

Morphology Transition of Bismaleimide-Modified Novolac Resin

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ABSTRACT: The bismaleimide (BMI)-modified novolac resin was synthesized by allylation of the novolac resin and its "Ene" reaction with BMI. The reactions were monitored by Fourier transform infrared analysis (FTIR). The morphology of the BMI-modified novolac resin changed with degree of allylation (i.e., the amount of BMI used). On the basis of the studies done by dynamical mechanical analysis (DMA), differential scanning calorimetry (DSC), and field emission scanning electron microscopy (FE-SEM), it was found that when the degree of allylation increased from 48 to 59%, the resin changed from a single-phase structure to a two-phase

structure. From the research by thermogravimetric analysis (TGA) and DMA, it was found that the higher allyl-content (when > 48%) caused a decrease of the thermal properties and mechanical properties of the resultant resin. The BMI-modified allyl novolac resin with 48% degree of allylation has the best thermal properties and the highest dynamic modulus in the current research. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 76–83, 2006

Key words: novolac resin; preparation; morphology; phase separation; thermal properties

INTRODUCTION

Having a century-long history, phenolic resins are still attracting a great deal of research interest. Phenolic resins show unique properties because of the high aromatic content and very high crosslinking density in the structure. These unique properties include high dimensional stability, superior mechanical strength, high char yield, flame retardation, as well as high resistance to chemicals such as acids, water, and some solvents. Therefore, they play an especially important role in modern vehicle construction, advanced structure materials, aerospace industry, and the semiconductor industry.¹

Phenol resins are usually cured through condensation reactions. For the matrix of composites, the major disadvantages of phenolic resins lie in the volatiles released upon the curing process. Many new alternative curing mechanisms have been studied to avoid the release of volatiles. A successful approach is to introduce allyl groups into the phenol-formaldehyde novolac, and the resin is cured thermally at 180°C without the evolution of volatiles. The mechanism of the thermal curing of this resin is polyaddition at allyl double bonds.² The applications of the allyl-functional phenolic resins are the manufacture of glass fiber-

reinforced plastics and moldings, and to be used as casting compositions in resin composites with high thermal properties, good mechanical strength, and excellent chemical resistance.³ The disadvantages of the allyl phenolic resins lie in the difficulty to achieve complete allyl curing and the thermal instability of the resultant matrix caused by curing at high temperature (>250°C), which is needed to complete the curing process and initiated degradation of other fragile parts of the crosslinking network.⁴

To overcome this problem, the decreased curing temperature is needed. And to improve the thermal stability of allyl phenolic resins, bismaleimide (BMI)^{5–7} has been incorporated to cure the resin via the "Ene" reactions and "Diels-Alder" reactions.^{8–10} The curing mechanism has been exploited by many researchers, and it varies with different feeding ratio of allyl : BMI, preparation process, and the cure schedule. Although an unambiguous mechanism has not been proposed, the generally accepted mechanism is allyl group and BMI's "Ene" reactions and "Diels-Alder" reactions, plus the condensation of phenol OH groups.^{11–21}

Many high performance polymers based on allyl phenol-BMI system have been developed, such as commercial available Matrimide-5292 of Ciba-Geigy (containing 4,4'-Bismaleimidodiphenyl methane (BMI) and 2,2'-Diallyl Bisphenol A (DABA))⁷ and their further development.^{22,23} Recently, a partially allylated novolac, cured with BMI and molded under pressure at high temperature has been developed by Yan et al.²⁴

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TABLE I
Compositions of the BMI-Modified Novolac Resin Prepolymers

Sample	N^a	Molar feed ratio ^b	P^c (%)	BMI/allyl group molar ratio	M_n^d
BMI-APN-1	8.1	0.40 : 1	39.0	1 : 1	1750
BMI-APN-2	7.9	0.50 : 1	48.3	1 : 1	1870
BMI-APN-3	7.5	0.60 : 1	59.2	1 : 1	1960

^a Refers to degree of polymerization of the novolac resins.

^b Refers to molar ratio of $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}:\text{—OH}$ in the novolac resins.

^c Degree of allylation.

^d $M_n = 200 + 105N + 220 \times P \times N$.

The cured resin showed excellent heat resistance and good flexural properties with the T_g of 288°C and 122 MPa of the flexural strength, as well as 3.5 GPa of flexural modulus. Another example of this type is partially allylated Xylok (polyaralkyl phenol)-BMI system, which exhibits superior heat resistance (no mass loss up to 490–500°C) and good mechanical properties.²⁵

To get good thermal and mechanical properties of the BMI-modified allylated novolac resins, it is necessary to study the morphology of the resultant complex resin. In the present work, we synthesized three kinds of BMI-modified Novolac resins with different BMI content, then used DMA, DSC, and SEM to study the

morphology transition of the resin. At the same time, TGA and DMA were used to characterize their thermal and dynamic properties.

