The Effect of Allylation Degree on Processing Properties, Thermal Cure, and Thermal Properties of BMAN Resins

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ABSTRACT: A series of allyl-functional novolac (AN) resins with various allylation degree, from 32.4 to 114.6%, were synthesized and blended reactively with 4,4′-bismaleimide biphenyl methane (BMI) at a weight ratio of 2.50 : 1 to get BMI-modified and allyl-functional novolac (BMAN) resins. Structural characteristics of the resins were determined by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}HNMR) techniques. Processing properties of BMAN resin system was evaluated by solubility, rheology, and thermal gelation, and the results show that processing properties of BMAN resins were excellent and could be tailored by changing allylation degree of AN resins. Differential scanning calorimetry (DSC) was used to evaluate cure reactivity of BMAN resin system, and the results reveal that the resins with higher allylation degree possessed better cure reactivity. Thermal properties were evaluated by means of dynamic mechanical analysis (DMA) and thermogravimetry analysis (TGA) techniques. The results reveal that with increase in allylation degree of resins the thermal stability of BMAN resins increased because of increase in crosslinking density, but char-yields of the above resins at 800°C decreased in turn. Understanding of the relationship between allylation degree and properties of the resins would be useful to direct the design of material to meet different requirements of applications. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2822–2829, 2007

Key words: thermosets; allylation degree; processing property; thermal cure; thermal property

INTRODUCTION

Phenolic resins are preferred in a wide range of applications from commodity and construction materials to high technology aerospace industry because of their desirable characteristics, such as superior heat and flame resistance, excellent ablative properties, and high strength retention at elevated temperatures, as well as, low fire, smoke and toxicity properties, and low cost.[1–3] However, their acceptance as a universal material in many engineering areas is hampered by their three major shortcomings, including inherent brittleness, limited shelf life of resin at ambient conditions, and evolution of volatiles during a condensation cure. The concept of addition-cure gains significance in view of its improved processing properties in deriving void free components and composites without impairing the thermomechanical characteristics of phenolic resins.[4–6] Structral modification involving phenolic hydroxyl groups is one of the major strategies in designing addition-cure phenolics,[6] such as allyl-functional phenolics,[7–10] propargyl ether functional phenolics,[11,12] phenol-epoxy system,[13] novolac cyanate[14] et al. Allyl-functional novolac (AN) resin have attracted a great deal of

attention because of being readily available in large quantities, easy synthesis and low cost. AN resin cures thermally without the evolution of volatiles. They can be used for the manufacture of glass fiber-reinforced plastics and moldings, casting or impregnating composites of high heat resistance, mechanical strength, and chemical resistance.[15] However, achieving complete allyl group curing is difficult and the cured matrix is not thermally stable due to the thermal fragility of crosslinking arising from polymerization of allyl groups. The thermal stability of AN resin can be further improved by reactively blending with bismaleimide (BMI), and the cure temperature can be lowered at the same time. Compared with pure BMI resin, the production cost of BMAN resin can be reduced obviously because it can be prepared from inexpensive AN resin and a small quantity of BMI. In addition, comparing with BMI resin, BMAN resin possesses better processing properties and can be tailored to fit for different processing requirement, such as RTM, solution impregnation process, and melt impregnation process.[9,10] So the processing cost of BMAN resin is lowered significantly. From earlier-mentioned discussion, BMAN resin possesses higher performance cost ratio than BMI resin. There are several reports [7–10] on polymer systems based on the blending of allyl phenol and bismaleimide (BMAN resin). Yan et al.[9] worked on this resin system and found that three major parameters were responsible
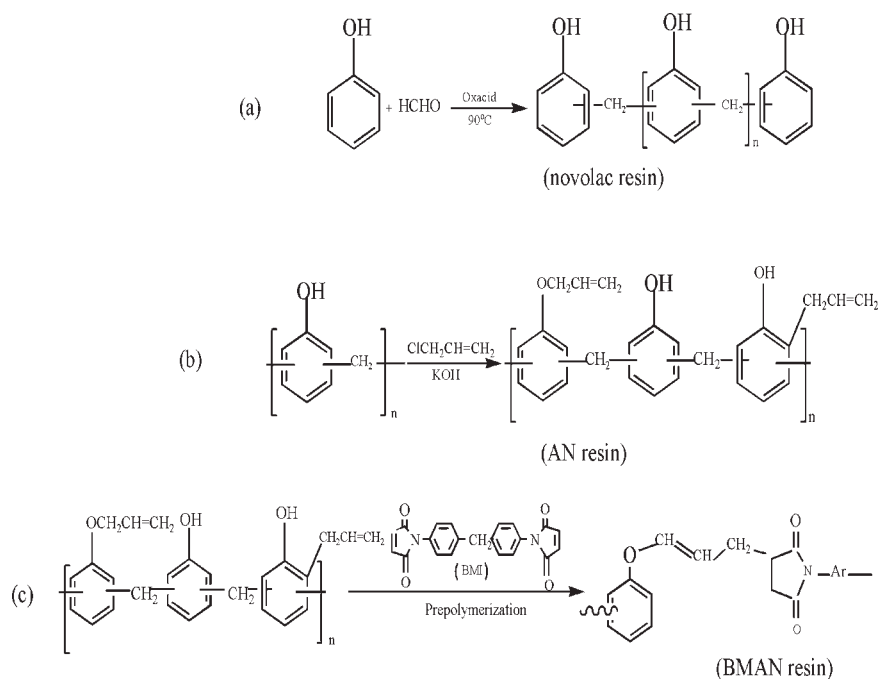
Scheme 1 Preparation of BMAN resin: (a) Synthesis of novolac; (b) Synthesis of AN resin; (c) Prepolymerization between AN resin and BMI.

