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European Polymer Journal 41 (2005) 903–912

EUROPEAN POLYMER JOURNAL

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Cure study of addition-cure-type and condensation–addition-type phenolic resins

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Received 11 November 2004; received in revised form 19 November 2004; accepted 29 November 2004
Available online 25 January 2005

Abstract

By the incorporation of propargyl and methylol groups on to novolac backbone, a series of addition-curable phenolic resins and condensation–addition dual-cure type phenolic resins (novolac modified by propargyl groups referred as PN, and novolac modified by propargyl and methylol groups simultaneously referred as MPN) were synthesized. The processing characteristics, thermal cure and catalytic cure behavior for both resins were investigated mainly by means of viscosity measurement and non-isothermal differential scanning calorimetry (DSC) techniques. The effect of propargyl and methylol content of PN and MPN, the molecular weight and the configuration of the parent novolac, on the processing and cure behavior was studied in details. Processing parameters and curing kinetic parameters were obtained. Both resins exhibit excellent processing properties. Thermal cure of PN resins possessed one cure mechanism and that of MPN resins possessed two cure mechanisms according to DSC analysis. The dual-cure-type mechanism made MPN resins superior to PN resins in terms of a mild and controllable cure process. Compared with thermal cure, catalytic cure of PN resins showed lower initiation temperature and cure temperature by about 60 °C. These novel resins have a bright prospect of application as matrix for thermal–structural composite materials.
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Keywords: Phenolic resins; Ethynyl; Cure

1. Introduction

As the first commercial synthetic resin, phenolic resins have been extensively studied for nearly 100 years and are still among the best commercially available heat-resistant resins [1]. However, conventional phenolic materials from either novolac or resole type resins suffer from the common shortcomings of brittleness and release of volatiles upon curing via condensation reactions. Another disadvantage is the lack of molecular design flexibility imposed by the phenolic chemistry employed [2]. New chemistry is needed to modify the cure mechanism of phenolic resins. The condensation cure can be replaced by addition mechanism by designing phenolic resins possessing thermal stable addition-curable groups [3]. Addition-curable phenolic resins could avoid many drawbacks of conventional phenolics, such as the processing problems associated with the evolution of volatiles during curing. For example, ethynyl-containing phenolic oligomers (see Fig. 1) can be polymerized via addition mechanism at elevated temperatures with

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doi:10.1016/j.eurpolymj.2004.11.036

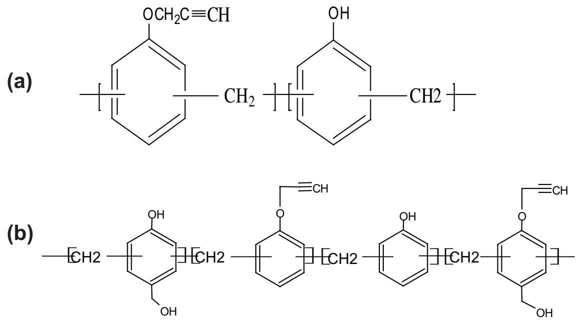

Fig. 1. Molecular structures of ethynyl-containing phenolic resins: (a) PN resin and (b) MPN resin.

or without catalyst to facilitate the fabrication of desirable void free components owing to the elimination of volatiles. Cured ethynyl-containing phenolic resins provide many desirable properties such as solvent-resistance, moisture-resistance and good mechanical properties as well as high thermal stability, which make ethynyl-containing phenolic resins good candidate as matrices for advanced composite materials. To incorporate methanol groups and propargyl groups into navolac backbone simultaneously will have improvements on processing and final properties. To the best of our knowledge, there is no report on this subject.

The major objectives of this research included:

1. To develop propargyl-novolac ether resins (PN resins) with varying propargyl contents, with varying molecular weights and with varying ortho/para in bridged methylenic linkage, respectively;
2. To develop methylol propargyl-novolac-ether resins (MPN resins) with varying methylol contents and with varying propargyl contents, respectively;
3. To characterize the cure processability of the above novel resins; and
4. To estimate the cure kinetics of the above novel resins and to have an insight into the relationships between curing behaviors and molecular structures.

2. Experimental

2.1. Materials

Novolac resins were prepared in our laboratory (Mn = 320, 576 and 770, respectively). Formalin (37% solution, Beijing Yili, PR China) and KOH (A.R., Beijing Yili, PR China) were used as received. Propargyl bromide (80% toluene solution, Jiangsu Yangnong, PR China) was distilled before use. $NiCl_2(PPh_3)_2$ was synthesized from $NiCl_2 \cdot 2H_2O$ and PPh_3 according to a reported procedure [4].