EXPERIMENTAL

Materials

Phenol (CP) and formaldehyde (37% in water, CP) were purchased from the Beijing Organic Chemicals Factory (China) and were used as received. Allyl chloride was purchased from Qilu Petrochemical Co. (China) and used after distillation. 4,4'-Bismaleimido-diphenyl methane (BMI) was obtained from the Fenguang Chemical Co., Ltd. (China). It is a crystalline compound with melting point of 151–154°C, and purity greater than 99%. Tetrahydrofuran (THF) and *n*-butanol (BuOH) were analytic reagents from the Beijing Chemical Factory (China). THF was purified by reflux over $\text{Na}/\text{CO}(\text{C}_6\text{H}_5)_2$ and distillation.

Synthesis of the BMI-modified novolac resin

The novolac resin was prepared through condensation of formaldehyde and phenol catalyzed by oxalic acid. The molar ratio of phenol to formaldehyde was 1 : 0.9. For the allylation of the novolac resin, 0.4, 0.5, and 0.6 mol of allyl chloride were used for one mole of the phenol group in the novolac resin, respectively. The

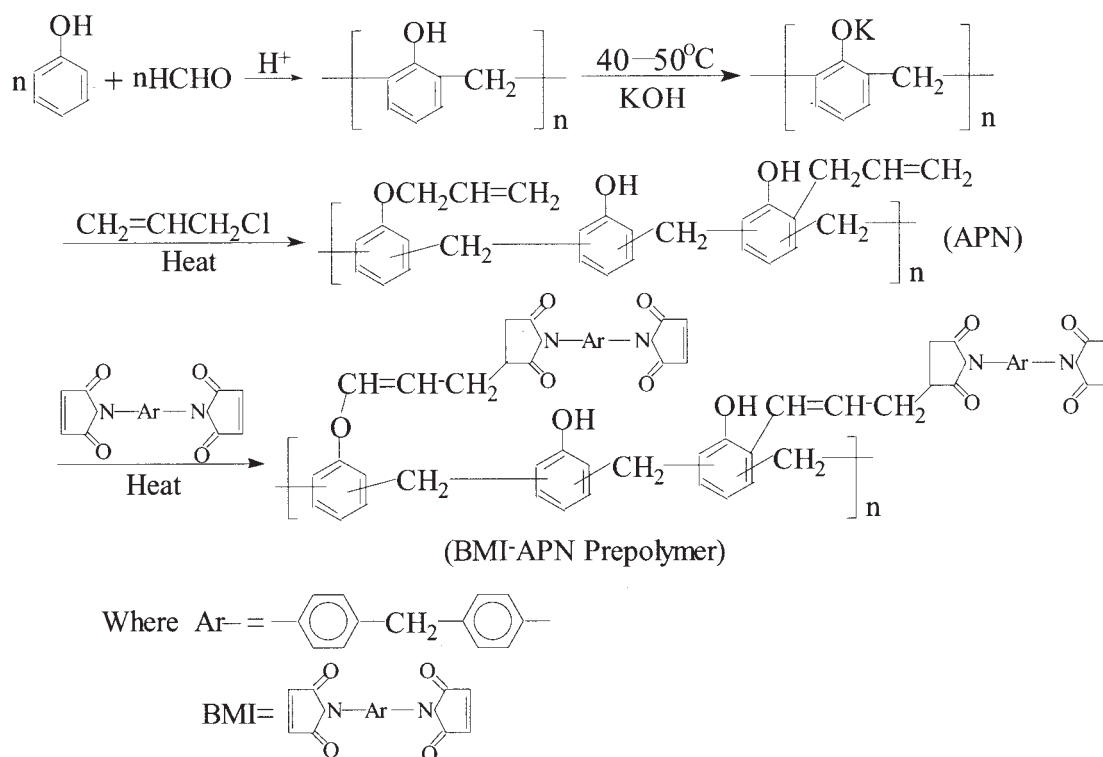


Figure 1 Preparation of the BMI-modified novolac resin prepolymer.

