Properties and curing behavior of reactive blended allyl novolak with bismaleimide using dicumyl peroxide as a novel curing agent

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ABSTRACT: For reducing the cure temperature and improving the thermal stability and mechanical properties, a thermosetting resin system composed of novolak and bismaleimide (BMI) was developed by reactive blending and using dicumyl peroxide (DCP) as a novel curing agent. Novolak was allylated and reacted with BMI to produce bismaleimide allylated novolak (BAN), and the effect of DCP on flexural, impact and heat distortion temperature of cured resin were investigated. On the basis of improved mechanical and thermal properties at 0.5% DCP contents, the curing behavior of DCP/BAN resin system was evaluated by DSC analysis. Ene, Diels-Alder, homo-polymerization and alternating copolymerization which occurred in DCP/BAN resin system were further verified using FTIR at sequential cure conditions from 140 to 200°C. Kissinger and Ozawa-Flynn-wall methods were used to optimize the process and curing reactions of DCP/BAN resin system. The results showed that the addition of 0.5% DCP in BAN reduced the curing temperature and time of the modified resin. For evaluating process ability of the modified system, composite samples using polyvinyl acetyl fiber were molded and tested for flexural properties. The resulting samples showed better flexural properties when compared with the composite made with neat BAN. The modified 0.5% DCP/BAN resin system with good mechanical properties and manufacturability can be used for making bulk molding compounds and fiber reinforced composites required in various commercial and aerospace applications. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41829.

INTRODUCTION

Solid novolak is a versatile and stable type of phenolic resin that cures with a latent source of formaldehyde (hexa) or heat reactive conditions. Phenolic resins are preferred for aircraft interiors due to the extraordinary fire, smoke, and toxicity characteristics. Due to their excellent ablative properties, they are also used to manufacture carbon–carbon composites, rocket nozzles and heat shields.[1–6] However, the major shortcoming is the evolution of volatiles during high temperature curing, which necessitates application of expensive processing equipment like autoclave, hydroclave, or hot press.[7–10] Keeping in view of this problem, a new chemistry is needed to modify the cure of phenolic resin without production of volatiles. The concept of addition curing is gaining popularity among the people working on modification of phenolic resin. Addition curable phenolic resins with improved thermo-oxidative properties will be desirable in many aerospace applications.[11–13] Furthermore, these addition curable phenolics are relatively catalyst free.

A strategy to solve the above problems is the reactive blending of structurally modified phenolic resin with a functional

reactant.[7,14] Structurally modified allyl ether type phenolic, synthesized by the allylation of novolak, minimizes the problem of evaluation of volatiles upon curing.[15,16] However achieving complete allyl cure is difficult, requiring prolonged heating (nearly 6 h) at 250°C, which degrades other fragile groups in the network.[17] For reducing the cure temperature and improving the thermal stability of allyl phenolic, bismaleimide (BMI) is a novel choice due to its tremendous flexible molecular design, versatile performance and good thermal and mechanical properties.[18,19]

BMI resin is a new generation of thermosetting matrices for structural composite applications. It has many excellent properties such as high thermal stability, great mechanical properties and good radiation, moisture and corrosion resistance. In addition, BMI is similar to typical epoxies in terms of workability and moldability. However, the high curing temperature makes it difficult to manufacture BMI matrix composites using common bagging and autoclaving process.[20] BMI-modified allyl-functional novolak resin is expected to maintain the mechanical properties of phenolic and improve the heat resistance as well

as the resin molding process when mixed in optimum ratio and cured under required cure schedule.[21–23] BMI concentration lower than stoichiometry leads to a very low number of cross-links in the system. Conversely an excess of allyl novolak leads to more chances of Ene homo-polymerization resulting in more linear structures than does the Diels-Alder cyclo-adduct.[7] In this case, the viscosity is lower, which is desirable for molding compounds, but the resin system has inferior thermal properties after curing. A stoichiometric excess of BMI could lead to increased cross-linking reactions resulting in a more rigid and brittle matrix. Ideally, a molar ratio 1 : 3 gives a maximum crosslink density and enhanced thermal stability. In most cases, a compromise of various properties is achieved at a ratio of 1 : 1.[15] Limited data is available on reactive blending of allyl novolak with BMI. In the current research, reactive blending of these two components in the presence of a free-radical initiator has been studied which is novel for resin formulators. This method would enable creation of resin with good curing performance and could possibly broaden the application range of novolak resin. Dicumyl peroxide (DCP, C_6H_5C $(CH_3)_2$ OOC $(CH_3)_2$ C_6H_5) was selected as a novel curing agent for improving the curing process of allyl novolak and BMI reactive blend, hereafter called as bismaleimide allylated novolak (BAN). DCP is a strong free-radical source and is used as a polymerizing initiator, catalyst, vulcanizing agent and flame retardant for alkyl aromatic resins.[24–28] It is a special purpose high temperature initiator for the curing of unsaturated polyester, vinyl ester and acrylic thermosetting resins in the temperature range of $100-140°C$. Its thermal instability and reactivity is due to the peroxy group ($-O-O-$). The effect of DCP contents on the mechanical and thermal properties of BAN has been investigated and optimized the weight percentage on the basis of mechanical properties. The curing behavior of optimized DCP/BAN was evaluated by differential scanning calorimetry (DSC). The methods of Kissinger and Ozawa-Flynn-wall were used to investigate the process and mechanism of curing reaction. At last, a complementary study on molding composite materials based on the modified resin system and polyvinyl acetal fiber (PVA) was also performed and improvement in flexural strength was discussed in line with the fractured morphology.

EXPERIMENTAL

Materials

Phenol (99+ %) was purchased from Fuchen Chemical (Tianjin, China). Allyl chloride and DCP [having active peroxide (PO) content of 40% and specific gravity of 1.53 g/cm^3 at 23°C] was supplied by Sinopharm Chemical Reagent. Paraformaldehyde was obtained from the hongyan Chemical (Tianjin, China). 4,4′-Bismaleimide biphenyl methane (BMI) was purchased from the Fengguang Chemical (Hubei, China). Acetone, oxalic acid, magnesium oxide, zinc oxide, zinc stearate and pulvistalci were obtained from Shanghai Reagent (Shanghai, China). All chemicals were used as received.

Synthesis of BAN Resin

At first, novolak resin was prepared by a typical condensation polymerization of paraformaldehyde and excess phenol (molar ratio of phenol to paraformaldehyde was 1 : 0.8) using oxalic
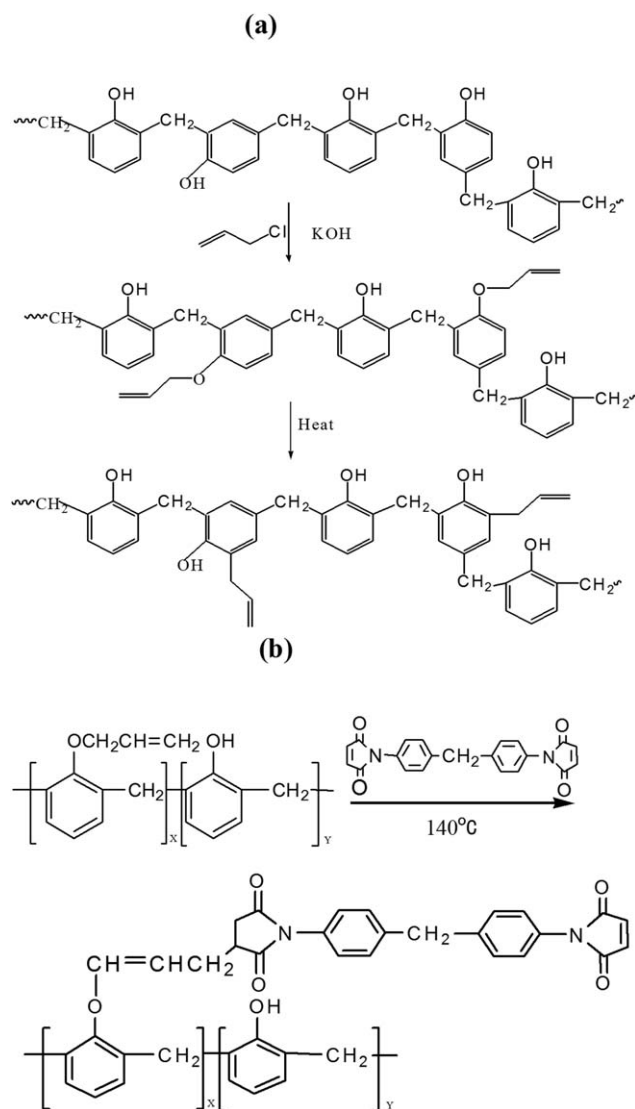