2.2. Characterization methods

The chemical structures of the resins were identified by FTIR (Perkin-Elmer, IR2000) and ^1H NMR (Bruker, AV400) spectroscopic methods. Solution ^1H NMR spectra were measured using DMSO-d_6 as solvent and tetramethylsilicane as internal standard. Thermal cure and catalytic cure were analyzed by non-isothermal DSC (Mettler-toledo, DSC822^e) in N_2 atmosphere at various heating rates (5, 10, 20, 30 °C/min) for estimation of cure kinetics and determination of processing parameters. Rheologic property of viscosity was determined using NDJ-79 rotating viscometer and dynamic mechanical analysis (DMA) on thermal cure. DMA scans (Perkin-Elmer, DMA7) were recorded in compression mode using a single ply of carbon prepreg with 10 mm radius at a heating rate of 5 °C/min and at a frequency of 1 Hz. Gel time of resins was determined according to GB-7193.1-1987 using home made apparatus in our lab.

2.3. Synthesis of PN resins

The PN resins were synthesized via Williams reaction between novolac resins and propargyl bromide catalyzed by KOH in butanol solution [5]. The synthetic scheme is shown in Fig. 2. In a typical experimental, novolac (10.4 g, 0.1 mol) and butanol (12 ml) were placed in a

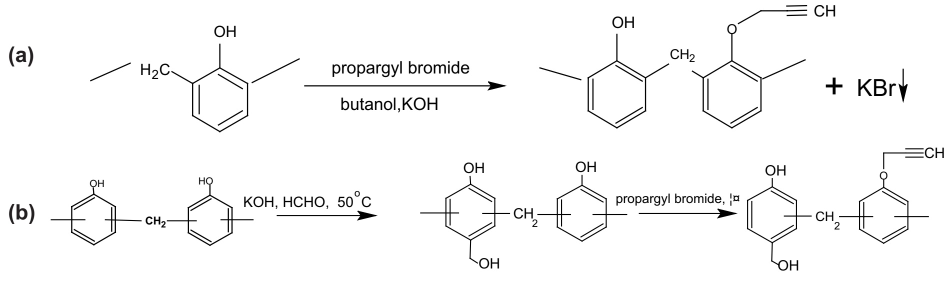

Fig. 2. Synthetic protocols for (a) PN resin and (b) MPN resin.

three-neck flask equipped with a mechanical stirrer, a thermometer and a condenser. The mixture was stirred to form a solution; then KOH (5.33 g, 0.08 mol) was added slowly under agitation to form a purple solution. To the above solution at 80 °C in a water bath, propargyl bromide (9.52 g, 0.08 mol) was introduced dropwise under vigorous agitation over a period of 15 min. The reaction mixture was kept at 80 °C for another 3 h till the mixture turned pale yellow and its PH value was about 7. The filtrate was washed with hot distilled water till the water phase was negative to Ag^+; then the butanol phase was rotating evaporated at 100 °C to obtain a brown-red viscous resin. Thus, PN resin with 80% propargyl content was prepared. Yield (11 g, 91.7%). IR (KBr) cm^{-1} 3400 (–OH), 3288 (≡C–H), 3033 (aromatic C–H), 2122 (C≡C); HNMR (DMSO) δ 3.35–3.53 (≡C–*H*), 3.70–3.81 (–ϕ–CH_2-ϕ–), 4.7–4.8 (–OCH_2C≡C–), 6.6–7.3 (aromatic hydrogen). PN resins with varying propargyl contents or with varying molecular weights were also prepared as per the same procedure.

PN resin based on high ortho novolac precursor (PHON resin) was synthesized utilizing a similar procedure as mentioned above.