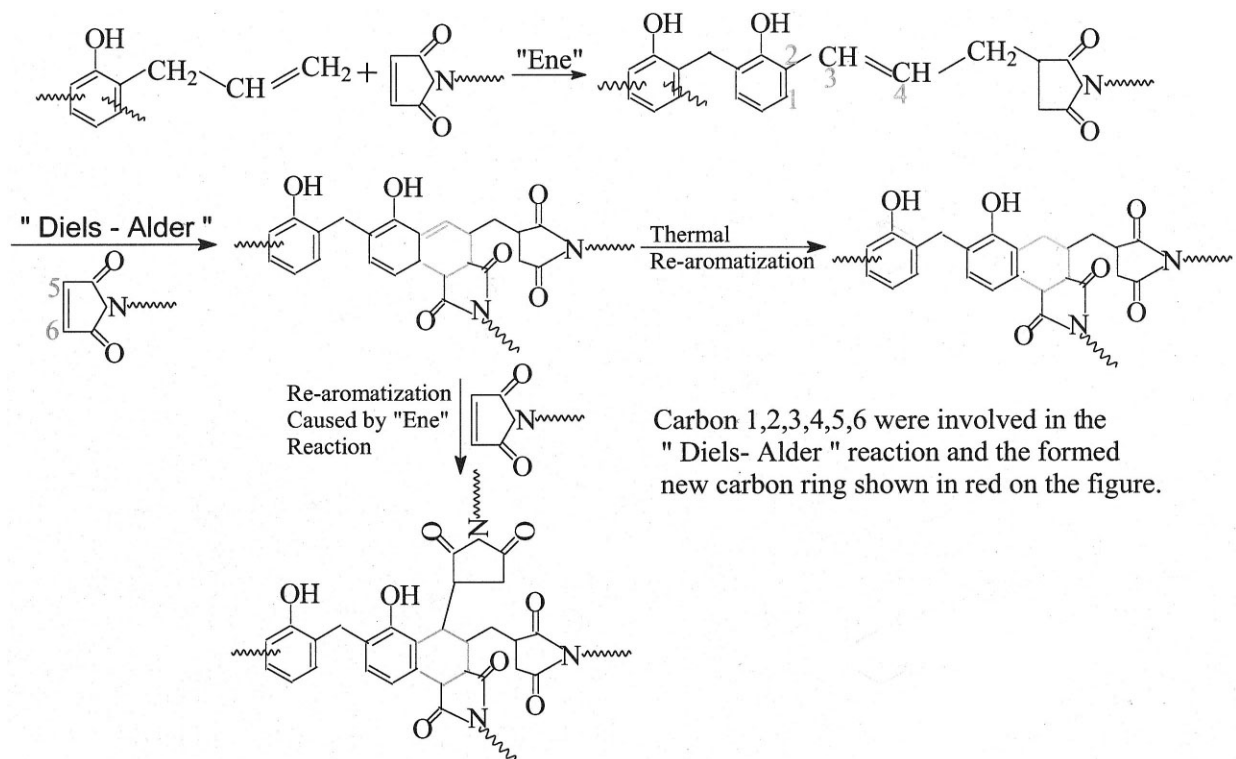


Figure 2 (a) Proposed curing mechanism for the BMI-modified novolac resin. (b) Additional curing paths for the BMI-modified novolac resin.

reaction was carried out at 50°C in butanol for 5 h, and then heated to 80°C for another hour. The degree of allylation of the phenol groups in the novolac resins was 39%, 48%, and 59%, respectively, determined by ^1H NMR.²⁶ The allylated novolac resin was heated to 120°C in oil bath, and then BMI was introduced at the molar ratio of allyl group to maleimide group, 1:1. After the prepolymerization was carried out at 120°C for 40–90 min (for different allylated degrees), clear homogenous BMI-modified novolac resins were obtained. The formation of BMI-PN was confirmed by FTIR and ^1H NMR (CD_3COCD_3) spectra.

Preparation of the cured resin

The resin mixtures were degassed in a vacuum oven to make the mold powder. Specimens were prepared by compression molding. The cure schedule was 170°C/2 h + 200°C/6 h, and the post cure procedure was 250°C/6 h, according to Yan et al.²⁴ The compositions of the three BMI-modified novolac resin prepolymers are listed in Table I. The molecules of the three BMI-modified novolac resin prepolymers have been calculated based on the following formula:

$$M_n = 105N + 220 \times P \times N \quad (1)$$

where P denotes the total allylation degree of phenol-OH, N denotes the polymerization degree of phe-

nolic resin, and the coefficient 220 has been calculated by adding the molecular weight of $-\text{CH}_2-\text{CH}=\text{CH}_2$ and half of BMI (because there are two double bonds in one BMI molecule).