for properties of the cured resin, including molecular weight of novolac resin, allylation degree and the molar ratio of allyl group to maleimide group. But those work focused on the resins with allylation degree not higher than 50%. Yao et al.[10] reported that the thermal properties of the resin and composites could attain a good level without being affected by the amount of BMI when allylation degree of the resin was high enough. However, to the best of our knowledge, the relationship between allylation degree and properties of BMAN resins, such as processing properties, cure reactivity, and thermal stability, has not been investigated in details. Now our work focused on this subject and the results must be useful to improve the properties of this resin system.

EXPERIMENT

Materials

Phenol (A.R., Beijing Yili Chemicals Factory, China), Formalin (A.R., 36–40% aqueous solution, Jinan Shengquan Chemicals Company, China), Oxalic acid (A.R., Beijing Chemical Reagents Corp., China), Butanol (A.R., Beijing Yili chemicals factory, China), Potassium hydroxide (A.R., Tianjin zhonghengxing chemicals corp., China), and 4,4′-Bismaleimide biphenyl methane (BMI) (Fengguang chemicals Co. Ltd., Honghu, China) were commerically available and used as received. Allyl chloride (Qilu petrochemical Co. Ltd., China) was distilled before use.

Instruments

FTIR spectra were recorded with a Bruker IFS 45 spectrometer. Solution ^{1}HNMR spectra were run on a Bruker AV400, DMSO-d_6 as solvent and TMS as internal standard. DSC was performed on Mettler-Toledo DSC822^e, at a heating rate of 10°C/min and a N_2 purge rate of 50 mL/min. DMA analysis was performed on DMA 242c (Netzsch, Germany) at a fixed requency of 1 Hz and the oven was heated at a rate of 5°C/min from room temperature up to 420°C. The specimens were deformed under flexural mode using a dual cantilever clamp arrangement. Thermal stability was evaluated by TGA on Netzsch STA409PC at a heating rate of 10°C/min in N_2. Viscosity of resin melts was determined using NDJ-79 rotating viscometer. Gel time was determined by means of a home-made apparatus according to Chinese standard of GB-7193.1-1987 (Corresponding to ASTM2471-71).

Synthesis of novolac precursor

The novolac precursor was synthesized by reacting phenol and formaldehyde under acid condition.[9] In a typical synthesis, phenol (1000 g, 10.62 mol) and oxalic acid (4.33 g, 0.048 mol) were taken in a three-necked flask and stirred at 90°C for 1.5 h in oil bath. Formaldehyde (765.4 g, 37.5 wt % formalin) was added drop-wise to the mixture over 50 min. The reaction was conducted for 3 h under stirring at 90°C and stopped by neutralization with 0.1M potassium hydroxide aqueous solution. The crude product was

washed several times with hot distilled water to remove unreacted phenol and catalyst followed by rotary evaporation to remove water to obtain pale-yellow transparent novolac resin. The synthesis protocol is shown in Scheme 1(a). The fraction selected for precursor of allyl-functional resin was characterized by FTIR and ^{1}HNMR techniques.