Figure 1. Schematic of synthesis: (a) AEN and (b) BAN.

acid as a catalyst. Allyl novolak was synthesized through Williamson reaction between allyl chloride and novolak in the presence of a base catalyst.[15] Novolak was dissolved in butanol and reacted with allylchloride for 6 h in the presence of KOH as catalyst to obtain allylated novolak resin (AEN). The degree of allylation of the phenol groups in the resin was 90%. Prepolymerization of AEN and BMI was carried out at 140°C for about 30 min to obtain BAN resin. BAN resin with proper prepolymerization degree is a clear, homogeneous and reddish brown resin, which can easily be dissolved in commonly known low toxic solvents like acetone and tetrahydrofuran, which makes them suitable for prepreg preparation. To improve mechanical and thermal properties at lower curing temperature, a molar ratio of 1 : 1 of allyl to maleimide group was chosen. The schematic is illustrated in Figure 1.

Curing of the BAN Resin

The BAN resin was blended with different amounts of DCP ranging from 0.2 to 0.7 wt %, and then slowly stirred at 110°C for 30 min to obtain a homogeneous blend. The blend was
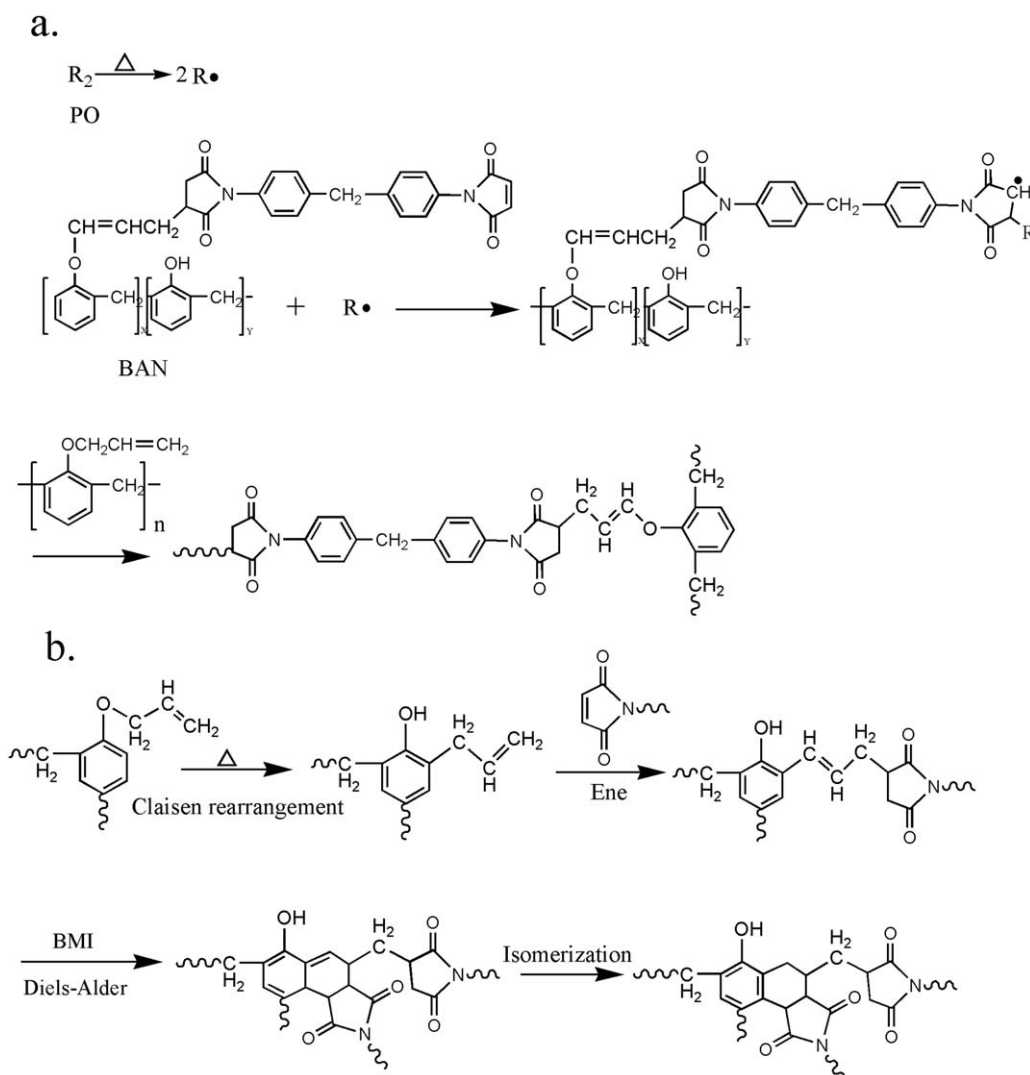
Figure 2. Proposed curing mechanism for the BMI-modified novolak resin.

poured into a rectangle mold and degassed in a vacuum oven at 125°C for 0.5 h. Then the resin was thermally cured in an electric oven according to curing cycle of 140°C/2 h + 160°C/2 h + 180°C/2 h + 200°C/2 h, and a post-curing at 220°C for 2 h to attain a complete cure and to release internal stresses produced during curing.

Preparation of Composites

Polyvinyl acetal (PVA) fibers (14 micron diameter, 260 MPa strength, 35GPa modulus, 6–15 mm length) were used to make composite using a hot press. The molding compound was prepared by a wet process. Acetone was used as the distribution medium for the resin to be adhered to the fibers. About 30–35% by weight of fibers were added in 0.5DCP/BAN resin system containing lubricant and inorganic fillers and mixed vigorously to homogeneously impregnate all the fibers. Then the prepreg was torn and loosen by hand and placed on a flat surface at room temperature for 3–5 days. After, the prepreg was dried at 50°C for 3 h in an air circulating drying oven, the pregreg was molded at 160°C using a hot press at a pressure of 30 MPa for 20 minutes. After de-molding of the samples, a post cure heat treat-

ment was performed to attain complete cure and to release internal stress produced upon high pressure processing. The post-curing process was 140°C/2 h + 160°C/2 h + 180°C/2 h + 200°C/2 h. For comparative analysis, composite specimens were also fabricated using the neat BAN resin and the same curing cycle.

Characterization

Thermo gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris1 thermo gravimeter in inert atmosphere from 25°C to 900°C at a heating rate of 20°C/min. Ca. 10 mg of sample was placed in a platinum crucible and a nitrogen flow rate over it was adjusted to 100 mL/min.

Fourier Transfer Infra-Red (FTIR) was used to quantify the extent of succinimide formation and to identify the cross-linking process. Spectra were recorded in the transmission mode on a WQF-310 FTIR spectrometer supplied by the Optical Instrument Factory (Beijing, China). The samples were prepared using KBr with a sample to KBr ratio of 1 : 100.