2.4. Synthesis of MPN resins

Briefly, the MPN resins were prepared by two independent reactions stepwise [6]. The synthetic scheme is shown in Fig. 2. First, novolac and formaldehyde were reacted in butanol with alkali as catalyst; then, propargyl bromide was added and Williams reaction was conducted. Typically, to a solution of novolac (10.4 g, 0.1 mol) in 12 ml butanol, KOH (5.33 g, 0.08 mol) was added in batches under agitation to form a transparent purple red solution at ambient temperature. Formaldehyde (0.6 g, 37 wt% aqueous solution) was added when the mixture was heated to 50 °C in water bath and the condensation reaction was allowed for about 6 h. Then propargyl bromide (9.52 g, 0.08 mol) was introduced dropwise in an interval of 30 min, and etherification reaction lasted for another 3 h at 65 °C. The reaction mixture turned pale yellow, and large amount of KBr salt deposited. The salt was separated by filtration and the filtrate was washed with hot distilled water till the water phase was negative to Ag^+. Finally, the butanol phase was rotating evaporated at 100 °C to give a brown red transparent viscous resin. Thus, MPN resin with 20% methylol content and 80% propargyl content was prepared. Yield (11.3 g, 94.2%). IR (KBr) cm^{-1} 3393 (–OH), 3288 (≡C–H), 3032 (aromatic C–H), 2122 (C≡C); HNMR (DMSO) δ 3.50–3.53 (≡C–*H*), 3.69–3.79 (-ϕ-CH_2-ϕ-), 4.4–4.5 (ϕ-CH_2OH), 4.7–4.8 (–OCH_2C≡C–), 6.6–7.3 (aromatic hydrogen). MPN resins with varying propargyl contents or with varying methylol contents were prepared as per the same procedure.

3. Results and discussion

3.1. Processability studies

The resins studied in this paper were listed in Table 1.

FTIR spectra of typical PN and MPN resins shown in Fig. 3 exhibited the characteristic absorptions of –OH around 3390 cm^{-1}, ≡C–H around 3288 cm^{-1} and C≡C around 2122 cm^{-1}. The results of ^1H NMR of typical PN and MPN resins also ascertained the existence of ethynyl groups.

Solubility, rheologic properties and cure characteristics are crucial processing parameters of a matrix-resin for the preparation of composite materials. The PN and MPN resins were soluble in common organic solvents such as acetone, methylethylketone and tetrahydrofuran, etc.

Rheologic properties of thermosetting resin are principal parameters for processing. From the data in Table 2, PN and MPN resins both possessed low viscosities (less than 400 mPa s when heated 2 h) even under 100 °C, which was far below their gel temperatures (for PN resin it is about 190 °C, while for MPN resin it is about 170 °C). This implied that they have wide process window. It can be seen that these resins were suitable for compression molding or transfer molding process.

In addition, they had long shelf life in comparison to conventional resole type phenolic resins; e.g. after storage for three months, the viscosity of PN resin or MPN resin remained nearly unchanged while conventional resole got gelled.

Table 1
The resins studied in this paper

Resins	30%PN	50%PN	70%PN	80%PN	80%PN	100%PN	MPN-1	MPN-2	MPN-3	MPN-4	60%MPN
Propargyl content (%)	30	50	70	80	80	100	80	80	80	40	80
Methylol content (%)	0	0	0	0	0	0	15	45	20	20	20
Molecular weight[a]	578	578	578	578	767	578	578	578	578	578	578

[a] Here it is the molecular weight of novolac precursor resin.

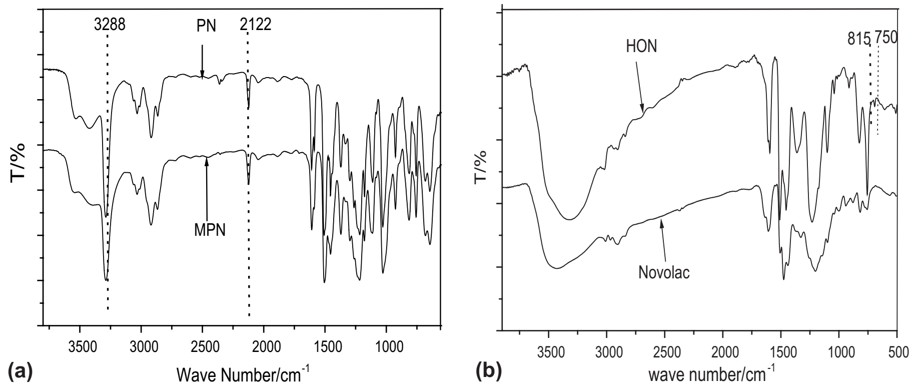

Fig. 3. FTIR spectra of (a) typical PN and MPN and (b) conventional novolac and HON (high ortho novolac).

Table 2
Viscosity–temperature and viscosity–time relationships for typical PN and MPN

Polymer	Viscosity[a]/mPa s				Viscosity[b]/mPa s				
	90 °C	100 °C	110 °C	120 °C	1 h	2 h	3 h	4 h	5 h
PN[c]	400	260	170	95	125	125	120	115	110
MPN[d]	1400	544	291	238	544	344	333	337	331

[a] Samples were dwelt at each temperature for 1 h before measurement.
[b] PN was measured at 110 °C, while MPN was measured at 100 °C.
[c] Propargyl content is 80%.
[d] Methylol content is 20%, propargyl content is 80%.