Measurements

^1H NMR spectra were obtained with a Bruker MW 300 spectrometer with CDCl_3 as solvent. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermogravimeter with a heating rate of 20°C/min under a nitrogen flow rate of 100 mL/min. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°C/min and nitrogen flow of 100 mL/min. Dynamical mechanical analysis (DMA) was performed on a Perkin-Elmer DMA-7 dynamical mechanical analyzer at a heating rate of 20°C/min and the three-points tensile style. The samples were measured at a 2-Hz frequency and for a temperature range from 40 to 350°C, with the dimension $15 \times 4 \times 1.5 \text{ mm}^3$ (Length \times Width \times Height). The microstructure features of the complex materials were examined with a Hitachi S-900 field emission scanning electron microscope. The fracture surfaces of the samples were coated with gold to eliminate charging effects, and a high voltage (10 KV) was used.

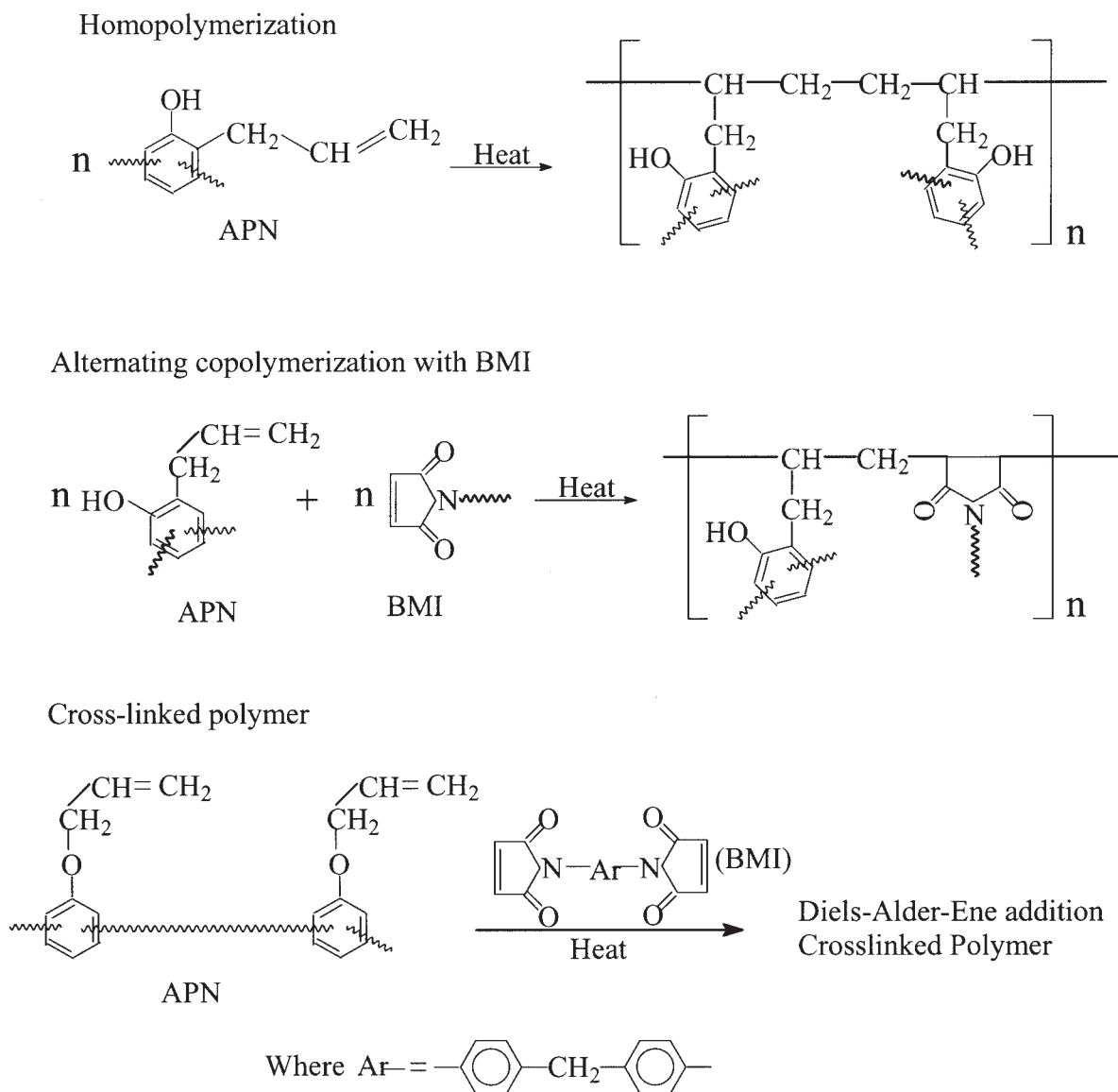


Figure 2 (Continued from the previous page)