Differential scanning calorimetry (DSC) analysis, used to monitor the curing process, was performed on a MDSC2910 thermal

analysis system supplied by the TA Co. (USA). The scanning range was from 25 to 400°C with different heating rates of 5°C/min, 10°C/min, and 15°C/min under nitrogen atmosphere and a dynamic mode.

Scanning electron microscope (SEM, SM-6700F) was employed to examine the morphologies of the fracture surfaces of the samples of cure resin. The specimen surface was coated with a thin conductive layer of gold using a plasma vapor deposition technique in a fine coat ion sputterer JFC-1100.

The flexural strength of composite specimen was studied using the SANS CMT 5105 (100KN) mechanical testing machine. The vertical moving speed of the crosshead was set at 2 mm/min (corresponding to a strain rate of $8.3 \times 10^{-3}s^{-1}$) with the load and displacement being recorded. Based on ASTM D 790, the specimens were cut to a size of $4 \times 10 \times 70$ mm (±0.2 mm variation). The specimens were washed and dried in a drying oven at 110°C for 120 min before the tests. Five samples were tested in each experiment and the average value was reported.

Gel time was determined by means of a home-made apparatus according to Chinese standard of GB 7193.1–1987 (Corresponding to ASTM 2471-71). Water absorption was recorded by immersing the specimens in water for 24 h, and measured according to the standards GB/T 1033.1–2008. The viscosity was determined on an NDJ-79 viscometer. The measurement of composite density, impact strength, flexural strength and modulus, and HDT were determined according to GB/T 1033.1–2008, GB/T 451–2005, GB/T 1449–2005, and GB/T 1634.2–2004, respectively.

RESULTS AND DISCUSSION

Reaction Mechanism

The multitudes of reactions in the curing process of BAN were mainly Ene-reaction, Diels-Alder reaction, homo-polymerization, and alternating copolymerization.[29,30] The reaction between ally phenyl and maleimide ensued via the Ene-reaction was studied by Enoki et al.[31] Reyx et al.[32] investigated the curing process through reaction of model compounds and gave a strong support to the Enoki mechanism. It was difficult to achieve complete allyl curing and a high temperature (250°C) could lead to thermal instability of the resultant resin. Therefore, a curing agent was needed to accelerate the curing of modified resin at a lower temperature. According to the reaction mechanism, a PO like DCP was selected as a free-radical initiator to add into the modified resin. The reaction sequence involved in the curing process is shown in Figure 2. DCP can be a popular choice because of its favorable decomposition rate and generation of reactive free radicals at normal processing temperatures. The reactive free radicals attacked C=C bonds of the BAN resin system. Therefore, the unreacted BMI and unsaturated maleimide groups in BAN resin reacted with allyl group of AEN resin through diene addition. In addition, the Claisen rearrangement of allyl ether into 2-allyl phenol occurred at a higher temperature. The final network formed was through the Diels-Alder reaction.

Effect of DCP on Mechanical Properties

Figure 3 shows the impact and flexural strengths of BAN with different amounts of curing initiator. As expected, the mechanical properties of the BAN were markedly affected by the content
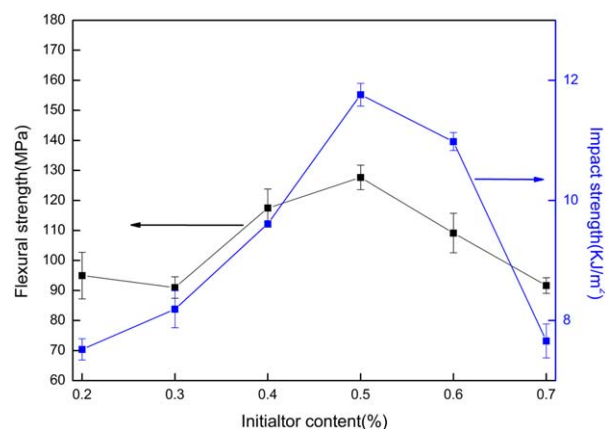

Figure 3. Impact and flexural strength of BAN resin with different DCP contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of initiator. The impact and flexural strengths first rose and then fell down, when the amount of DCP was varied from 0.2 to 0.7 wt %. The maximum values were obtained at 0.5 wt %. Generally, the strength of polymeric materials is related to the backbone of molecular chain. Moderate crosslinking and hetero-cyclic groups also improve the strength to a greater extent. A suitable amount of curing initiator lowered the curing temperature of BAN and resulted in a higher strength and thermal stability. When the DCP content was lower than 0.5 wt %, it produced fewer reactive radicals insufficient for a complete curing reaction. When the contents were more than 0.5 wt %, the amount of reactive radicals increased resulting in more reactive sites. The chances of collision of active radicals with each other increased resulting in a decreased of overall activity. As a result, the curing rate and the mechanical properties of BAN decreased. The influence of different amount of curing initiator on BAN can be evaluated by the change of fracture morphology. Photographs of the impact fracture of 0.2−0.7 wt % DCP contents are shown in Figure 4. It can be seen that the fracture surfaces of all specimen were smooth and flat indicating a typical brittle fracture with crack propagated uninterrupted. However, when DCP content was 0.7% there were many particulates in fractured surfaces. Due to higher DCP content, the concentration of free radicals was too large which caused the curing reaction to proceed very fast. In fact, in the present work, it can be concluded that a maximum improvement in impact strength and flexural strength was achieved with 0.5 wt % DCP.

Table I shows the properties of BAN with different DCP contents. It can be seen that at 0.5 wt % DCP contents, the flexural strength (127.7 MPa), modulus (4.59 GPa) and HDT (295°C) are higher than that (122.4MPa, 3.53GPa and 273°C respectively) of the resin cured and 250°C and developed by Yan et al.[15] For amorphous polymers in general, and thus for thermosets, one can consider that the glass transition temperature, T_g, is related HDT (usually, HDT is 10–15°C is below T_g).[33] Therefore, the T_g of the 0.5DCP/BAN was in the range of 305–310°C.

Thermal Stability Analysis

The thermal stability of the 0.5DCP/BAN resin was compared with the neat BAN by TGA under a nitrogen atmosphere
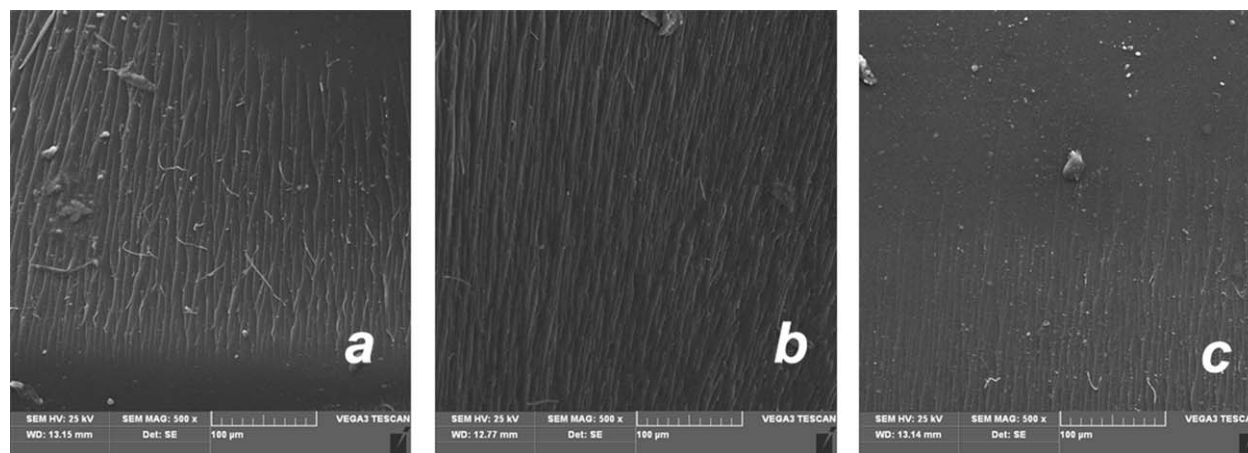
Figure 4.   SEM images of fracture surface of cured resin with different DCP contents; (a) 0.2%, (b) 0.5%, and (c) 0.7%