DSC and DMA techniques were used to determine the cure characteristics and cure parameters. The cure characteristics of PN resin by DSC in Fig. 4 showed a single, well defined exotherm with an onset temperature about 190 °C, a peak temperature about 260 °C and an endset temperature about 300 °C, which indicated one addition cure mechanism. DSC for MPN resin in Fig. 4 showed two fused exotherms, indicating dual cure mechanism, which revealed that MPN resin was condensation–addition dual-cure-type phenolics. The first exotherm at 170–240 °C is due to the condensation reaction of methylol groups, and the second exotherm at 250–300 °C is due to the addition polymerization of propargyl groups [5]. So MPN resin could be cured at lower temperatures. The cure characterization by DMA using single ply of carbon prepreg shown in Fig. 5 manifested the results revealed by DSC method. Gel

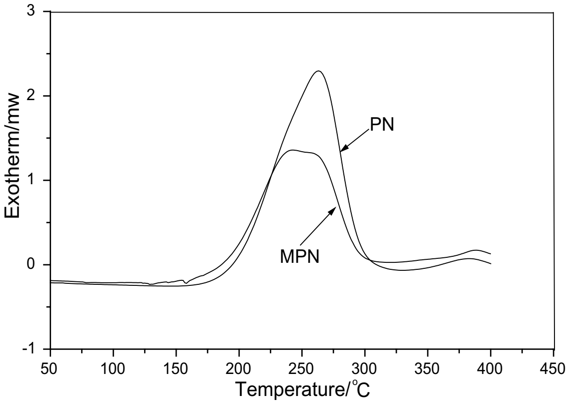

Fig. 4. DSC profiles of typical PN and MPN (heating rate 10 °C/min, N_2 50 ml/min).

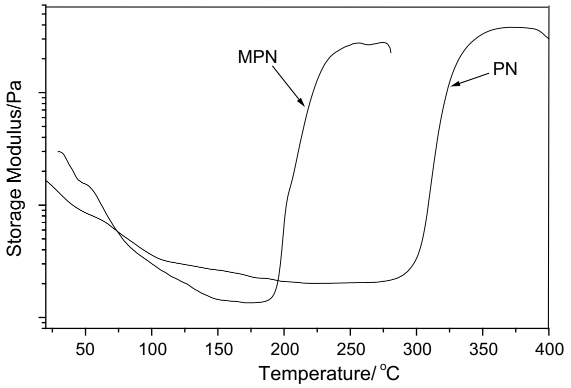

Fig. 5. DMA scans of PN and MPN (heating rate 5 °C/min, frequency 1 Hz).

time for MPN resin at 170 °C was 58′, while for PN resin was several hours; MPN can be processed at lower temperature and in short time.

The present work was not to establish the cure mechanism. In fact, the exact cure mechanism is still obscure because of the numerous ways in which polymerization can proceed combined with the fact that few characterization techniques are available to study these complex thermosetting structures [7,8].

In a word, the processability of PN and MPN resins were excellent and nearly suitable to all processing techniques.

3.2. Cure studies on PN resins

The major objective of this work was to derive information on cure behaviors and cure kinetics of these novel matrix resins in view that understanding the cure kinetics is essential for defining final properties, process development and quality control.

3.2.1. Thermal cure of PN resins with varying propargyl contents

DSC scans for PN resins with varying propargyl contents are shown in Fig. 6. All the PN resins were from the same novolac precursor with a molecular weight of 586 g/mol. The enthalpy of curing exotherm increased nearly linearly with increase in propargyl content of PN resins [5]. All of the curing scans had nearly identical sharp exotherm occurring around 190–200 °C corresponding to the onset of the crosslinking reaction and with a peak temperature around 255–265 °C, which revealed that the crosslinking reaction was dominated only by propargyl groups.

It has been reported earlier that the cure kinetics of ethynyl groups is dependent much on their concentration in the backbone [9]. Table 3 summarizes the effect of propargyl content on curing rate represented by gel time at 200 °C. The results confirmed that the thermal cure can be facilitated by higher concentration of propargyl groups.

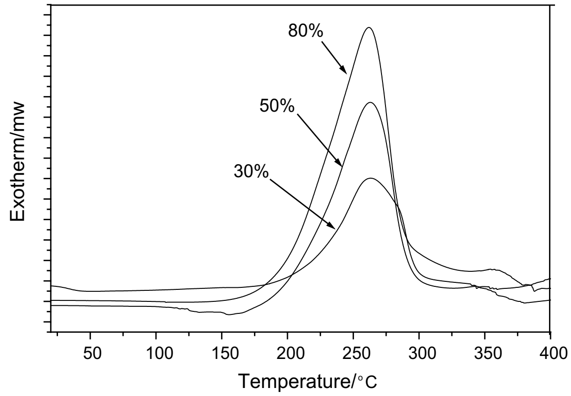

Fig. 6. DSC profiles of PN resins with varying propargyl contents (heating rate 10 °C/min, N_2 50 ml/min).

