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ScienceDirect
European Polymer Journal 43 (2007) 5084–5096
EUROPEAN POLYMER JOURNAL
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Benzoxazine–bismaleimide blends: Curing and thermal properties

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Received 15 February 2007; received in revised form 10 August 2007; accepted 19 September 2007
Available online 26 September 2007

Abstract

A blend of bisphenol A based benzoxazine (Bz-A) and a bismaleimide (2,2-bis[4(4-maleimidophenoxy) phenyl] propane (BMI), was thermally polymerised in varying proportions and their cure and thermal characteristics were investigated. The differential scanning calorimetric analysis, supplemented by rheology confirmed a lowering of the cure temperature of BMI in the blend implying catalysis of the maleimide polymerisation by benzoxazine. FTIR studies provided evidences for the H-bonding between carbonyl group of BMI and –OH group of polybenzoxazine in the cured matrix. The cured matrix manifested a dual phase behaviour in SEM and DMTA with the minor phase constituted by polybenzoxazine dispersed in an interpenetrating polymer network (IPN) of polybenzoxazine and cured BMI. The IPN possessed improved thermal stability over the constituent polybenzoxazine. A benzoxazine monomer possessing allyl functional groups, 2,2′-bis(8-allyl-3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) propane (Bz-allyl) was reactively blended with the same bismaleimide in varying stoichiometric ratios (Bz-allyl/BMI), where the curing involved mainly Alder-ene reaction between allyl- and maleimides groups and ring-opening polymerisation of benzoxazine. The rheological analysis showed the absence of catalytic polymerisation of BMI in this case. The overall processing temperature was lowered in the blend owing to the co-reaction of the two systems to form a single-phase matrix. The cured resins of both Bz-A/BMI and Bz-allyl/BMI blends exhibited better thermal stability than the respective polybenzoxazines. The T_g of the IPN was significantly improved over that of polybenzoxazine (Bz-A). However, the co-reaction resulted in a marginal decrease in the T_g of the system in comparison to the polybenzoxazine (Bz-allyl).

Keywords: Allyl polymers; Polybenzoxazine; Bismaleimide; Alder-ene reactions; IPN

1. Introduction

High temperature resistant polymers are in great demand for high-speed aircraft structures and as structural components of space vehicles. Polybenzoxazine is a novel class of phenolics and it can be used as the matrices of high performance composites because of its superior mechanical

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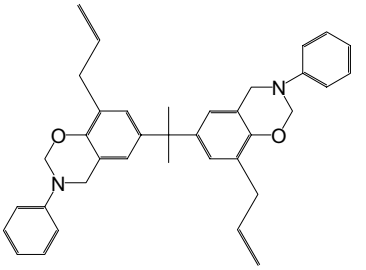
0014-3057/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2007.09.012

properties and high temperature stability. It possesses excellent processability through a wide range of molecular design flexibility [1–8]. This high performance polymer possesses high T_g, low volumetric shrinkage on curing, low moisture absorption, excellent resistance to chemicals and UV light, thermal and dimensional stability and superior electrical properties [9,10]. Although, benzoxazines possess many advantages over other state-of-the-art thermosetting resins, their brittleness, long cure time and higher cure temperature point to the need of modifications on the matrix. The polybenzoxazine properties could be improved or modified via the formation of blends, alloys, copolymers [11–15] and organic–inorganic nanocomposites [16–19]. Blending with an epoxy resin significantly improves the processability of benzoxazines resins, but the resulting binary mixtures require higher curing temperatures than the pure benzoxazine resin [20,21]. Polybenzoxazine containing furan groups showed higher curing temperature (247 °C) [7] and polybenzoxazine–polyimide alloy exhibited a curing temperature of 241 °C [22].