Synthesis of allyl-functional novolac (AN) resin

AN resin was prepared via Williamson reaction between allyl chloride and novolac resin in the presence of alkali catalyst.[9,10] The synthesis procedure is shown in Scheme 1(b). The synthesis of AN324 resin is chosen as the example now. Novolac resin (104 g, 1 mol) and butanol (160 g) were placed in a three-necked flask equipped with a mechanical stirrer, thermometer, and condenser. The mixture was stirred at 60°C for 1 h in oil bath. Then potassium hydroxide (19.64 g, 0.35 mol) was added into the mixture in batches, then the mixture turned into a purple solution. To the solution, allyl chloride (30.6 g, 0.4 mol) was added dropwise during 30 min. The mixture was stirred at 80°C for 6 h till it turned to be pale-yellow and was filled with KBr. After filtration, residual salt in butanol solution of resin was washed away by hot distilled water. The butanol in the solution was removed by rotary evaporation, then a viscous transparent brow-red resin was obtained. Thus the resin with allylation degree of 32.4% (AN324) was prepared. Yield was 95% (to novolac). It was characterized by FTIR and ^{1}HNMR spectroscopy techniques.

AN resins with varying allylation degree were also prepared by the same procedure described already.
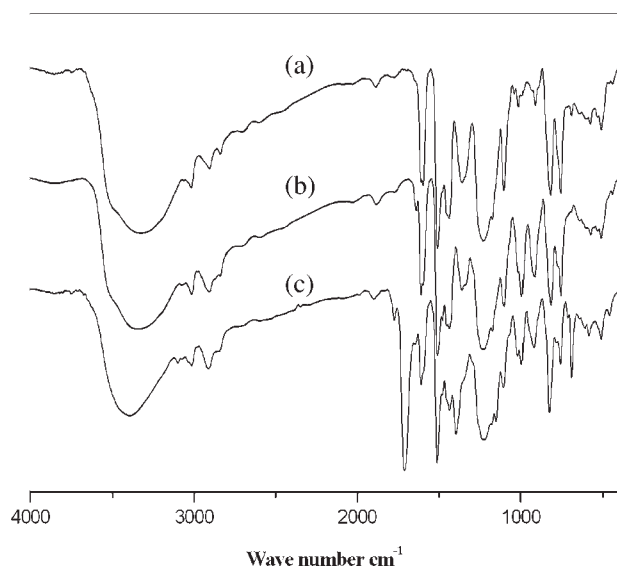
Figure 1 FTIR Spectra of (a) novolac resin; (b) AN324 resin; (c) BMAN 324 resin.
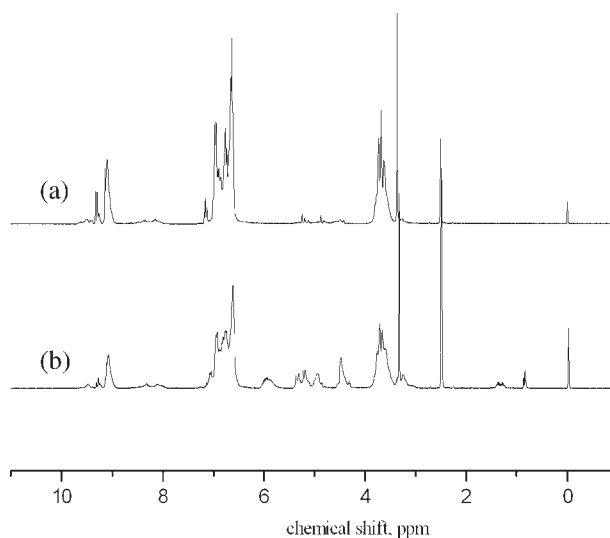
Figure 2 ^{1}HNMR Spectra of (a) novolac resin; (b) AN324 resin.