Table 3
Gel time of PN with varying propargyl contents

Polymers	Gel time[a] at 200 °C
70%PN[b]	17′
80%PN	11′
100%PN	5′18″

[a] Determined using NDJ-79 rotating viscometer.

[b] 70%PN designates PN resin with a propargyl content of 70%.

Cure kinetics of many thermosetting resins have been elucidated by DSC using non-isothermal scanning methods [10]. Here, kinetic analysis is performed using a general nth order reaction model without the consideration of cure reaction mechanism. The general rate equation may be written as:

$$d\alpha/dt = k(1-\alpha)^n \qquad (1)$$

$$k = A\exp(-E/RT) \qquad (2)$$

where α is the degree of cure, t is the reaction time, k is the rate constant defined by Arrhenius relationship, n is the order of the cure reaction, A is frequency factor, E is activation energy, R is the universal gas constant and T is temperature.

Combining Eqs. (1) and (2) yields:

$$\mathrm{Ln}(d\alpha/dt) = \ln A - E/RT + n\ln(1-\alpha) \qquad (3)$$

The non-isothermal DSC analysis for estimation of kinetic parameters capitalizes on the variation in peak exothem temperature (T_p) with the scanning rate (β). Here, Ozawa [11], Kissinger [12] and Crane [13] equations (integrated forms of Eq. 3) are used to calculate the cure kinetic parameters:

Ozawa equation $$E = (-R/0.4567) \times \{d\lg\beta/d(1/T_p)\} \qquad (4)$$

Kissinger equation $$E = -R\{d\ln(\beta/T_p^2)/d(1/T_p)\} \qquad (5)$$

$$A = E\beta\exp(-E/RT_p)/(RT_p^2) \qquad (6)$$

Crane equation $$n = (-E/R) \times \{1/(d\ln\beta/d(1/T_p))\} \qquad (7)$$

The characteristics of non-isothermal DSC scans for PN resins with varying propargyl contents are listed in Table 4, while the estimated kinetic parameters are complied in Table 5. Although activation energy showed a tendency to decrease slightly with increase in propargyl content, the frequency factor increased notably. As a result, the thermal cure was accelerated with increase in propargyl

Table 4
Characteristics of non-isothermal DSC scans for PN[a] resins with varying propargyl contents (N_2 50 ml/min)

Polymers	5 °C/min			10 °C/min			20 °C/min			30 °C/min		
	Onset[b]	Peak	Endset	Onset	Peak	Endset	Onset	Peak	Endset	Onset	Peak	Endset
50%PN	204.6	257.4	276	208	264.8	290	224	279	305	231	287	315
80%PN	190	251.7	277	196	262	291	200	270	300	208	273	303

[a] The two PN resins have the same novolac precursor.

[b] Onset temperature in DSC curve, °C.

Table 5
Cure parameters and kinetic parameters for PN resins with varying propargyl contents (N_2 50 ml/min)

Polymers	Cure parameters			Kinetic parameters		
	T_{gel}[a] (°C)	T_{cure}[a] (°C)	T_{post}[a] (°C)	E (kJ/mol)	A (1/s)	n
50%PN	198.7	252.5	272.3	134.3	6.12E12	0.937
80%PN	184.3	246.7	271	151.5	3.84E14	0.944

[a] T_{gel} designates gel temperature of the resin, while T_{cure} designates cure temperature and T_{post} designates post heat-treated temperature.

content. This conclusion is in close agreement with the results of gel time measurements.

The onset temperature, peak temperature and endset temperature in non-isothermal DSC were linear-fit with scanning rates (β) to obtain the intercepts which can be regarded as gel temperature, cure temperature and post-cure temperature, respectively. Thus, processing parameters for practical cure were determined as shown in Table 5. It can be seen that with increase in propargyl content the gel temperature and cure temperature of PN resin decreased. The results also lend direct support to accuracy of kinetic analysis.

3.3. Thermal cure of PN resins with varying molecular weights

Fig. 7 shows DSC scans for PN resins with varying molecular weights and an identical propargyl content of 80%. The profiles are nearly overlapped.