and dynamic heating conditions. For reference, the TGA curve for novolak resin has also been plotted with the modified system in Figure 5. There was only one stage of mass loss in the process. In both the cases, the mass loss occurred at above 400°C, which was due to the decomposition of the polymer network. DCP contents did not alter the degradation initiation temperature (Ti). It can be seen that 5% mass loss temperature ($T_{0.05}$), in both the cases, was higher than 400°C, indicating that the cured BAN possessed excellent thermal stability. This made the resin best suited as a matrix of heat-resistant composites. After 600°C, the mass loss rate of 0.5DCP/BAN decreased as compared with neat BAN. It was obvious that the DCP in the BAN affected the mass loss rate.

Furthermore, comparing the char yield of the neat BAN with 0.5DCP/BAN resin at 800°C, the char yield increased from 35% to 40%, which is expected since 0.5DCP/BAN resin showed better heat stability because of higher crosslink density. For BAN resins, the contribution of self-polymerization of allyl groups decreased with the incorporation of PO free-radical initiator. Aliphatic crosslinking network from self-polymerization of allyl groups was thermally fragile. When temperature was high enough, the aliphatic structure decomposed rapidly, resulting in an obvious mass loss. Compared with the neat BAN, 0.5DCP/BAN possessed relatively a higher proportion of aromatic structure in the cured resin resulting in a relatively slow decomposition rate and higher char yield.

Table II summarizes the mass loss rate of cured novolak, neat BAN and 0.5DCP/BAN resins at 400°C, 700°C, and 800°C. The residual weight at 700°C was 51.5 wt % which is similar to the resin developed by Lu[29] and Yan et al.[15] This behavior was characteristics of crosslink density of cured BAN resin. As appropriate amount of DCP was added in the BAN resin, there were more cross-linked networks of cured resin derived from polymerization of allyl and maleimide groups. This led to a high mass residue at 800°C. The active radicals provided by DCP improved the crosslink density and hence improved the thermal stability of the 0.5DCP/BAN resin. TGA weight loss curve of the cured novolak showed a typical and steady weight loss throughout the heating resulting from the loss of water and/or solvents at low temperatures, followed by water loss from the condensation reaction to form the cured resin. The lower molecular weight components of the polymer degrade before the higher molecular weight polymer components. As a result the degradation occurred over a broad temperature range, forming two major plateaus between 200−350°C and 550−800°C.

Gel Time and DSC Analysis

Figure 6 shows the non-isothermal DSC curves of 0.5DCP/BAN resin along with the neat BAN resin taken for 1 : 1 stoichiometry. As compared with the neat BAN resin, the 0.5DCP/BAN resin showed two sharp exotherms in the temperature ranges 130−180°C and 230−280°C, respectively. The peak temperatures for the two exotherms were 166.07°C and 257.15°C. Similar behavior has been reported in the literature.[7,34]
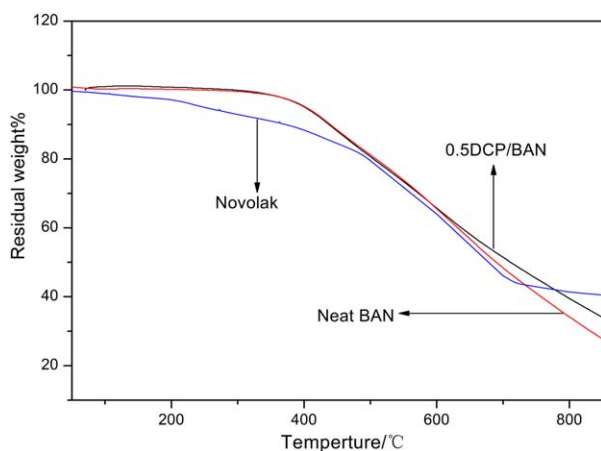
Table I. Properties of BAN with Different DCP Contents

DCP (wt %)	Density (g cm^{-3})	Water absorption (wt %)	Impact strength (kJ·m^{-2})	Flexural strength (MPa)	Flexural modulus (GPa)	HDT (°C)
0.2	1.24	0.32	7.52	94.98	4.34	291
0.3	1.31	0.27	8.19	91.32	4.25	302
0.4	1.27	0.33	9.61	117.44	4.74	287
0.5	1.25	0.20	11.76	127.66	4.59	295
0.6	1.38	0.21	10.98	109.15	4.12	294
0.7	1.33	0.28	7.66	91.64	4.27	298

Figure 5. TGA thermograms of nonolak, neat BAN and 0.5DCP/BAN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
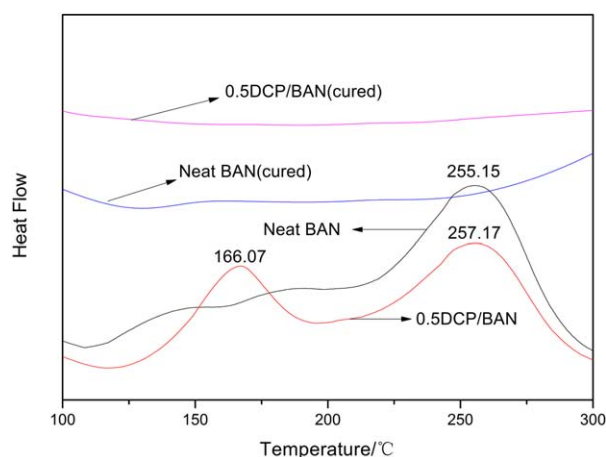

Figure 6. DSC curves of neat BAN and 0.5DCP/BAN resin systems before and after curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The mechanism of curing reaction based on model compound studies is very popular and hence the cure mechanism proposed for N-phenyl maleimide and 2-allyl phenol was extrapolated to the 0.5DCP/BAN resin system. The first exotherm (130−180°C) was assigned to the Ene-reaction between maleimide and allyl groups forming trans-Ene-adducts at 166.07°C. This transient intermediate was consumed by Diels-Alder (via an intermediate Wagner-Jauregg reaction step) reaction at 257.15°C to form tri-adduct. At still higher temperatures the copolymerization occurred to form highly cross-linked structure.[7] The neat BAN showed a sharp peak at 255.15°C. The active radicals produced by DCP promoted the reaction of the reactive groups and led to complete Ene-reaction and initiation of copolymerization below 200°C. For thermosetting resins, the low cure temperature was much more favorable for the cure process. Therefore, 0.5DCP/BAN resin can present better manufacturability of the composite system as compared with the neat BAN resin.

DSC scans of the neat BAN and 0.5DCP/BAN resin systems already cured at 200°C/2h, and a post cured at 220°C/2h are also shown in Figure 6. The neat BAN resin further showed an exotherm above 250°C showing that the neat resin was not fully cured. The partially cured BAN undergone further Diels-Alder reactions of phenyl and allyl groups. The 0.5DCP/BAN system showed no appreciable exotherms confirming the complete curing of the resin.