Preparation of the BMAN resins

The BMAN resins were prepared by prepolymerization of the AN resins with BMI. When AN resin was heated to 140°C, BMI was introduced at the weight ratio of AN resin to BMI of 2.50 : 1. A clear homogeneous BMAN resin was obtained after prepolymerization at 140°C for 30 min. The BMAN resin, which was prepared from AN resin with allylation degree of 32.4%, was designated as BMAN324, and so on.

Preparation of cured resins

The BMAN resins were preheated at 120°C for 1 h and cast into rectangular steel mold. Volatiles were removed by treatment in vacuum oven at 125°C for 1.5 h. The cure schedule was 170°C/2 h + 200°C/4 h and post curing was carried out at 250°C for 6 h.

RESULTS AND DISCUSSION

Synthesis and characterization of novolac precursor

The novolac precursor was synthesized by condensation reaction between phenol and formaldehyde using oxalic acid as catalyst. It was characterized by FTIR and ^{1}HNMR.

FTIR spectrum of novlac is given in Figure 1(a). The strong absorption at 3330 cm^{-1} is due to phenolic hydroxyl group, absorptions at 2850 and 2910 cm^{-1} due to bridging —CH$_2$—, strong absorptions at 1610 and 1509 cm^{-1} due to —C=C— of phenyl ring of novolac.

Figure 2(a) shows ^{1}HNMR characteristics of the novolac precursor. The signals at 8–10 ppm are due to phenolic hydroxyl proton, signals at 6.6–7.2 ppm are

due to aromatic protons, and signals at 3.5–4.0 ppm are due to bridging —CH$_2$— proton.

The average polymerization degree (n) of novolac resin and number average molecular weight (M_n) can be approximately calculated from integrals of ^{1}HNMR for novolac resin by means of the following equation:[16]

$$n = (2A_1 - 8A_2)/(3A_2 - 2A_1) \qquad (1)$$

$$M_n = 200.22 + 106.12 * n \qquad (2)$$

Where A_1 is the integral of aromatic protons of novolac resin and A_2 is the integral of bridging —CH$_2$— proton in novolac resin.

According to the earlier-mentioned method, it can be calculated that M_n of the novolac precursor is 442 and n is 2.28.

Synthesis and characterization of AN resin

AN resins bearing varying proportions of allyl function (AN) were synthesized by Willamons reaction between novolac resin and ally chloride. Scheme 1(b) shows the synthesis protocol for AN resin. By regulating the concentration of allyl chloride, allylation degree of AN resin, which is defined as the proportion of allyl group to phenyl ring, was controlled. When the molar ratio of allyl chloride to phenol in novolac exceeds 1 : 1, the allylation degree of AN resin would exceed 100% because of Claisen reaarangement during reaction.[10] For example, allylation degree of AN1146 is 114.6%, which means that all phenolic hydroxyl groups were converted to allyl ether, and each phenol ring carried 0.146 additional allyl group on average as a result of Claisen rearrangement. The allylation degree of AN resin can be determined by ^{1}HNMR. Figure 2(b) gives the typical ^{1}HNMR spectrum of AN324 resin. The signals at 6.6–7.2 ppm are due to aromatic protons, 5.2–5.5 ppm due to —OCH$_2$, 4.8–5.2 ppm due to —CH$_2$— proton of allyl group linked with phenyl ring and bridging —CH$_2$— proton appeared as a broad peak at 3.5–4.0 ppm. FTIR characteristics of AN resin are shown in Figure 1(b). The characteristic absorption at 3340 is due to phenolic hydroxyl group, absorptions at 1610, and 1509 cm^{-1} due to —C=C— of phenyl ring, absorption at 3085 and 917 cm^{-1} due to C=C—H of allyl group, and absorptions at 1000 and 1010 cm^{-1} are corresponding to —O—CH$_2$—.

The allylation degree was calculated from the integral of ^{1}HNMR for AN resin. The equations are given as follows:[16]

$$\text{Allylation degree (\%)} = (A_3 + A_4) * (n+1)/A_2 * (n+2) \qquad (3)$$

where n is the average polymerization degree of novolac precursor, A_3 is the integral of —OCH$_2$—

proton of allyl group, A_4 is the integral of —CH$_2$— proton of allyl group linking with carbon atom of phenyl ring.