With the same methods mentioned above, the kinetic parameters and processing parameters for two PN resins with deferent molecular weights were calculated and are listed in Table 6. As can be seen, molecular weights also had an undisputed effect on thermal cure. Although the curing temperatures for both resins were similar, the thermal cure was facilitated with increase in molecular weight (for PN-1 the gel time at 200 °C is 20 min, while for PN-2 it is 11 min). It maybe results from gel effect during crosslinking reaction.

3.4. Thermal cure of PN resins wherein bridged methylene having different o/p linkage ratios

In this part, the effect of configuration on cure kinetics was investigated. The samples were derived from conventional novolac having an o/p ratio of 1 and high ortho novolac (HON) having an o/p ratio of 3 (the former was designated as PN and the latter was designated as PHON). Both samples had the same propargyl content of 72%. The o/p ratio is semi-quantitatively proportional to the ratio of the absorbency of the two peaks at 815 cm^{-1} and 750 cm^{-1} in IR spectra (see Fig. 3b). The non-isothermal DSC scans are shown in Fig. 8.

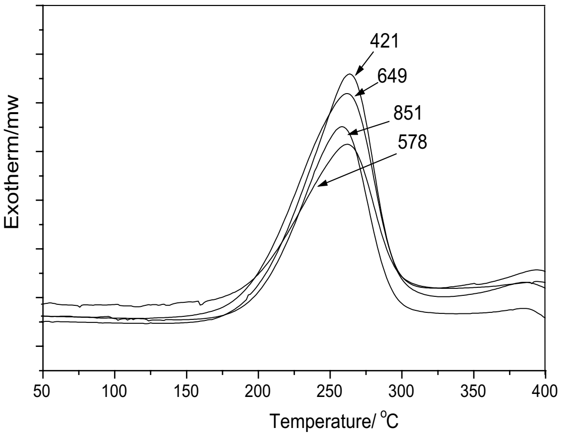

Fig. 7. DSC profiles of PN resins with varying molecular weights (heating rate 10 °C/min, N_2 50 ml/min).

Using the same methods mentioned above, thermal curing parameters and kinetic parameters of the thermal cure reactions for the resins were obtained, and are summarized in Table 7. Compared with PN resin, PHON resin possesses a lower cure temperature and higher frequency factor. The distribution of propargyl groups in PHON resin is more un-uniform than that in PN

Table 6
Cure parameters and kinetic parameters for PN resins with varying molecular weights (N_2 50 ml/min)

Polymers	Cure parameters			Kinetic parameters		
	T_{gel}[a] (°C)	T_{cure}[b] (°C)	T_{post} (°C)	E (kJ/mol)	A (1/s)	n
PN-1[a]	184.3	246.7	271	151.5	3.84E14	0.944
PN-2[b]	183.5	244	276	126.9	1.45E12	0.934

[a] PN-1 designates PN resin based on novolac with molecular weight of 578 g/mol.

[b] PN-2 designates PN resin based on novolac with molecular weight of 767 g/mol.

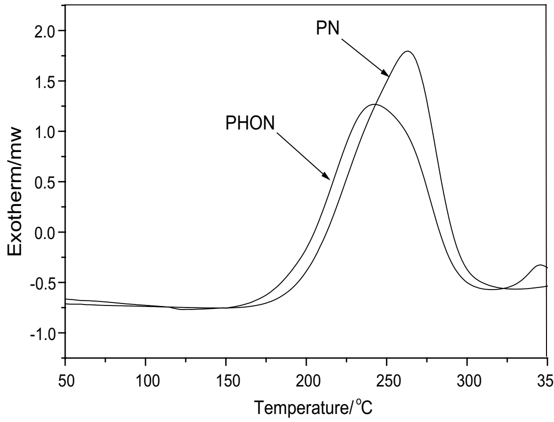

Fig. 8. DSC profiles of conventional PN resin and PHON resin (heating rate 10 °C/min, N_2 50 ml/min).

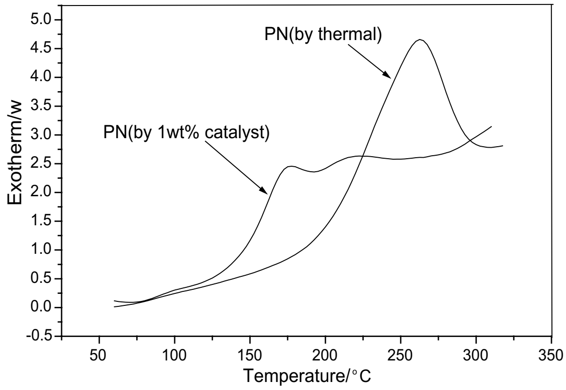

Fig. 9. DSC profiles of catalytic and thermal cure of PN resin (heating rate 10 °C/min, N_2 50 ml/min).