Gel time testing, reflecting the reactivity of the resin system, was performed to further evaluate the cure behavior of neat BAN and 0.5DCP/BAN resins. Figure 7 shows that the

Table II. Mass Loss Rate of Neat BAN and 0.5DCP/BAN Resins at Different Temperatures

Sample	Mass loss rate		
	400°C	700°C	800°C
Novolak cured at 250°C	12.0	52.5	58.7
Neat BAN	4.7	51.6	62.1
0.5% DCP/BAN	4.8	48.5	60.5

0.5DCP/BAN resin system took only 6 min to cure, while the cure time for neat BAN was 98 min at the same temperature of 150°C. DCP strongly influenced the gel time of BAN resin, which was almost independent of the system temperature. As shown in Figure 8, the viscosity decreased rapidly as the temperature increased in the range of 70–160°C. When heated above 150°C, the viscosity increased rapidly due to the formation of crosslinking network. A resin could be processed by resin transfer molding (RTM) when its viscosity is below 0.3 Pa-s. The viscosity was below 0.3 Pa-s at 100–150°C. In this temperature zone, the resin system is suitable for the RTM process. At temperatures below 75°C, the viscosity of the resin exceeded 1.0 Pa-s. For comparison with 0.5DCP/BAN, viscosity of neat BAN is also shown in Figure 8. Pre-polymerization degree of the BAN resin could be controlled by reaction condition. The BAN resin with proper pre-polymerization degree was a homogeneous resin system soluble in acetone without precipitation of BMI. The viscosity of BAN resins depend on the degree of allylation, showing an inverse relation. The degree of allylation in the neat BAN was 90% and a higher degree
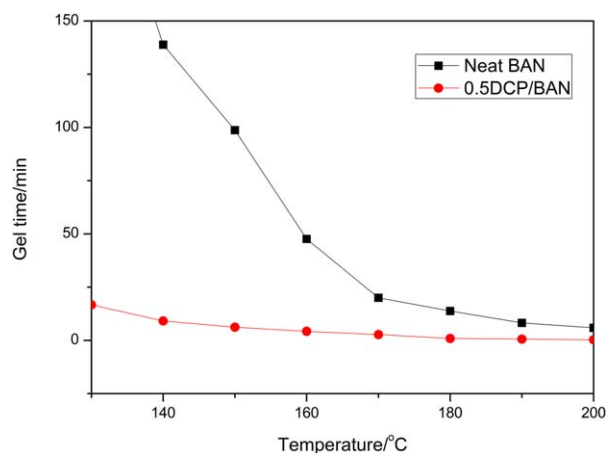

Figure 7. Gel time-temperature curves of neat BAN and 0.5DCP/BAN resin systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
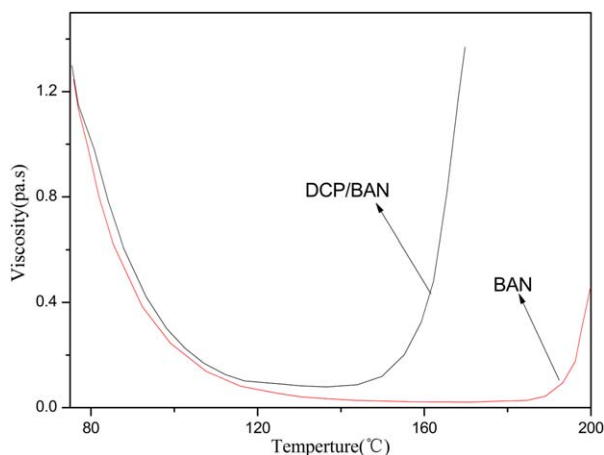
Figure 8. Viscosity-temperature curves of BAN and the 0.5DCP/BAN resin system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

promoted etherification of hydroxyl groups of novolac. This imparted more softness to molecular chains of novolac and hence lower viscosity. Moreover the viscosity temperature curve showed that the lower viscosity of BAN could be maintained for a longer time as compared to BAN/DCP.

Curing Behavior of 0.5DCP/BAN Resin

Curing Process. The parameters of curing process included curing temperature, curing time and the cooling rate. Generally, curing temperature can be determined using T-β extrapolation.[19] Figure 9 shows the DSC exotherms of 0.5DCP/BAN at different scanning rates β (5°C/min, 10°C/min and 15°C/min). Each DSC curve had two sharp peaks labelled as peak 1 and peak 2. With the increase in heating rate, the initial reaction temperature (T_i), peak temperature (T_p) and final temperature (T_f) shifted to higher temperatures. The curing time and temperature range became shorter and wider respectively. This was due to the greater thermal effects generated per unit time (dH/dt) with the rise in scanning rate. In other words, greater heat flow per unit time generated more thermal inertia and temperature differential moved reaction peaks toward higher temperatures. Table III shows the temperatures of different curing peaks at different scanning rates.

To eliminate the effect of heating rate on curing reaction temperature, T-β extrapolation was selected and the fitting curves are shown in Figure 10. Gel temperature ($G_{el} = 119.8$°C), curing temperature ($T_{cure} = 148$°C) and post-treatment temperature ($T_{treat} = 160$°C) of peak 1 were derived from the slope of T versus β plot when the value of β was zero.

Similarly, G_{el}, T_{cure}, and T_{treat} of peak 2 came out to be 193°C, 226°C, and 263°C respectively. Therefore, curing cycle was optimized as 140°C/2 h + 160°C/2 h + 180°C/2 h + 200°C/2 h. Curing at 220°C/2 h served as post-curing cycle to attain a complete cure and to release internal stresses produced during curing. The cure temperature and time of 0.5DCP/BAN resin proved to be lower and shorter respectively than that of the neat BAN.

FTIR Analysis

To verify the curing mechanism and extent of Ene-reaction in BMI and allyl groups, FTIR spectra of 0.5DCP/BAN resin was obtained at sequential cure conditions from 140 to 200°C. Figure 11 shows typical FTIR spectra of the modified BMI resin as a function of cure conditions.

IR bands at 690 cm^{-1} and 823 cm^{-1} were assigned to the maleimide C═C─H bonds,[35] the peak characteristic of the allyl double bonds was located at 916 cm^{-1},[36] the absorbance band at 1180 cm^{-1} corresponded to C─N─C succinimide,[37] appearance of a broad O─H band toward 3000–3800 cm^{-1} and the wide band at 3436 cm^{-1} was correspondent to the stretching vibration of C─OH meaning that the novolak hydroxyl groups were generated during the course of curing cycle.[38] It can be seen that both of the peaks at 690 cm^{-1} and 823 cm^{-1} were found to decrease with reaction time, thus confirming the gradual disappearance of maleimide double bonds. Moreover, at the same time, allyl double bond located at 916 cm^{-1} was also consumed indicating that the Ene-reaction between maleimide and allyl double C═C bonds completed after 2 h at 200°C. The absorbance peak at 1180 cm^{-1} assigned to the succinimide was found to increase as the curing temperature was increased showing the cross-linking reaction. As the curing schedule proceeded, the absorbance band associated with C─OH increased from stage (a) to stage (c), while the absorbance intensity of stage (e) showed a strong decrease in comparison with the spectra of stage (c). Claisen rearrangement mechanism showed that allyl phenyl ether changed to an ortho-substituted phenol leading to an increase of novolak hydroxyl just as the increase of absorbance peak shown in Figure 11. From the stage (d) onwards, 3436 cm^{-1} peak showed a strong decrease which was caused by the ether crosslinking reaction via hydroxyl dehydration reaction. Further post-curing at high temperature may lead to a further increase in ether crosslinks, however, the higher curing temperature may also make the ether crosslinks become unstable as described in the article. Therefore, it was confirmed
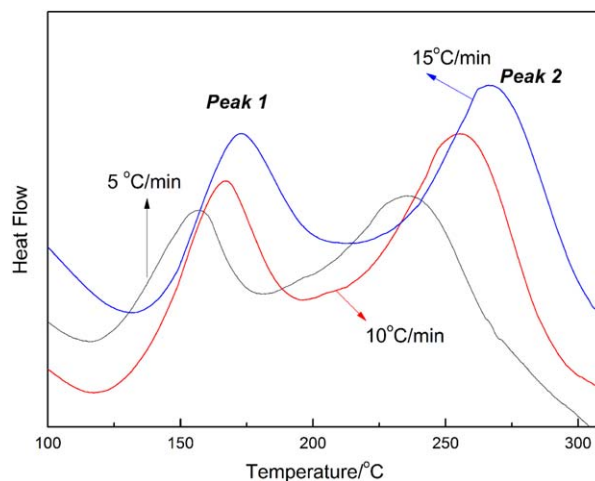