The AN resins with varying allylation degree of 32.4, 51.5, 65.6, 84.6, and 114.6% were synthesized and characterized by the same methods. The characterization of AN324 is chosen as example and the results are shown in Figure 1(b) and Figure 2(b).

Preparation and characterization of BMAN resins

The BMAN resins can be prepared via "Alder-ene" reaction between maleimide groups of BMI and allyl groups of AN resins.[10,19,21] Prepolymerization degree of the BMAN resin can be controlled by reaction condition. The BMAN resin with proper prepolymerization degree is a homogeneous, transparent and red-brown resin system, which can be easily dissolved in acetone without precipitation of BMI. The structural characteristics of BMAN resins were studied by means of FTIR techniques. Now the characterization of BMAN324 is chosen as example and the result is shown in Figure 1(c). Comparing with Figure 1(b), it can be seen in Figure 1(c) that new characteristic absorption appeared at 1770, 1710, and 690 cm^{-1}, which are ascribed to carbonyl of maleimide groups and bending mode of =C—H of maleimide group. In addition, the characteristic absorption at 820 cm^{-1} due to deformation of allyl groups decreased. According to the change of characteristics, absorption and experimental phenomena of prepolymerization reaction, it can be seen that the BMAN resins with structural characteristics given in Scheme 1(c) were obtained via "ene" reaction between maleimide groups and allyl groups.

Processing properties of BMAN resins

To determine the relationship between processing properties of BMAN resins and allylation degree, solubility, rheology, and thermal gelatin of BMAN resins were examined.

All BMAN resins show excellent solubility in common low toxic solvent such as acetone and tetrahydrofuran, which makes them suitable for solution preg preparation of composites.

Time dependency of viscosity of BMAN resins at 130°C is shown in Figure 3. It can be seen that viscosity of BMAN resins showed a decreasing trend with increase in allylation degree. This is attributed to etherification of hydroxyl groups of novolac, which imparted more softness to molecular chains of novolac. Besides, the lower viscosity of BMAN resins with higher allylation degree could be maintained for as long as 6 h, indicating that BMAN resin is suitable for RTM process. Certainly, it can also be processed by
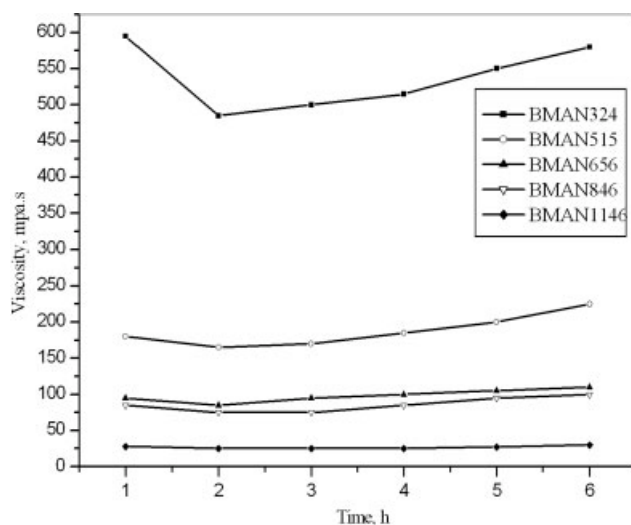
Figure 3 Viscosity–Time Curves of BMAN Resins at 130°C.

Figure 4 DSC Curves of BMAN resins and AN1146.

means of other techniques, such as compression molding, winding, and so on.