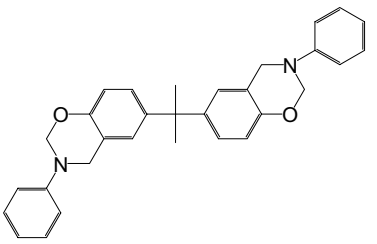
The bismaleimide systems dominate over the other polymer matrices primarily due to their high performance-to-cost ratio and relatively high temperature resistance [23]. They have superior thermal and oxidative stability, low propensity for moisture absorption and good flame retardance. They offer excellent thermomechnical properties and withstand high stress at high temperatures at which typical phenolics and epoxies as well as most high performance plastics are unstable. However, their processability and fracture toughness are not promising. Attempts to reduce brittleness by way of reduction of cross-link density through structural modification, toughening etc. adversely affect the high temperature performance.

Maleimides are known to react with allyl derivatives via Alder-ene reaction. Many studies on allyl-modified bismaleimides have been reported and these materials draw attention in view of ease of processing and good mechanical performance [24–29]. There are a few reports on polybenzoxazine containing imide units as part of the molecule. Preliminary investigations on the co-curing of polybenzoxazine containing BMI as part of the benzoxazine molecule have been reported [13,30–32].

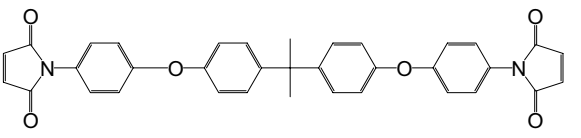
The objective of the present work is to examine the polymerisation and properties of the blends of traditional benzoxazine based on Bisphenol-A – [(6,6′-bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) isopropane] (Bz-A) and an allyl functionalised benzoxazine [2,2′-bis(8-allyl-3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) propane] (Bz-allyl) with a bismaleimide (2,2-bis[4(4-maleimidophenoxy) phenyl] propane) (BMI), all possessing closely resembling backbone structures based on bisphenol-A. Bisphenol-A based benzoxazine was blended with the bisphenol-A bismaleimide (Bz-A/BMI) and the curing pattern and thermal properties were studied. Allyl groups were introduced into benzoxazine monomer and then the monomer was reacted with the same bismaleimide. The components of the blends are Bz-A, Bz-allyl and BMI (structures are given in Scheme 1). The structural similarity is expected to facilitate good miscibilisation and thereby to reduce the probability of phase separation in the cured matrix. Apart from this, this bismaleimide is a low melting solid and affords a network with reduced brittleness due to the phenyl ether spacing between the two maleimide groups. The goal of this work also includes the preparation,



Bz-allyl



Bz-A



BMI

Scheme 1. Selected benzoxazines and bismaleimide resins for blending.

monitoring of polymerisation profile and comparison of the cure and thermal properties of Bz-A/BMI and Bz-allyl/BMI blends.

2. Experimental

2.1. Materials

The monomers Bz-A and Bz-allyl were synthesised and characterised as per previous reports from our group [33,34]. BMI was synthesised by a standard route developed in Vikram Sarabhai Space Centre.

2.2. Instrumentation

Samples weighing approximately 2–5 mg were sealed in aluminium pans and scanned in a TA instruments model 2920 modulated differential scanning calorimeter (DSC) calibrated with an indium standard. A stream of nitrogen at a flow rate of 20 ml/min was used to purge the DSC cell. The measurement was conducted at a heating rate of 5 °C/min under N_2. The heat of reaction was obtained as an instrument output from the area of the DSC thermogram. The samples for infrared analysis were mixed with dried KBr powder, pressed into a pellet for recording infrared spectra with a Perkin Elmer spectrum GXA Fourier transform infrared (FTIR) spectrophotometer at a resolution of 4 cm^{-1} in an optical range of 400–4000 cm^{-1}. Thermogravimetric analysis was done with TA instruments model SDT 2960 simultaneous thermo-gravimetric/differential thermal analyzer (TGA/DTA) at a heating rate of 10 °C/min under N_2. Microscope analysis of the cure blends was done in a PHILIPS XL-30 scanning electron microscope (SEM). The samples were sputter-coated with gold to impart electrical conductivity and reduce charging artifacts. The operation voltage of the SEM was 10 kV. Dynamic mechanical thermal analysis (DMTA) was conducted on a Rheometrics Scientific model Mark IV (UK) analyzer at a frequency of 1.0 Hz and a heating rate of 10 °C/min in a bending mode under N_2. Rheological characterization was done with a Reologica Stresstech Rheometer model Reologica Viscotech QC using a 20 mm parallel plate assembly in oscillation mode at a frequency of 1 Hz and a controlled strain of 0.01. The benzoxazine monomers, BMI and blends were melted and degassed for 30 min at 110 °C under vacuum before loading on the plate at 130 °C. The gap between the plates was maintained at 0.5 mm. The data analysis was done with the instrument software.