RESULTS AND DISCUSSION

Synthesis of the BMI-modified novolac resin

The synthesis of the BMI-modified Novolac resin prepolymer is shown in Figure 1. The BMI-modified novolac resin was prepared in the following steps: (a) synthesis of the novolac resin, (b) allylation of the novolac resin, and (c) prepolymerization of the allylated novolac resin with BMI. The first two steps are already characterized in Szymanski et al.²⁶ Here the third step receives focus. Figure 2 gives FTIR spectra for BMI, APN, and BMI-APN-1. It can be seen from Figure 2 that most of the characteristic peaks of BMI, which are at 687 cm^{-1} , 830 cm^{-1} , 1150 cm^{-1} , 1387 cm^{-1} , and 1515 cm^{-1} from benzene ring, 1710 cm^{-1} , 1770 cm^{-1} from carbonyl groups in imide ring, and 950 cm^{-1} , 3100 cm^{-1} from $-\text{CH}=\text{CH}-$ in imide ring,

appeared in the BMI-APN-1 spectroscopy, and the characteristic peaks of APN at 760 cm^{-1} , 820 cm^{-1} , 1230 cm^{-1} , 1610 cm^{-1} , 2853 cm^{-1} , 2922 cm^{-1} , 3020 cm^{-1} , 3440 cm^{-1} (all from phenolic resin), and 930 cm^{-1} , 990 cm^{-1} , 1643 cm^{-1} , 3080 cm^{-1} (from $-\text{CH}_2=\text{CH}-$) appeared as well. All these peaks show that BMI reacted with APN to give the BMI-APN prepolymer. The formation of BMI-APN is also shown from its ^1H NMR spectrum according to Szymanski et al.²⁶

The curing of the BMI-APN prepolymer was monitored by FTIR. The reactions involved in the curing process are shown in Figure 3(a, b), which are mainly Ene reactions, Diels-Alder reactions, homopolymerization, and alternating copolymerization.¹⁵ The detailed discussion of the curing process is presented elsewhere.²⁷

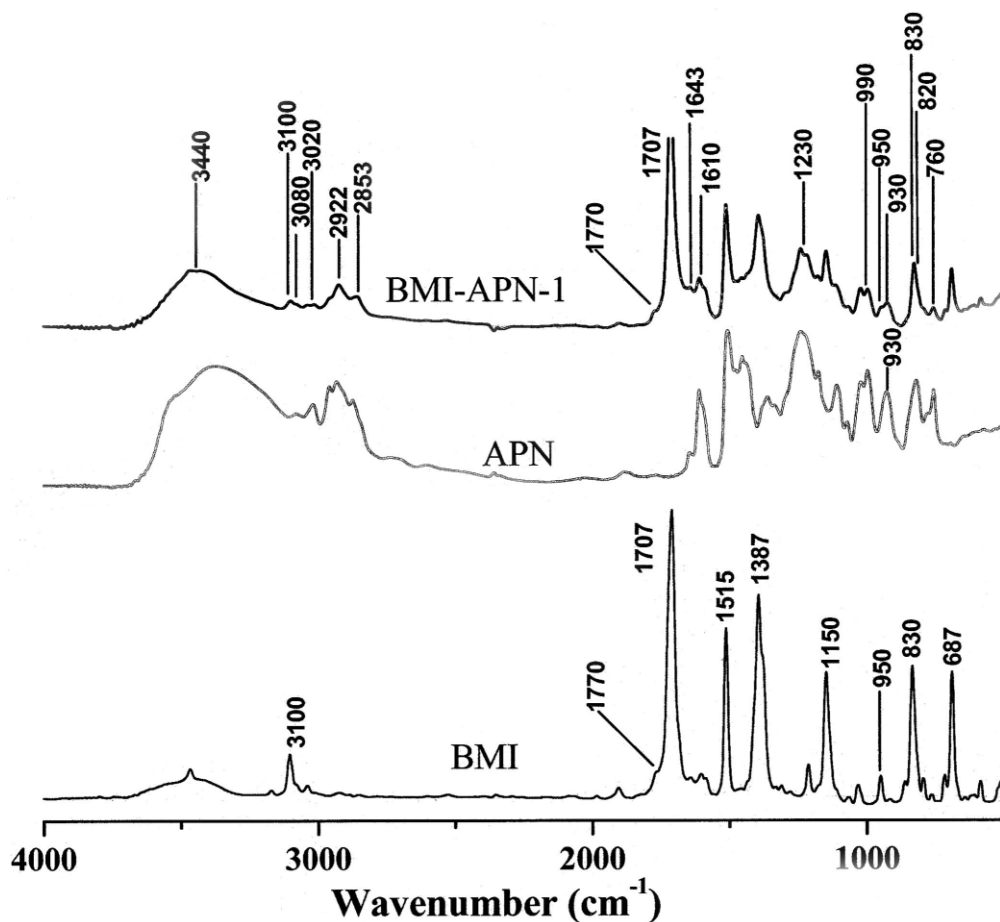


Figure 3 FTIR spectra of BMI, APN, and BMI-APN, respectively.