Figure 9. DSC curves for 0.5DCP/BAN resin at different scanning rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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Table III. DSC Data at Different Scanning Rates

Scan rate (°C/min)	Peak 1			Peak 2		
	T_i	T_p	T_f	T_i	T_p	T_f
5	127.85	155.43	173.82	206.86	239.58	276.66
10	138.40	166.07	195.38	223.33	257.17	297.78
15	145.21	171.78	204.94	236.18	267.95	307.80

that the curing cycle proposed according to the DSC analysis was reasonable.

Curing Kinetics Analysis

The investigation of cure kinetics of a new resin is an important subject for the development and optimization of the curing cycles used in the manufacturing of composite materials. Generally cure kinetics of resin systems are studied using non-isothermal and iso-thermal methods. The non-isothermal single heating rate method measures the curing process at a constant heating rate, while the multi heating rate method is suitable for systems with multiple reactions like the BAN. The two kinetic analysis models are extensively used to understand and predict the cure behavior of the resin systems.[39] The basic assumption for the application of DSC technique to the cure of the thermosetting resins is that the rate of kinetic process is proportional to the measured heat flow. Analysis of cure kinetics of 0.5DCP/BAN resin was necessary for the optimization and determination of the curing condition and thereby for the achievement of high performance thermosetting materials. Kissinger and Ozawa-Flynn-wall methods were used to analyze the non-isothermal curing kinetics, since the kinetic parameters like E_a and A could be simply obtained from Kissinger's and Ozawa-Flynn-wall's equations without any assumption about the equations related to reaction conversion. Activation energy is a function of degree of cure which changes with gel, glass transition temperature and reaction mechanism. Therefore, relationship of apparent activation energy and degree of cure was investigated through the method of Ozawa-Flynn-wall which eliminates the selection process of reaction models, reduce the workload of experiments and accurately describe the actual process of the reaction.

The rate constant is $K(T)$ is dependent on temperature and assumed to follow an Arrhenius equation:

$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

where E_a is the activation energy, R is the gas constant (8.314 J/mol/K), T is the absolute temperature and A is the pre-exponential factor (frequency factor). The kinetic parameters of the curing reaction, with special reference to E_a can be calculated using different computational techniques.[40–42] In case of Kissinger method, E_a was obtained by the iso-conversional methods using the logarithmic form of the kinetic equation from the slope of the plot of $ln(\beta/T_p^2)$ versus $1/T_p$ as follows:[43]

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_a} - \frac{E_a}{RT_p} \qquad (2)$$

where β is the heating rate, α is the degree of cure and T_p is the peak curing temperature. Ozawa and Kissinger methods relate E_a and heating rate and the peak exotherm temperature with the assumption that the extent of the reaction at the exotherm peak is constant and independent of the heating rate.[44] Having evaluated the value of E_a, the Crane method gives a relationship between β and the reaction order n and is expressed as follows:[45]

$$\frac{d(\ln\beta)}{d(1/T_p)} = -\left(\frac{E_a}{nR} + 2T_p\right) \qquad (3)$$

As long as the E_a/nRT_p is much greater than 2, the n can be derived from the slope of the plot of $ln\beta$ versus $1/T_p$. Furthermore, E_a derived from Ozawa-Flynn-wall method can also be
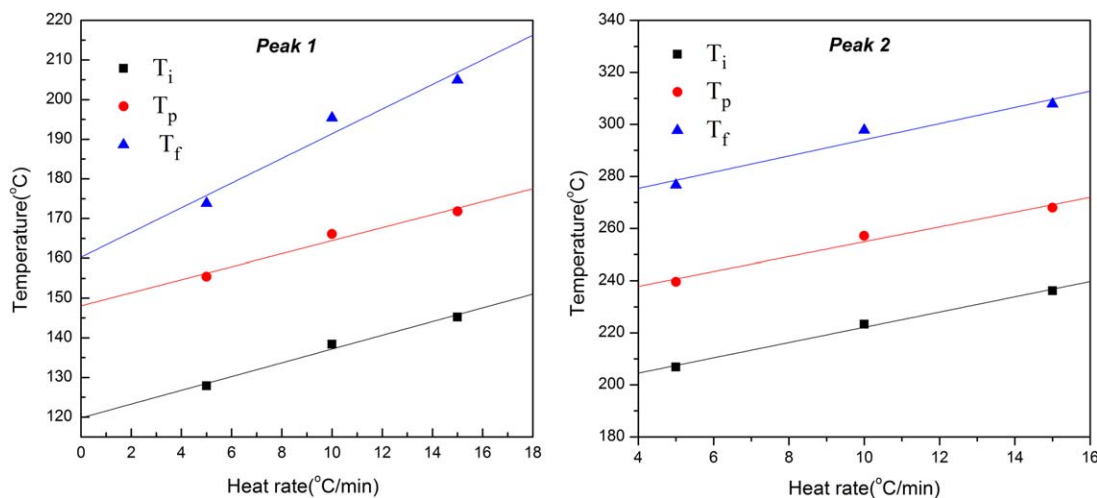

Figure 10. The plots of T versus β. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
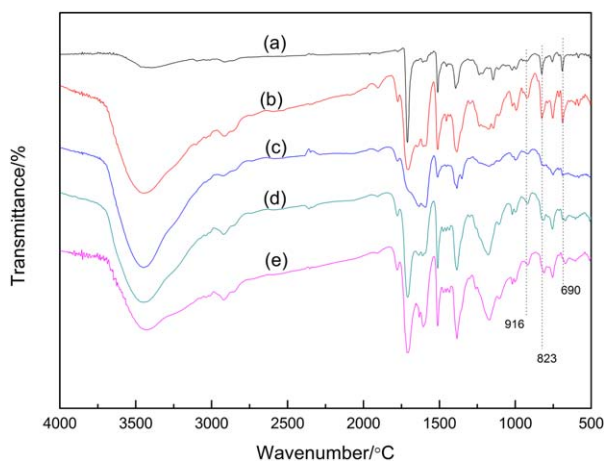
Figure 11. FTIR spectra of 0.5DCP/BAN resin as a function of sequential cure conditions. (a) Prepolymer; (b), (c), (d), (e), 2 h at sequential temperature of 140, 160, 180, 200°C, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtained from the slope of the plot of $ln\beta$ versus $1/T_p$ according to the equation expressed as follows:[46]

$$\ln\beta = -1.052\frac{E_a}{RT_p} + \ln\left(\frac{AE_a}{R}\right) - 5.331 \qquad (4)$$

Figure 9 shows the DSC thermo grams of 0.5DCP/BAN resin at various scanning rates, and corresponding data is summarized in Table IV.