2.3. Preparation of Bz-A/BMI and Bz-allyl/BMI blends and their analyses

Bz-A was blended with BMI in the molar ratio 1/0.5, 1/1 and 1/3 (Bz-A/BMI). The blends were prepared by solution blending. Both the monomers were dissolved in acetone and stirred for 30 min. The blend was kept at 50 °C in vacuum for removing the solvent. Subsequently, a cure profile (140 °C/2 h, 160 °C/2 h, 180 °C/2 h, 210 °C/2 h and 230 °C/3 h) was applied for curing the blend. Bz-allyl monomer was blended with BMI in various molar ratios. The chosen molar ratios were 1/0.5, 1/1, 1/1.75 and 1/2.5 (Bz-allyl/BMI)). The weighed amounts of monomers were mixed in a beaker, melted at *ca.* 100 °C and kept in vacuum for 30 min. The mixture after melt blending was subjected to curing in a stepwise manner. The adopted cure temperature profile was 150 °C/2 h, 180 °C/2 h, 210 °C/3 h and 240 °C/3 h. The cure schedules were drawn based on IR investigations. Neat BMI was cured by heating it at 240 °C/10 h [35]. The curing behaviour was examined by DSC, rheology and IR analyses and thermal properties were investigated by TGA/DTA, and DMTA. Scanning electron microscopy was carried out for morphological investigations.

3. Results and discussion

3.1. Cure Profile by DSC and rheological analyses

3.1.1. Bz-A/BMI systems

The cure behaviour of Bz-A/BMI blends as investigated by DSC is shown in Fig. 1. The DSC traces of the individual resins are also included for comparison. The DSC thermogram of the benzoxazine monomer showed a typical sharp curing exotherm with a peak (T_p) located at 218 °C attributed to the benzoxazine ring-opening polymerisation. The endotherm that corresponds to melting was observed at 60 °C. The initial curing temperature (T_i) at 156 °C indicates a controllable curing window (CCW) of 62 °C. The CCW implies the easiness/control over processing. The more the temperature gap between initial and peak curing, the easier it is for keeping and curing the material at low temperature with a good control over processing. On the other hand, the melting of BMI

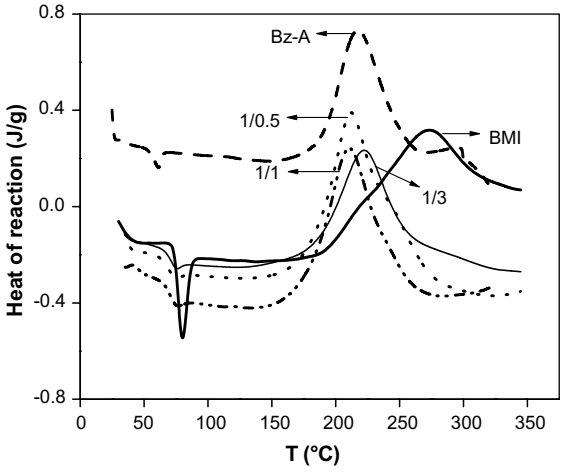


Fig. 1. DSC of neat Bz-A, neat BMI and Bz-A/BMI blends.

was observed as an endotherm at 80 °C and it started curing at 195 °C with the peak exotherm appearing at 270 °C, providing a CCW of 75 °C. But the higher initial cure temperature of 195 °C outweighs the reasonable CCW of 75 °C for BMI.