Gel time of BMAN resins at 170°C is summarized in Table I. Table I shows that gel time of the BMAN resins decrease from about 1 h to 10 min as the allylation degree increases from 32.4 to 114.6%. The trend reveals the influence of density effect of allyl group on the crosslinking reaction. According to Carothers equation, the gel point of BMAN resins could be attained at a lower reaction degree with increase in allylation degree of BMAN resins.[17]
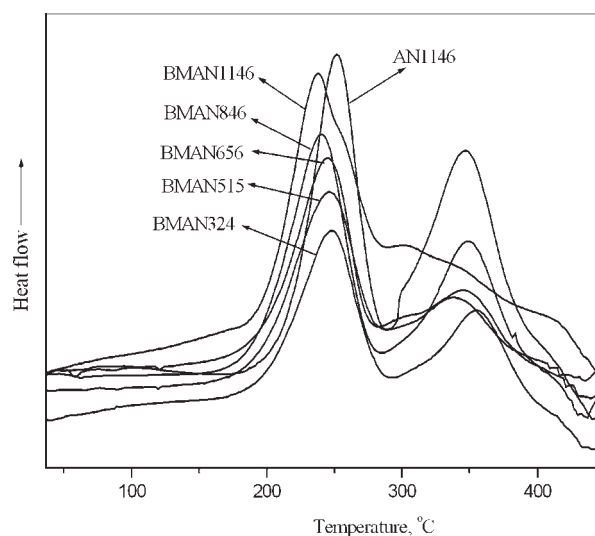
From what has been discussed earlier, it can be concluded that the processing properties of BMAN resins is excellent and can be tailored by changing the allylation degree of AN resin.

Thermal cure studies

DSC profiles of the BMAN resins and AN1146 are given in Figure 4. As shown in Figure 4, during thermal cure of AN1146, two exothermic peaks are observed in the temperature range of 170–280°C and 280–400°C. The former peak is corresponding to thermal Claisen rearrangement reaction of allyl ether group, and the latter one is resulted from the thermal polymerization of allyl groups.[18] This is the typical characteristic of DSC curve of AN resin.

TABLE I
Gel time for BMAN Resins with Different Allylation Degree at 170°C

System	Gel time
BMAN324	55.29
BMAN515	37.12
BMAN656	28.25
BMAN846	18.45
BMAN1146	10.25

As for DSC profiles of the BMAN resins, it can be seen in Figure 4 that the cure reaction of BMAN324, BMAN515, BMAN656, and BMAN846 showed two distinct exothermic peaks in the temperature ranges of 150–300°C and 300–400°C. The similar observation was reported by Gu et al.[8] The thermal cure reactions of blend resin system based on BMI and allyl phenol resin are very complicated and possible reaction occurring during thermal cure have been widely studied.[19–21] According to the earlier results reported, the first exothermic peak locating at 170–280°C can derived from several reactions, including Wangner–Jauregyg reaction (160–220°C), Diels–Alder reaction (225–275°C), thermal rearrangement reaction (180–280°C), and self-polymeriztion of BMI (170–280°C). As allylation degree increased, the peak temperature slightly shifted to lower temperature, indicating that reactivity of BMAN resin increased with increase in allylation degree. As for the second exothermic peak locating at temperature range of 280–400°C, it was mainly resulted from self-polymerization reaction of allyl groups. Comparing with other BMAN resins, the first exothermic peak of BMAN1146 showed an obvious shoulder peak due to thermal rearrangement reaction of excess allyl groups, and this exothermic peak changed into main exothermic peak locating low temperature range, indicating that BMAN1146 resin possessed better reactivity. Accordingly, it can be concluded that the higher allylation degree, the better reactivity of BMAN resin.

Thermal stability

DMA analysis

Thermal properties of the cured BMAN resins were evaluated by means of DMA and TGA techniques.
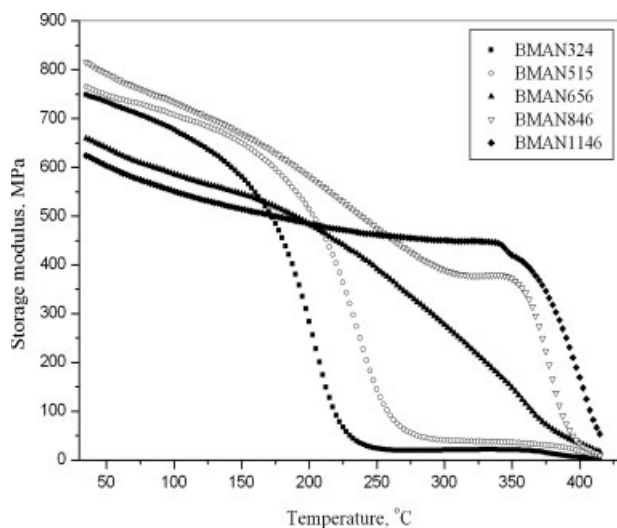
Figure 5 Storage modulus–Temperature curves of cured BMAN resins.