Table 8
Cure parameters and kinetic parameters for catalytic and thermal cure of PN resin (N_2 50 ml/min)

Curing methods	Cure parameters			Kinetic parameters		
	T_{gel} (°C)	T_{cure} (°C)	T_{post} (°C)	E (kJ/mol)	A (1/s)	n
Thermal	184.3	246.7	271	167.2	1.56E16	0.950
Catalytic	123.7	191.5	243.5	159.8	3.14E17	0.953

resin, so higher local concentration in PHON resin conduces a larger A which results in the lowered cure temperature.

PHON resin is comparable to PN resin in terms of the cost of production. It has brightly prospective applications in the area of heat-resistant materials.

3.5. Catalytic cure vs. thermal cure of PN resins

Many transition metal complexes are well known to catalyze acetylene to polymerize [14], and their use in the cure of PN resins is expected to affect the curing behaviors dramatically. However, reports on this subject have been scarce.

DSC was usually used to screen potential catalyst for activity, here the catalysis of $NiCl_2(PPh_3)_2$ on PN was ascertained. $NiCl_2(PPh_3)_2$ was chosen because it is stable in air at cure temperature and soluble in PN melt. The non-isothermal DSC results (see Fig. 9 and Table 8) showed that $NiCl_2(PPh_3)_2$ remarkably lowered the initiation temperature and the peak temperature. Catalytic gelation at 130 °C is mind enough, which is about 60 °C lower than the thermal gel temperature. The cure temperature is lowered by about 45 °C in comparison

Table 7
Cure parameters and kinetic parameters for PN resins with different o/p ratios (N_2 50 ml/min)

Polymers	Cure parameters			Kinetic parameters		
	T_{gel} (°C)	T_{cure} (°C)	T_{post} (°C)	E (kJ/mol)	A (1/s)	n
PN	183.5	244	276	126.9	1.45E12	0.934
PHON	178	227.2	276	134.6	2.9E13	0.939

with that of thermal cure. To our surprise, the activation energy for catalytic cure was similar to that for thermal cure. Maybe it is the remarkable increase of frequency factor (A) that leads to the higher curing rate and the lower cure temperature.

In all, catalytic cure of PN has a broader exotherm, smaller enthalpy and lower cure temperature, which enables PN resins to be cured in a controllable and safe way.

3.6. Thermal cure of MPN resins

The viscosity of PN resin is very low, in some cases, the viscosity is too low to avoid flowing out of the frame at processing temperatures. MPN resin was condensation–addition dual-cure-type phenolics, and methylol groups can induce partial crosslinking or chain extending at lower temperatures and render the resin melt a proper viscosity for processing. MPN resin could be cured at a lower temperature compared with PN resin with the same propargyl content (vide supra). The content of methylol groups in MPN resin was controlled so that the amount of the volatiles upon cure was acceptable. In view of this, MPN has an advantage over PN, and is suitable for fabrication of large-scale composite materials. In this part, the cure kinetics of various MPN resins will be discussed.

3.6.1. Thermal cure of MPN resins with varying methylol contents

Fig. 10 shows the non-isothermal DSC of MPN resins with varying methylol contents. The first exotherm at 190–240 °C due to the condensation reaction of methylol groups grew stronger with the increase of methylol content, and slightly shifted to lower temperature. The second exotherm at 250–290 °C due to the polymerization of propargyl groups varied slightly amongst all the MPN resins, the peaks were comparatively less pronounced when methylol content is higher. This implies the condensation of methylol groups and the addition polymerization of propargyl groups are not separate, there must be some combined reaction between them [15–17].

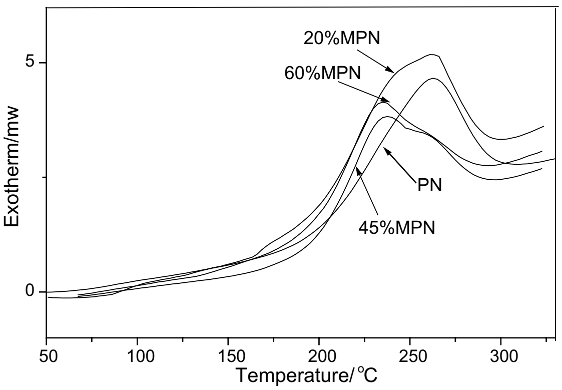

Fig. 10. Non-isothermal DSC profiles of MPN resins with varying methylol contents (heating rate 20 °C/min, N_2 30 ml/min).