In all blend compositions, the endotherm corresponds to melting was observed around 70 °C. In the 1/1 molar blend of these two systems, the T_i got reduced to 142 °C and the T_p was shifted to a lower temperature of 211 °C. Thus, a curing window of about 70 °C was maintained. The processing of a thermosetting polymer is always carried out at or near the T_p. It is preferred to process a thermosetting polymer at lower temperatures to avoid void formation. If the polymer is processed at higher temperature, due to a sudden increase in exothermicity (release of heat), hot spots can be formed. This eventually leads to the formation of voids. As far as the processing is concerned, peak curing temperature is the primary concern. In this respect, the processing of the blend of Bz-A/BMI was improved. The T_p of the blend decreased to 211 °C in comparison to those of BMI (270 °C) and Bz-A (218 °C). Moreover, the final cure temperature (T_f) of the blend was 284 °C compared to 339 °C of BMI. Hence, from the view of BMI also, the processing characteristics of the blend are improved. A wide cure regime between 142 and 284 °C was observed for the blend. Hence, by realising a blend of these resins, the initial and peak curing temperatures are lowered in comparison to those of the component resins or in other words, the processing is facilitated. The curing profile of two more compositions of Bz-A/BMI blends was investigated to confirm the catalytic effect of Bz-A on the curing of BMI. The 1/0.5 (Bz-A/BMI) molar blend showed a cure profile matching with that of 1/1 blend. When the Bz-A ratio decreased significantly as in the 1/3 ratio, though the T_i was in the same range, the T_p and T_f increased. These results imply that the Bz-A catalyses the polymerisation of BMI and the extent of catalysis increases with the amount of Bz-A in the blend. All these observations are compiled in Table 1.

The lowering of cure temperature implies that the maleimide polymerisation is catalysed by benzoxazine whereas benzoxazine ring-opening is not influenced by maleimide significantly. The ring-opening polymerisation of benzoxazine is susceptible for acid catalysis and in the absence of any such catalysts, the polymerisation occurs at the same temperature. But, the presence of amino group of benzoxazine is sufficient to catalyse the maleimide polymerisation [8]. It has also been postulated that the iminium ions, which are formed during the ring-opening polymerisation of benzoxazine could catalyse the maleimide polymerisation [31].

Table 1
DSC observations of monomers and Bz-A/BMI blends

Samples	T_i (°C)	T_p (°C)	T_f (°C)	CCW (°C)	Cure window (°C)	Heat of reaction (J/g)	
						Experimental	Theoretical
Bz-A	156	218	270	62	114	257	–
BMI	195	270	339	75	144	130	–
Bz-A/BMI (1/0.5)	128	212	293	81	165	225	209
Bz-A/BMI (1/1)	142	211	284	69	142	180	191
Bz-A/BMI (1/3)	130	224	342	118	212	174	157

T_i – initial curing temperature.
T_p – peak curing temperature.
T_f – final curing temperature.
CCW – Cure controllable window ($T_p - T_i$).
Cure window – $T_f - T_i$.

The enthalpy of reaction of individual neat resins viz: benzoxazine and bismaleimide was 257 J/g and 130 J/g, respectively whereas the exothermicity of the 1/1 blend was found to be 180 J/g which is comparable to the theoretical value of 191 J/g. Similarly, for the other two compositions too, there is a good match between experimental and theoretical heat of curing, within experimental error (data in Table 1). This observation rules out any co-reaction between two components and postulates the formation of an interpenetrating polymer network (IPN). A single exotherm in the DSC of the blend further points out that the IPN formed is a simultaneous interpenetrating network (SIPN).