The E_a and n of peak can be derived from the plot of $-\ln(\beta/T_p^2)$ and $ln\beta$ versus $1/T_p$ respectively. As shown in Figure 12, the activation energy and reaction order of 0.5DCP/BAN resin system obtained by slope of the straight line came out to be 99.01 KJ/mol, 0.932 and 81.12 KJ/mol, 0.901 for peak 1 and peak 2, respectively. The percentage conversion for different heating rates as calculated from the DSC data is shown in Figure 13(a). The curves did not intersect, indicating similar cure kinetics at different heating rates. Curing temperature became higher when the heating rate was higher provided the degree of cure was unchanged. Computational results of α-T curves are plotted in Figure 13(b). Peaks shifted to a higher temperature and became more acute with the increase in heating rate. This could be attributed to the shifting of exothermic curing peak to higher temperatures because of the greater thermal effects generated per unit time. The multi heating rate technique adopted in this

study is an iso-conversional method that assumes that the E_a change with conversion.

Figure 14(a) illustrates the Ozawa plots for the curing of 0.5DCP/BAN resin at different degrees of cure. Each data point on the curve was an average of three values corresponding to three heating rates of 5, 10, and 20°C/min. The shape of the activation energy curve indicated the simplicity or complexity of the reaction. For simple processes, it is practically constant as defined by the nth order kinetics model. Simple process does not mean that it is a single step reaction. It may be a multistep process that is controlled by the rate of the slowest step as seen in the case of BAN. Activation energy, which is corresponding to the curing rate, can be obtained from the calculation of the slopes plotted against degrees of cure in Figure 14(b). The E_a curve does not reveal the reaction mechanism but provide significant information about kinetically controlled and diffusion controlled mechanisms.

It can be seen from Figure 14(b) that in the early stage, the value of E_a was higher and had relatively small fluctuation with the increase in curing rate. An increase in the activation energy means that more energy is required for the reaction components to complete the reaction in addition to the exothermic reaction indicating an acceleration effect; this phenomenon was exhibited in the case of BAN resin system.

At the start of curing reaction, addition reaction played a dominated role and the variation of E_a had very little effects on the curing reaction. Later the value of E_a had two slight decreases with the increase of degree of cure and marked as "a" and "b" on the line. At the initial stage of "a," curing reaction was difficult to occur smoothly due to presence of water in the resin, but after a short while, due to evaporation of water, the curing reaction was relatively easier to proceed as evident from the decreasing trend of activation energy. A slight rise in activation energy was due to the DCP present in the system. DCP needed more energy to form free radicals because its E_a was higher than BAN resin. Once free radicals were formed, less energy was needed for the reaction of double bonds and activation energy showed again decreasing trend as marked "b" on the curve. E_a reduced to minimum when the value of α was 55% and then started increasing afterwards as the curing reaction proceeded to final stages. The reason for this phenomenon was that the reaction of curing system was gradually hard to sustain after the resin transformed into gel state. At this stage, the system formed

Table IV. Curing Kinetic Parameters Obtained from DSC Analysis for 0.5DCP/BAN Resin

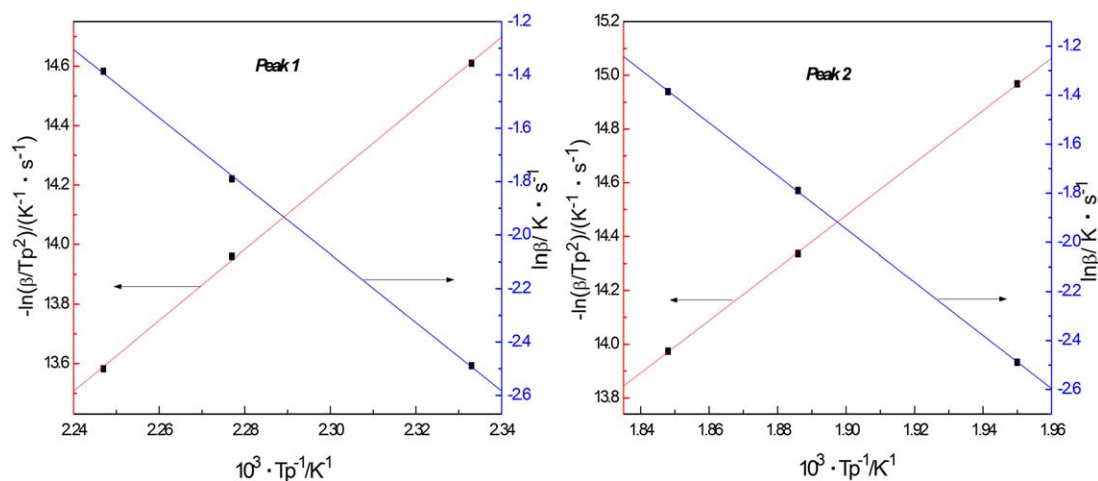| 0.5 DCP/BAN | β | | T_p (K) | $-\ln(\beta/T_p^2)$ (K^{-1} s^{-1}) | $\ln \beta$ (K·s^{-1}) | $10^3 \cdot T_p^{-1}$ (K^{-1}) |
	K/min	K/s				
Peak 1	5	0.083	428.58	14.610	−2.489	2.333
	10	0.167	439.22	13.960	−1.790	2.277
	15	0.250	444.93	13.582	−1.386	2.247
Peak 2	5	0.083	512.73	14.968	−2.489	1.950
	10	0.167	530.32	14.337	−1.790	1.886
	15	0.250	541.10	13.974	−1.386	1.848

Figure 12. Kissinger's plots for the 0.5DCP/BAN curing system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

three-dimensional network with a rise in relative molecular mass. When the relative molecular mass become infinite, it was more difficult to maintain the balance of concentration among the functional groups and to keep the collision frequency at the required level. As a result, the concentration of activated macromolecule gradually reduced. All of this led to the cease of intermolecular motion and therefore E_a gradually increased. During curing process, Ene-reaction followed by a Diels-Alder reaction at a higher temperature with the formation of succinimide by the conversion of maleimide moieties occurred resulting in a steady increase in E_a. This cure kinetics of the resin system approached the model-free kinetic model. The difference in the activation energy between Ozawa and Kissinger models was constant and within the acceptable limits of the two models.

The kinetic studies were considered to be appropriate because the value of E_a calculated by the methods of Kissinger and Ozawa-Flynn-wall were very close. But it must be pointed out that the curing reaction of thermosetting resins is a very complex process and non-homogeneous system of solid and liquid.

It was chemical reaction controlled before gelation and diffusion controlled afterwards. Therefore, it still needs to modify the current kinetic equation if the kinetic parameters of curing system need to be calculated accurately. As the two methods of dynamics were linear regressions and had very good linear correlations, both were considered to be suitable for solid-phase reaction system of DCP/BAN.

Properties of Composite

Table V shows the flexural properties of PVA fiber composites using neat BAN and 0.5DCP/BAN resin systems. Flexural tests were performed to evaluate the efficiency of the modified resin system. As can be seen, the flexural properties of the 0.5DCP/BAN resin were better than that of the neat BAN resin. Flexural behavior was dominated by the matrix properties. Improving the degree of cure and cross-linked density of the matrix improved the flexural properties. It was important to highlight that direct correlation between the interfacial strength and degree of cure with the flexural properties of a composite was rather complex. Interfacial adhesion strength in a composite
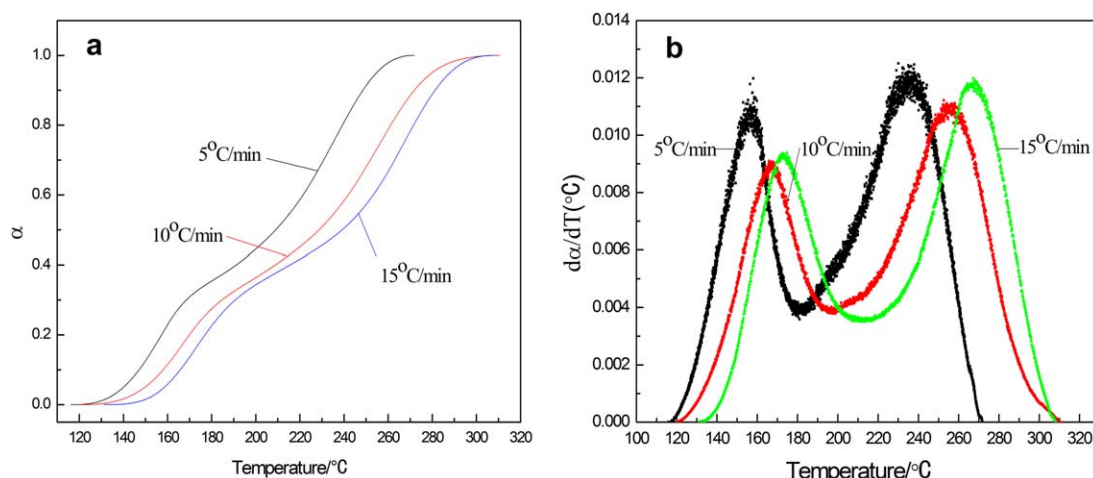