It is well known that the onset temperature of storage modulus (T_{onset}) in storage modulus–temperature curve can be used to evaluated thermal stability of materials: The higher T_{onset}, the better thermal stability of resin.[22]

The storage modulus–temperature curves from DMA testing of cured BMAN resins, including BMAN324, BMAN515, BMAN656, BMAN846, and BMAN1146, are illustrated in Figure 5.

As seen in Figure 5, T_{onset} of cured BMAN resins increased gradually with the increase in degree of allylation, indicating that thermal stability of BMAN resins increased with allylation degree increasing. When allylation degree is not higher than 70%, the T_{onset} is not higher than 300°C. But as allylation degree increases to 84.6%, T_{onset} increases to 360°C because of increase in crosslinking density of cured BMAN846 resin. In addition, it is noticeable that T_{onset} of BMAN1146 is as high as about 380°C. This makes it possible for BMAN1146 to be used as matrix of high performance thermostructural composites.

The tan δ-temperature curve can provide some useful information about molecular mobility in resin.[23] There are three parameters deserving to pay attention to: (1) The temperature, where the peak of tanδ appears, is interpreted as T_g (Glass transition temperature) used to evaluated the thermal stability of material; (2) The peak value of tan δ, which is associated with the movement of small groups and chains of molecules within the polymer structure, is a signature of the cooperative motion of small chains of the network[24]; (3) The area under the tan δ-temperature curve, which gives an indication of the total amount of energy that can be absorbed by the material during the experiment; A larger area means better damping properties and more energy absorbed and dissipated.[25]

From Figure 6, it can be seen that the tan δ peak temperature of cured BMAN324, BMAN515, and BMAN656 are 228, 257, and 274 °C, respectively, indicating that heat-resistant property of cured resin improved in turn. For cured BMAN846, two tan δ peaks are observed in the temperature range of 150–320°C and 330–400°C. The first tan δ peak of cured BMAN846, which is far obscure than that of cured BMAN324 and BMAN515, should be ascribed to glass transition of crosslinking network of cured resin. The second one with the peak temperature of 410°C reflected an effect of the increased mobility of the chains of cured resin. As for cured BMAN1146 resin, no glass transition occurred during the temperature range of 150–350°C. Besides, it can be seen from tan δ-temperature curve of cured BMAN1146 that the tan δ peak temperature caused by increased mobility of the chains would be higher than 420°C. All these indicate that cured BMAN1146 possessed excellent heat-resistant property. The excellent heat-resistant of cured BMAN1146 should derive from very high crosslinking density, which is ascribed to polymerization of BMAN prepolymer and self-polymerization of excess allyl groups.

It is also noted in Figure 6 that both the peak tan δ value and the area under the tan δ curve decreased as the degree of allylation increased. This characteristic showed that the mobility of molecules in the resins declined and material exhibit some rigidity at higher degree of allylation. This valuable information helps us to understand the relationship between structure and property of BMAN resins.

TGA analysis

TGA profiles of cured BMAN resins with varying allyl contents are shown in Figure 7. Figure 7 shows
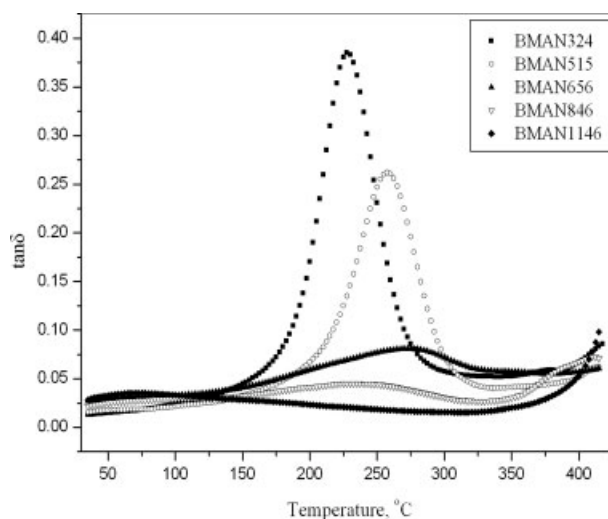
Figure 6 Tan δ-Temperature curves of cured BMAN resins.