A rheological cure analysis was carried out on 1/1 molar blend of Bz-A/BMI system because rheology offers the more precise temperature region where real mechanical property build-up sets off. In Fig. 2 dynamic rheological analyses of Bz-A, BMI and Bz-A/BMI (1/1) blend are shown (100–350 °C). Rheological analysis supports the DSC observation. It is seen that the cure temperature in the blend shifts to a lower regime due to the catalytic activity of benzoxazine on BMI and consequently a simultaneous polymerisation occurs. Thus, a simultaneous interpenetrating network (SIPN) is expected to be formed.

3.1.2. Bz-allyl/BMI systems

The curing of allyl containing benzoxazine–bismaleimide blends (Bz-allyl/BMI) was also studied by DSC. Fig. 3 shows the DSC traces of Bz-allyl/ BMI system of varying molar ratios along with thermograms of neat benzoxazine and BMI. In the 1/0.5 (Bz-allyl/BMI) blend, two exotherms were observed, at 228 °C and 269 °C, respectively. The first exotherm is the co-curing of allyl-bismaleimide and the second exotherm corresponds to the ring-opening of benzoxazine. Further addition of bismaleimide to benzoxazine resulted in a decrease in overall curing temperature. As the BMI concentration is enhanced from 0.5 to 1 molar ratio, a broad exotherm was observed predominantly due to the reaction between allyl groups in benzoxazine with the maleimide groups [26,28]. Also the T_p was lowered to 229 °C from 273 °C. Beyond this composition, bismaleimide did not influence the cure significantly, as the T_p and heat of reaction remain constant. The heat of reaction for independent curing of Bz-allyl is 40 J/g and for BMI is 130 J/g. Meanwhile, the heat of reaction in the 1/1 blend was found to be 190 J/g indicating a change in mechanism of cure.

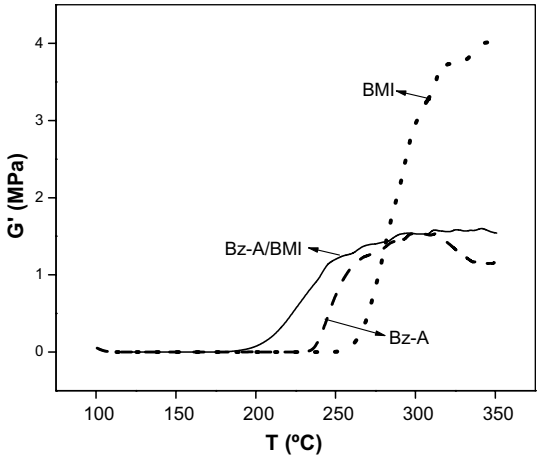


Fig. 2. Rheograms of neat Bz-A, neat BMI, and Bz-A/BMI (1/1).

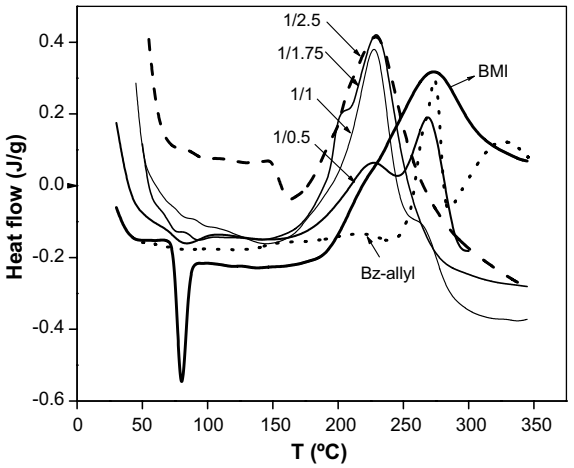


Fig. 3. DSC thermograms of various formulations of Bz-allyl/BMI blends.