Morphology of the BMI-modified novolac resin

Figure 4 gives the DMA diagrams of the cured BMI-modified Novolac resins. It can be clearly seen in Figure 4 that BMI-APN-3 has two glass transitions, which is a strong proof that there exists a two-phase structure in this material. But there is only one glass transition for BMI-APN-1 and BMI-APN-2.

Table II lists the T_g values of the BMI-modified Novolac resins obtained both from DMA and from DSC. It can be seen from this table that the BMI-modified novolac resin with 48% degree of allylation has the highest T_g and the one with 59% degree of allylation has two different T_g 's, which correspond with the microphase-separated structure. Table I in Yan et al.²⁴ gives glass transition temperatures of the cured BMI-modified Novolac resins with varied molecular weight and degree of allylation. There, all the allyl-novolac resins have similar molecular weights (334–618 g/mol), and when keeping the same degree of allylation (48%), with MW increasing from 334 to 551 g/mol, the T_g increases from 181 to 297°C. Keeping the same MW (454 g/mol) and increasing degree of allylation from 39 to 57%, the T_g increases from 243 to 314°C. There is no phase-separation phenomenon

observed. The probable reason for the difference between Yan's paper and this work is that in the present work, the allyl phenol novolac resin with much higher molecular weight (~ 1100 g/mol) was used to synthesize the complex resin, and the higher molecular weight resin has higher BMI content, compared with the lower MW resin at the same degree of allylation. This higher BMI content may cause the polymerization of BMI itself and formation of a two-phase structure, in which one phase is rich in APN (mainly APN homopolymerized product, secondarily APN-BMI alternating copolymerized product, as shown in Figure 3(a, b)) and the other phase is rich in BMI (mainly APN-BMI alternating copolymerized product, secondarily BMI homopolymerized product, as shown in Figure 3(a, b)). The cure schedule is important for the thermal properties of the cured resin; here, it was 170°C/2 h + 200°C/6 h, and the post cure procedure was 250°C/6 h. According to the research by Mijovic and Andjelic,¹⁴ the principle reaction was the alternating copolymerization by maleimide and allyl double bond when the curing temperature range from 140 to 250°C, and maleimide homopolymerization only started at temperature larger than 200°C. Then, we can

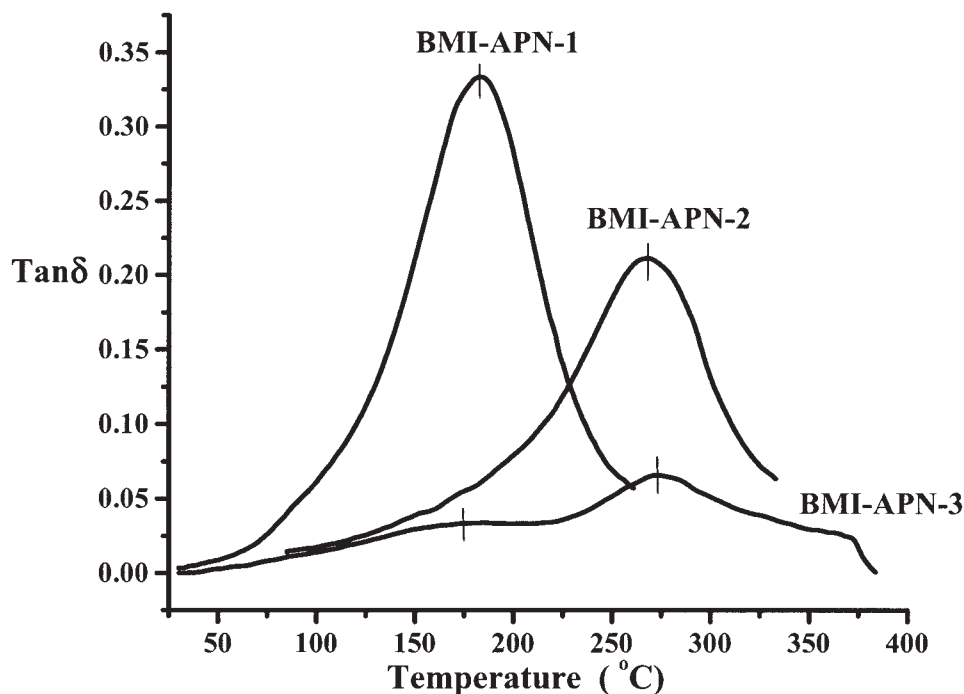


Figure 4 $T_{g,s}$ of the BMI-modified novolac resins with different degree of allylation measured by DMA.