that the initial decomposition temperature shifted to higher temperature in turn as allylation degree increased. From results in Table II, it can be seen that the respective $T_{0.05}$ (Temperature where the mass loss of cured resin is 5%) of cured BMAN resins are 375°C for BMAN324, 395°C for BMAN515, 400°C for BMAN656, 406°C for BMAN846, and 416°C for BMAN1146, showing the trend that $T_{0.05}$ increases with increase in allylation degree. The trend reveals that thermal stability of cured resins increased with increase in allylation degree. In addition, it is noteworthy that the T_i and $T_{0.05}$ of cured BMAN1146 resins are 422°C and 416°C, respectively, indicating that the cured BMAN1146 possesses excellent thermal stability. This makes the resin an ideal candidate for matrix of heat-resistant composites.

On the other hand, comparing char yield of cured BMAN324 and cured BMAN1146 at 800°C, the char yield value decreased from 55 to 36%, which is unexpected because cured BMAN1146 showed better heat-resistant property because of higher crosslinking density. After careful analysis we think that this unexpected behavior should be ascribed to characteristics of crosslinking network of cured BMAN resins. As for BMAN resins with higher allylation degree, the crosslinking network of cured resins derived from polymerization of BMAN prepolymer and self-polymerization of excess allyl groups. Moreover, the contribution of self-polymerization of allyl groups increases with increase in allylation degree, imparting cured resin-improved heat-resistant property. However, it is well-known that aliphatic crosslinking network from self-polymerization of allyl groups is thermally fragile. So when temperature is high enough, the aliphatic structure would decompose rapidly, resulting in obvious mass loss. Comparing with BMAN resins with higher allylation degree, the
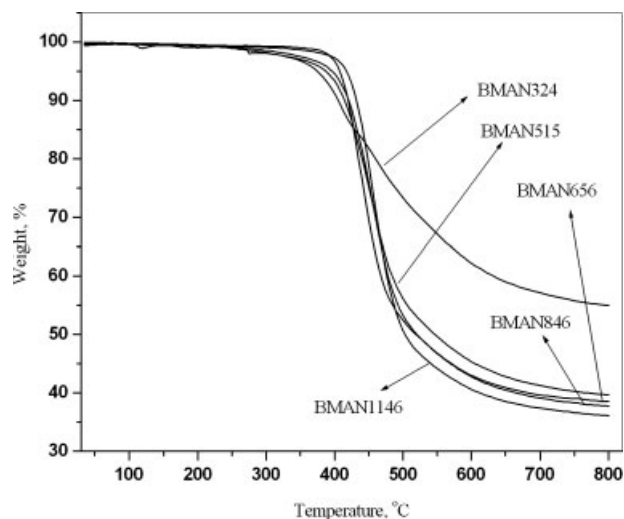
TABLE II
Typical Parameters for TGA Profiles of BMAN Resins

System	Allylation degree (%)	T_{onset} (°C)	$T_{0.05}$ (°C)	Residual mass at 800°C (%)
BMAN324	32.4	368.8	375	55.0
BMAN515	51.5	405.5	395.2	44.3
BMAN656	65.6	407.8	400.6	38.5
BMAN846	84.6	411.5	406.5	37.7
BMAN1146	114.6	422.3	416.1	36.1

BMAN324 resin possesses relative high proportion of aromatic structure in cured resin, which has better thermal stability and higher char yield. This characteristic of BMAN324 imparts the cured resin higher char yield at 800°C and relative slow decomposition rate.

CONCLUSIONS

Allyl-functional and BMI-modified novolac (BMAN) resins with different allylation degree were prepared and characterized. The effect of allylation degree on processing properties, cure characteristics, and thermal stability were studied. With increase in allylation degree, viscosity and gel time of the BMAN resins decrease in turn, indicating they can be tuned by changing the allylation degree of AN resin. The cure peak of prepolymer between AN resin and BMI tends to shift to lower temperature with increase in allylation degree of resin, indicating the BMAN resins with higher allylation possess better cure reactivity. As allylation degree increased, thermal stability of cured resins showed an enhancing trend because of increase in crosslinking density, but char yield of the above resins at 800°C decrease in turn. These conclusions revealed that the properties of BMAN resins can be tailored and it must be useful to direct design of materials.

Figure 7 TGA profiles of cured BMAN resins.

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