The 1/0.5 Bz-allyl/BMI blend showed two exotherms unlike the 1/1 Bz-A/BMI blend. In the former case, there is a reaction definitely between the allyl group and maleimide, which triggers off at about 150 °C. The reaction between allyl groups and BMI proceeds through the Alder-ene reaction involving an Ene, Wagner–Jauregg and Diels–Alder reactions at different temperature regimes. This is well documented in literature [26–28,36] and several polymeric systems based on this cure chemistry have been reported [37]. As a good proportion of maleimide is consumed by this reaction, the BMI curing cannot be catalysed by the amine (*N*,*N*-dialkyl ani-

line), which originates from the ring-opening of benzoxazine unlike in the case of Bz-A/BMI. This explains the observed DSC trends in the two cases. It is also implied that the incorporation of bismaleimide into allyl benzoxazine matrix does not alter the ring-opening of benzoxazine groups in the blend. Fig. 4 shows the rheograms of Bz-allyl, BMI and Bz-allyl/BMI (1/1) blend. The blend starts curing at a lower temperature and the Alder-ene reaction contributes to the modulus build-up (due to cross-linking). The high temperature regime of the rheograms of the blend resembles the profile in the rheogram of Bz-allyl. This implies that the benzoxazine polymerisation is unaltered in the co-reacted blend.

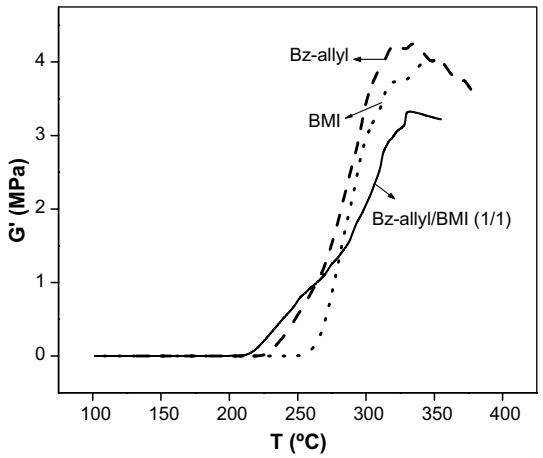


Fig. 4. Rheograms of Bz-allyl, BMI and Bz-allyl/BMI (1/1).

This was different from the observations in DSC (1/1 blend) where the high exothermicity of the Alder-ene reaction masked the cure exotherm of benzoxazine polymerisation. It may be noted that the benzoxazine group in Bz-allyl polymerises at a temperature higher than Bz-A, due to an altered cure mechanism [34].

3.2. FT-IR analysis

3.2.1. Cure analysis

The cure reaction of the Bz-allyl/BMI (1/1) was investigated by FT-IR. Fig. 5 represents the vibrational spectra of blend in the ratio 1/1. Cure monitoring by IR of the Bz-allyl/BMI system was done by observing the changes in the peaks at 831 cm^{-1} (=C–H, maleimide), 949 cm^{-1} (oxazine), 1638 cm^{-1} and 997 cm^{-1} (allyl group) (allyl peaks especially at 997 cm^{-1} are merged with other peaks, so a clear view is given in Fig. 6), 1713 cm^{-1} (–C=O), 1393 cm^{-1} (C–N bond), 693 cm^{-1} and 755 cm^{-1} (maleimide associated finger print region). Upon curing, the intensity of allyl peaks at 1638 cm^{-1}, and 997 cm^{-1} decreased to a considerable extent indicating ene-reaction between allyl and maleimide groups. The intensity of maleimide carbonyl (stretching C=O) at 1713 cm^{-1} decreased as the cure progressed. It has been observed previously that the C=O intensity decreases significantly on polymerising the maleimide ring in the presence of allyl groups. On transforming maleimide to succinimide during polymerisation, the absorptivity of