Figure 13. Relationship at different heating rates; (a) degree of cure with temperature and (b) $d\alpha/dT$ versus T. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
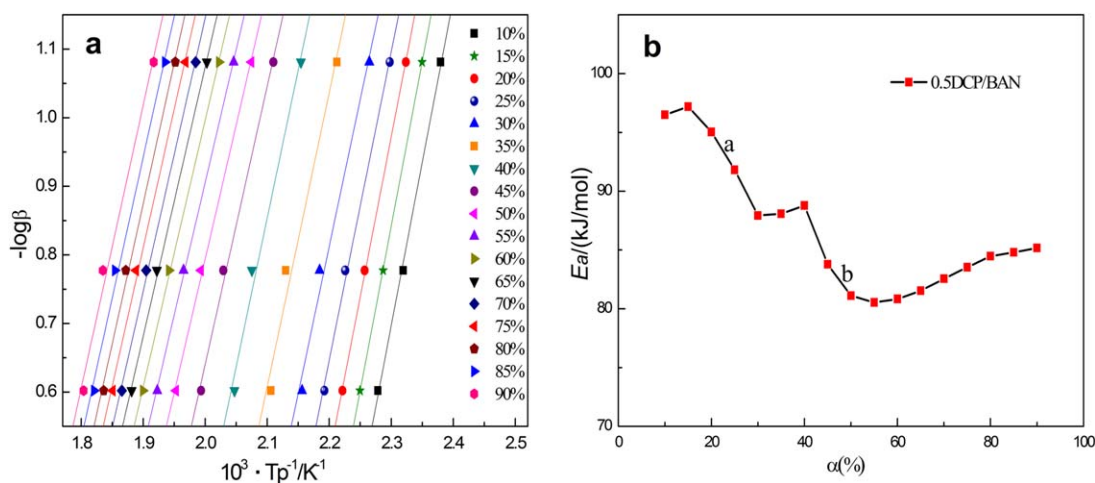
Figure 14. Activation energy; (a) Ozawa's plots for the curing of 0.5DCP/BAN at different α and (b) Correlation between E_a and α. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Flexural Properties of PVA Fiber Composites Using Neat BAN and 0.5DCP/DCP Resins

Composite system	Density (g cm^{-3})	Fiber weight fraction (%)	Flexural strength (MPa)	Flexural modulus (GPa)
0.5DCP/BAN	1.26 ± 0.01	~33	205 ± 15	7.85 ± 0.15
Neat BAN	1.25+0.01	~33	190 ± 25	7.70 ± 0.15

had a dominating effect on the flexural strength of composites but had minor effects on the flexural modulus. Degradation of fiber–matrix adhesion (due to low degree of cure) most likely resulted in the observed loss of flexural strength. Flexural strength was affected more than the modulus. It can also be noticed in Figure 15 that during crack propagation, energy absorbing mechanisms, such as crack deviation at the fiber–matrix interfaces occurred in the composite made with 0.5DCP/BAN resin. Delamination was the dominating phenomena in case of neat BAN resin. The modified resin possessed several

virtues. It had low viscosity and good adhesion between the resin matrix and the reinforced fibers. Such adhesion promoted the formation of a better interface in composite and hence achieved better mechanical properties. Due to addition of DCP, copolymerization between BMI and allyl ether novolak was a dominant process which belonged to addition-reaction class. As a result, no low molecular byproducts were generated during curing. This made the cured structure dense and defect-free as can be inferred from a higher density values for 0.5DCP/BAN resin system shown in Table V.
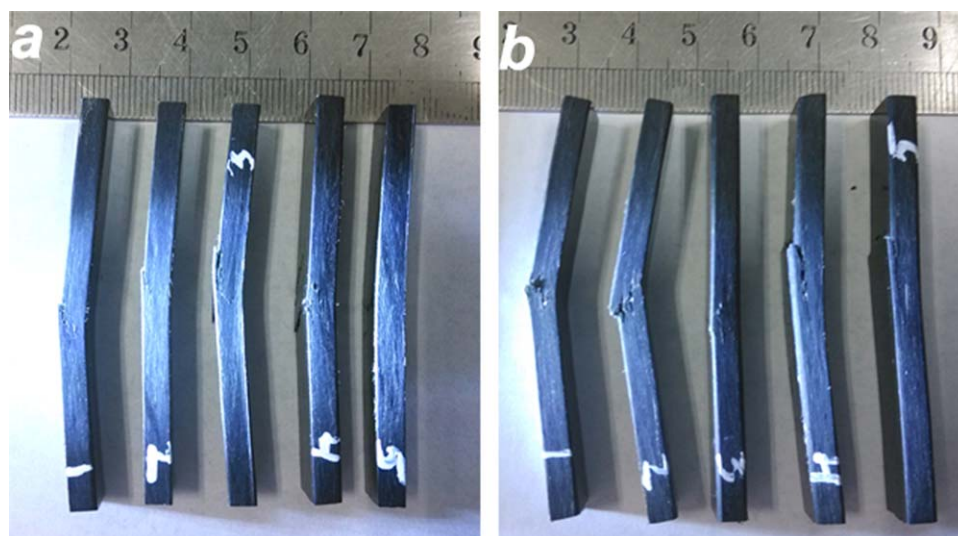

Figure 15. Macroscopic aspects of the fracture of composite; (a) with 0.5DCP/BAN and (b) with neat BAN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

With the incorporation of DCP as a novel curing initiator, BAN resin system was developed using allylated novolak and BMI. A remarkable improvement over the long-scolded curing process of modified BAN resin was achieved. The effect of DCP on flexural, impact and HDT of cured resin were investigated. The results indicated the cured resin represents relatively excellent properties with 0.5% DCP contents. It was evident that the incorporation of DCP significantly reduced the curing temperature and time of BAN resin, and improved the thermal stability of BAN resin at high temperature ($T > 600°C$). In addition, curing reactions of the resin system were investigated by DSC analysis. Ene, Diels-Alder, homo-polymerization and alternating copolymerization which occurred in DCP/BAN resin system were verified by FTIR at sequential cure conditions from 140 to 200°C. With curing kinetics analysis, it was confirmed that the Kissinger and Ozawa-Flynn-wall methods were suitable for optimizing of curing reactions in DCP/BAN resin system. The resulting modified resin system was used to manufacture PVA fiber based molded composites. The composite showed better density and flexural properties as compared to that made with a neat BAN system. Therefore, owing to the excellent properties and good manufacturability, the resulting 0.5% DCP/BAN resin system can be used in making bulk molding compounds and various manufacturing techniques applied in composite manufacturing for commercial and aerospace fields.

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