attribute the major glass-transition at 275°C to APN-BMI alternating copolymer and the minor glass-transition at 175°C to APN homopolymer (the separated phase). The phase-separation lowers the glass-transition temperature and thermal resistance of the material. Much more research is needed to be done to make clear the compositions of both the phases and the curing mechanism through fluorescence, real-time FTIR, and UV-Reflection spectroscopy.¹⁶

A similar result has been observed when Diallylbisphenol-formaldehyde (ABPF)-bisphenol A bismaleimide (BMIP) (1 : 1 stoichiometry) matrix resin was modified by polysulfone (PS) and polycarbonate (PC).²⁸ In this case, except for resin-rich phase and additive (PS or PC here)-rich phase, there exists a cocontinuous phase, which has an intermediate $T_{g'}$ between the T_g 's of the separated phase and the matrix, by the DMA study. SEM also has been used to observe the morphology transition of the complex resin.²⁸ This example indicated that the phase separa-

tion is not a rare phenomenon for the BMI/Allyl phenolic resin system, considering its complicated curing mechanism and many effect factors to the structures of the resin. However, through careful designed cure schedule, the phase-separation could be avoided in most situations.

Figure 5 gives the FE-SEM photographs of the BMI-modified novolac resins with 39 and 59% degree of allylation. It can be seen from Figure 5 that the BMI-modified novolac resin with 59% degree of allylation has a two-phase structure and the one with 39% degree of allylation is a uniform one-phase structure. This result was consistent with the T_g measured from the DMA study.

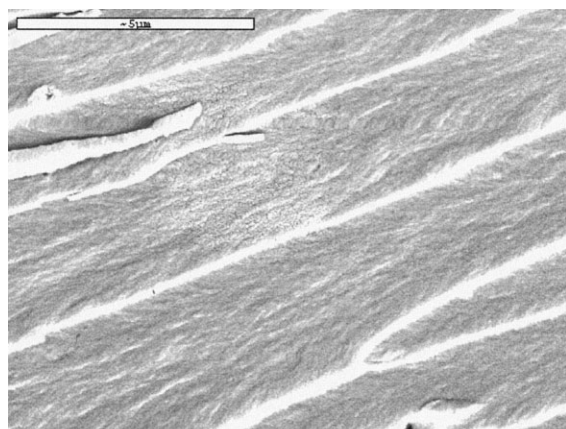
Thermal properties of the BMI-modified novolac resin

TGA diagrams of the BMI-modified Novolac resin with different degrees of allylation are shown in Figure 6. It can be seen that there were two stages in the weight-loss process of the resins. The elimination of trapped solvent or moisture accounted for the minor weight loss starting at ~150°C. The major weight loss occurred at > 450°C, which was due to the decomposition of the polymer network. Table III summarizes the inflection temperature (start main decomposition), temperature at 5% weight loss, temperature at 10% weight loss, and weight retention at 700°C in the TGA diagrams.

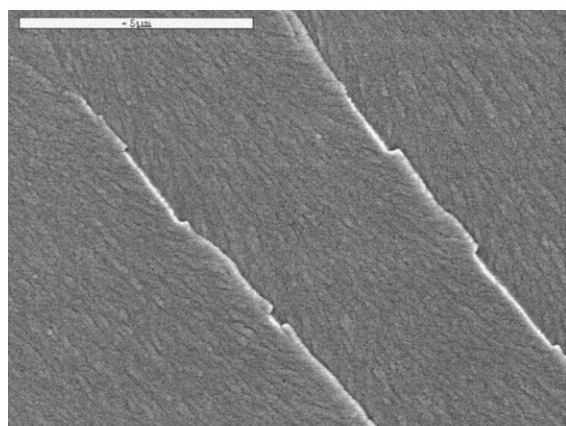
It is observed that the increase of degree of allylation from 39 to 48% dramatically increases the tem-

TABLE II
 T_g of the BMI-Modified Novolac Resins Measured by DMA and DSC

Sample	T_g measured by DSC (midpoint, °C)	T_g measured by DMA (tan δ , °C)	
		First	Second
BMI-APN-1	198	182	—
BMI-APN-2	295	274	—
BMI-APN-3	—	175	275



(a)



(b)

Figure 5 FE-SEM photographs of the BMI-modified novolac resins with different degree of allylation (scale bar = 5 μm). (a) BMI-APN-1 and (b) BMI-APN-3.