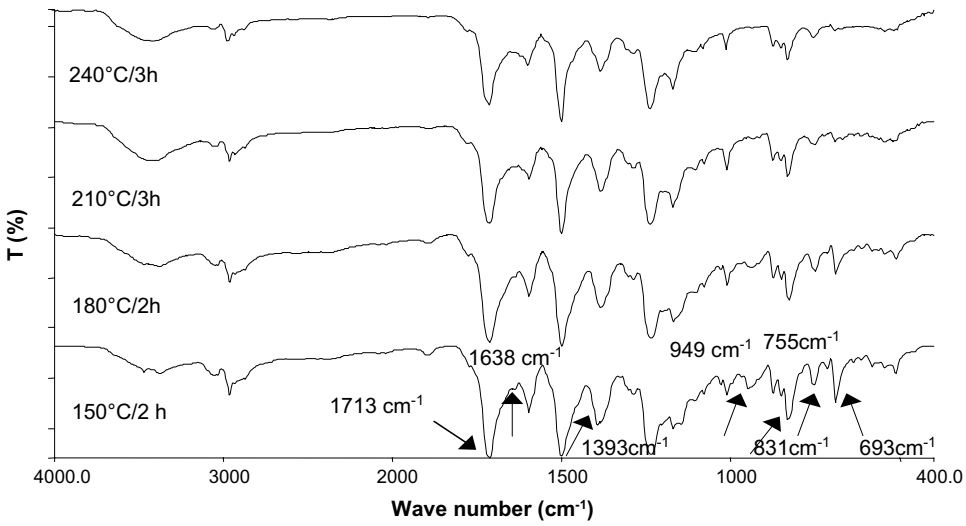


Fig. 5. IR spectroscopy of 1/1 blend of Bz-allyl/BMI at different curing stages.

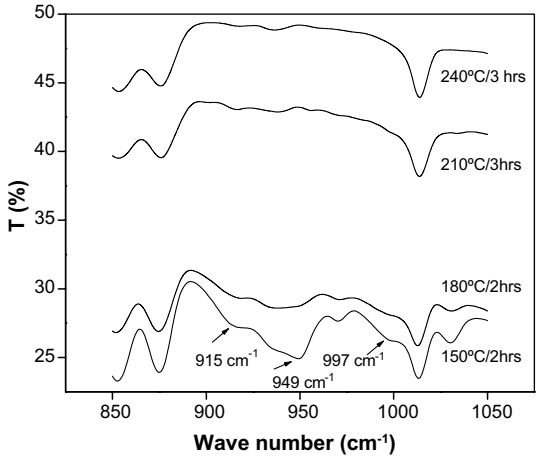


Fig. 6. Benzoxazine curing and disappearance of allyl groups in the (1/1) Bz-allyl/BMI blend at various curing stages.

carbonyl peak in the IR spectrum generally decreases without any shift in the frequency of absorption [38]. A decrease in C–N bond absorption intensity (1393 cm^{-1}) is also observed. Also, the maleimide absorption peak intensity at 831 cm^{-1} got reduced and the peak at around 693 cm^{-1} vanished. The characteristic peak of benzoxazine at 949 cm^{-1} vanished during the progress of curing. The intensity of –OH absorption in the range of 3300 cm^{-1} increased as the cure reaction advanced indicating the ring-opening of benzoxazine as one of the modes of polymerisation. Thus, the spectral evidences are all supportive of the expected cure sequences.