The kinetic and processing parameters for MPN with varying methylol contents are listed in Table 9. It showed that the more methylol the lower the cure temperatures (including condensation cure temperature and addition cure temperature). The decrease of conden-

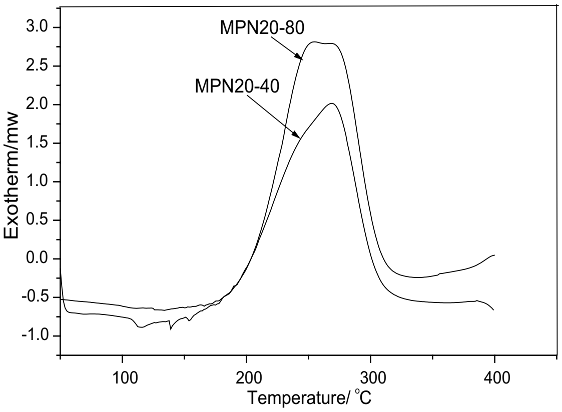

Fig. 11. Non-isothermal DSC profiles of MPN resins with two different propargyl contents (heating rate 10 °C/min, N_2 30 ml/min).

Table 9
Cure and kinetic parameters for thermal cure of MPN with varying methylol contents (N_2 50 ml/min)

Polymers	Cure parameters			Kinetic parameters		
	T_{gel} (°C)	T_{cure} (°C)	T_{post} (°C)	E (kJ/mol)	A (1/s)	n
MPN-1[a]	182.7	228.2	277	126.6	3.85E12	0.923
		247.7		158	2E15	0.95
MPN-2[b]	183.5	219.7	271	129.4	1.1E13	0.938
		240.4		121.8	5.1E11	0.932

[a] MPN-1 designates MPN resin with a methylol content of 15% and a propargyl content of 80%.

[b] MPN-2 designates MPN resin with a methylol content of 45% and a propargyl content of 80%.

Table 10
Cure and kinetic parameters for thermal cure of MPN resins with two different propargyl contents (N_2 50 ml/min)

Polymers	Cure parameters			Kinetic parameters		
	T_{gel} (°C)	T_{cure} (°C)	T_{post} (°C)	E (kJ/mol)	A (1/s)	n
MPN-3[a]	182.7	228.2	277	126.6	3.85E12	0.923
		247.7		158	2E15	0.95
MPN-4[b]	171.5	213	273.8	123.2	4.2E12	0.96
		238.5		121.9	5.6E11	0.932

[a] MPN-3 designates MPN resin with a propargyl content of 80% and a methylol content of 20%.

[b] MPN-4 designates MPN resin with a propargyl content of 40% and a methylol content of 20%.

sation temperature can be interpreted by the larger frequency factor for condensation reaction of methylol groups; and the slightly decrease of addition temperature might resulted from more hindrance to termination of radical during solid curing reaction of propargyl groups.

On the other hand, the more methylol groups in MPN resins, the more amount of volatile by-products during condensation reaction. In view of processability and thermal properties, moderate methylol content is appreciated.

3.6.2. Thermal cure of MPN resins with varying propargyl contents

Fig. 11 indicates the non-isothermal DSC scans of two MPN resins with a constant methylol content of 20% and two different propargyl contents of 40% and 80%, respectively. It was revealed that propargyl polymerization after the gelation of methylol groups exhibited similar characteristics in comparison to those of PN resins.

The processing and kinetic parameters calculated from DSC analyses are listed in Table 10. It can be seen that MPN resin with lower propargyl content possessed lower cure temperature. This might result from more hindrance to termination of radical during solid curing reaction of propargyl groups.

4. Conclusions

A facile synthetic route to PN resins and MPN resins was developed via Williams reaction between novolac resins and propargyl bromide. Both resins have excellent processability and nearly suitable to all processing techniques. Based on the results of non-isothermal DSC analyses, the cure parameters and kinetics of PN and MPN resins were estimated using linear-fit method and dynamic equations. The results revealed that propargyl contents, molecular weights and phenolic configuration had more or less effect on the thermal behavior of PN resins. Compared with thermal cure, catalytic cure of PN resins showed a lower initiation temperature by about 60 °C and a lower cure temperature by about 45 °C. For MPN resins, the thermal cure could be facilitated with increase in methylol content and with decrease in propargyl content, and the content of methylol groups of 20% is appreciated in view of proccessibility and thermal properties. These novel non-conventional addition-type and condensation–addition duel-cure type phenolic resins are structure-diverse and property-adjustable, which fulfill the requirements of high temperature matrices for advanced thermo-structural composites.

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