autocatalyzed reactions are described by the following equation:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha^n) \qquad (5)$$

where m and n are reaction order, and $m + n$ is overall order, k_1 and k_2 are the rate constant.

Shown in Figure 8 were the results of plotting the rate of conversion versus time for 10 wt % PDMS-modified AN/BDM resin and the parent AN/BDM resin. In all cases, the maximum rate of conversion appeared at $t = 0$, which meant that the cure reaction followed an nth-order reaction, and the presence of PDMS did not change the nature of the curing reaction.

To further investigate the curing kinetics, the Eq. (4) can be rewritten as:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k + n \, \ln(1 - \alpha) \qquad (6)$$

For the nth-order reaction, the plot of $\ln(d\alpha/dt)$ against $\ln(1 - \alpha)$ should be linear, with the slope representing the value of n and the intercept representing the value of $\ln k$.

The values of the rate constants, k, and the reaction orders, n, were tabulated in Table II.

It could be seen that the values of the reaction order, n, changed at different isothermal curing temperature. As discussed in "Dynamic DSC Analysis" Section, the proposed curing mechanism for the PDMS-modified AN/BDM resins and the parent AN/BDM resin was the combination of "Ene" reaction and Diels–Alder reaction between allyl groups and maleimide groups as well as Claisen rearrangement reaction of allyl groups. It was generally believed that "Ene" reaction between allyl groups and maleimide groups might occur below 200°C and Diels–Alder reaction between allyl groups and maleimide groups might occur at higher temperature.[26,28] At a lower temperature, "Ene" reaction might be dominant. At a higher temperature, more reactions might occur. Because of different propor-

TABLE II
Isothermal Kinetic Parameters for the PDMS-Modified AN/BDM Resins with
Different PDMS Content and the Parent AN/BDM Resin

PDMS Content (wt %)	190°C		200°C		210°C		220°C		230°C	
	$k \times 10^{-3}$ (s^{-1})	n	$k \times 10^{-3}$ (s^{-1})	n	$k \times 10^{-3}$ (s^{-1})	n	$k \times 10^{-3}$ (s^{-1})	n	$k \times 10^{-3}$ (s^{-1})	n
0	0.74	3.24	1.32	2.70	2.33	2.43	3.29	1.69	5.12	1.75
5	0.89	3.71	1.42	2.66	2.41	2.05	2.91	1.37	4.53	1.36
10	0.90	3.11	1.32	2.97	2.51	2.44	3.30	1.83	4.87	1.68
15	0.87	3.45	1.49	2.59	2.21	1.96	3.03	1.58	3.82	1.28
20	0.73	5.09	1.38	3.63	2.03	2.85	2.66	1.52	4.35	1.66

tion of the curing reactions, the reaction order changed at different isothermal curing temperature.

For the 20 wt % PDMS-modified AN/BDM resin, the reaction orders at lower temperature (such as 190, 200, and 210°C) were higher than those of other PDMS-modified AN/BDM resins and the parent AN/BDM. This might result from the improvement of the molecular mobility. Incorporation of PDMS into the AN/BDM resin might affect the curing reaction in two aspects. On the one hand, the curing reaction might be retarded because of the phase separation and the decreased reaction probability. On the other hand, because of the flexible chain of PDMS, the molecular mobility could be improved, which might promote the diffusion of the reactive groups and might lead to more complete ''Ene'' reaction at lower temperature. In the 20 wt % PDMS-modified AN/BDM resin, the molecular mobility might be improved significantly, therefore, the reaction order increased.

CONCLUSIONS

In the present work, the curing behavior of the PDMS-modified AN/BDM resins was studied and the effect of PDMS on the curing reaction and curing kinetics was evaluated. The proposed curing reactions for the PDMS-modified AN/BDM resins included ''Ene'' reaction and Diels–Alder reaction between allyl groups and maleimide groups, as well as the enhanced Claisen reaction of allyl groups. Because of the reduction in allylation degree, the total enthalpy of the curing reaction for the PDMS-modified AN/BDM resins decreased. The curing process of the PDMS-modified AN/BDM resins and the parent AN/BDM resin followed nth-order mechanism. The isothermal curing temperature and PDMS content had influence on the curing kinetic parameter.

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