TABLE III
The Thermal Resistance of the BMI-Modified Novolac Resins Measured by TGA

Sample	Inflection temp. ($^{\circ}\text{C}$)	Temp. at 5 wt % loss ($^{\circ}\text{C}$)	Temp. at 10 wt % loss ($^{\circ}\text{C}$)	Wt retention at 700 $^{\circ}\text{C}$ (%)
BMI-APN-1	396	331	408	19
BMI-APN-2	402	410	445	51
BMI-APN-3	402	415	452	42

peratures for 5% weight loss, 10% weight loss, and the weight retention at 700 $^{\circ}\text{C}$. But when degree of allylation is increased from 48 to 59%, the temperatures for inflection, 5% weight loss, and 10% weight loss do not increase significantly, but the weight retention at 700 $^{\circ}\text{C}$ decreases largely. The decrease of the thermal resistance of the material in the BMI-modified Novolac resin with 59% degree of allylation is due to the higher allyl-content than that with 48% degree of allylation. It is understandable that thermal stability decreases due to enhanced incorporation of the fragile aliphatic groups.

Table IV shows the change in storage modulus with temperatures for BMI-APN-1, BMI-APN-2, and BMI-APN-3. It can be seen that the BMI-modified Novolac resin with 48% degree of allylation has the highest dynamic modulus at all temperatures. This is consistent with the results from the TGA study. The previous explanation for the decrease of the thermal resistance also holds true for this situation.

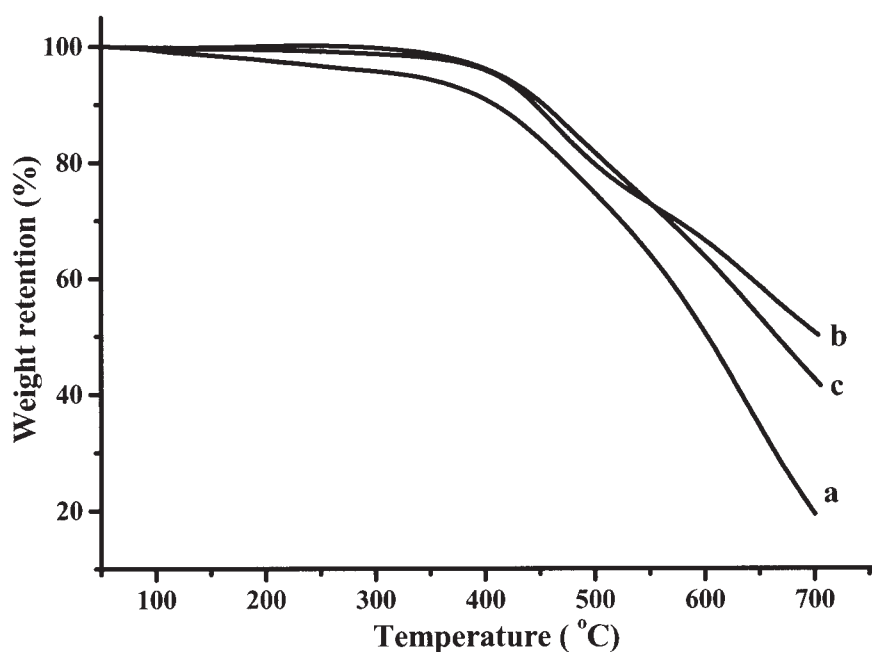


Figure 6 TGA diagrams for the BMI-modified novolac resins with different degree of allylation. (a) BMI-APN-1, (b) BMI-APN-2, and (c) BMI-APN-3.

TABLE IV
The Dynamical Mechanical Properties of the BMI-Modified Novolac Resins Measured by DMA

Sample	Dynamical modulus (GPa) at			
	25°C	200°C	250°C	300°C
BMI-APN-1	1.92	0.07	0.04	0.04
BMI-APN-2	3.53	3.20	2.95	2.75
BMI-APN-3	1.48	0.99	0.71	0.68

CONCLUSIONS

The morphology of the BMI-modified novolac resin changed with degree of allylation (i.e., the amount of BMI used), which affected the properties of the modified resins. When degree of allylation is increased from 48 to 59%, the BMI-modified novolac resin transitioned from a single-phase structure to a phase-separated structure. The higher allyl content (when > 48%) caused a decrease in the thermal properties and mechanical properties of the complex resin. The BMI-modified novolac resin with 48% degree of allylation has the best thermal properties and the highest dynamical modulus in this research.

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