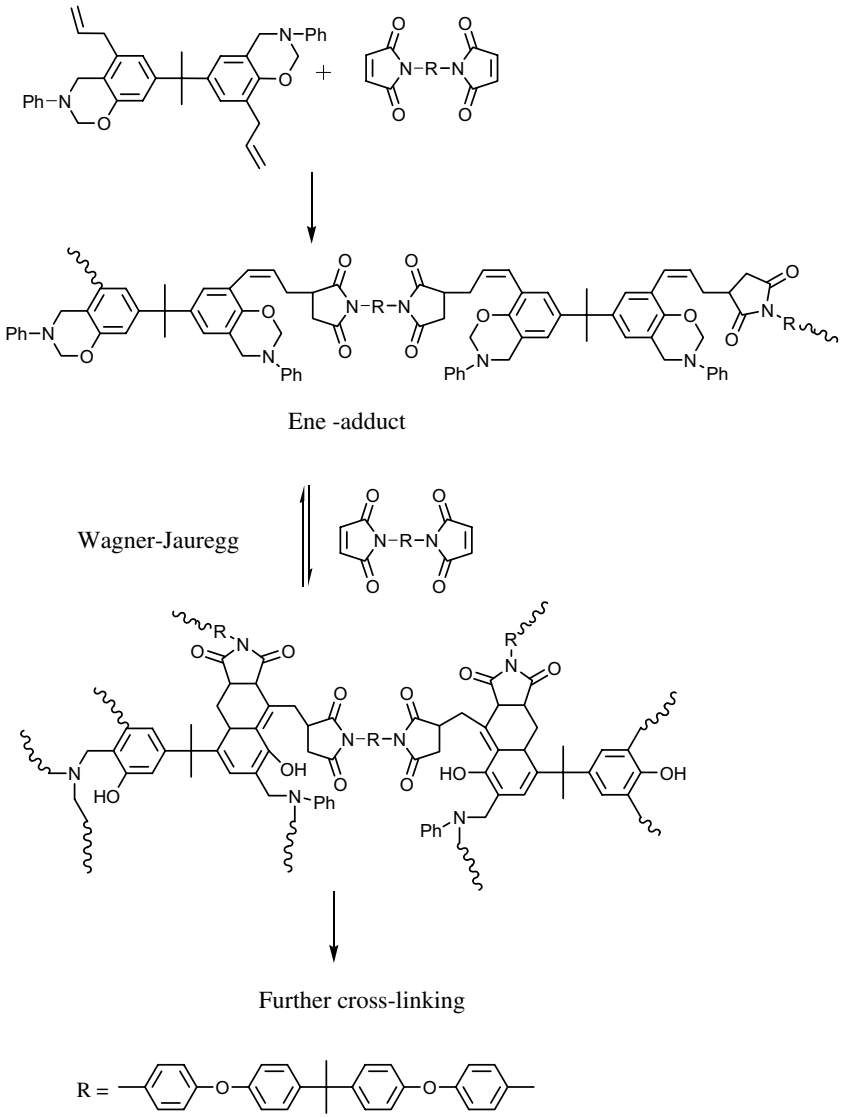
It is necessary to determine the cure temperature regimes of allyl moieties in the blend. Fig. 6 shows the disappearance of allyl groups (915, 997 cm^{-1}) and ring-opening of oxazine (949 cm^{-1}) moieties with the progress of curing. Benzoxazine polymerisation is nearly completed after the third stage curing (210 °C/3 h) whereas allyl groups persist even after that stage and completely vanishes after the fourth stage curing (240 °C/3 h) only. The present observations are supportive of the reported bismaleimide-allyl Alder-ene reactions [28,39]. Based on these observations, the probable reaction pathways for Bz-allyl/BMI blend are depicted in Scheme 2.

3.2.2. Cured blends

It has been previously reported that intermolecular hydrogen bonding plays a dominant role in the miscibility of polar polymers containing carbonyl groups [40]. In the Bz-A/BMI blend, there are two areas of interest in the FT-IR spectra of the blends; one is the carbonyl region (1800–1650 cm^{-1}) and the other is the hydroxyl region (3600–3000 cm^{-1}). The spectra of the cured Bz-A/BMI (1/1) and the cured BMI are shown in Fig. 7. In the cured blend, the characteristic carbonyl band was observed at 1714 cm^{-1}. In addition, two relatively weak bands were observed at 1702 $cm^{-1}$and 1687 cm^{-1}. These two bands are assigned to the H-bonded carbonyl groups generated in different environments in the blend. The two different possibilities are depicted in Scheme 3. The hydroxyl group may be H-bonded with the carbonyl moiety of the bismaleimides and hydroxyl groups which are already H-bonded (intermolecular H-bonding) may be bonded to carbonyl moiety of another bismaleimide group. The H-bonded carbonyl groups have been reported in polybenzoxazine/polycarbonate and polycarbonate/epoxy blends [41,42]. The absorption difference between the free and H-bonded carbonyl bands shows that the strength of H-bond is fairly good. In Fig. 8, the absorption of H-bonded hydroxyl groups in pure polybenzoxazine is observed at 3440 cm^{-1}. In the blend, the hydroxyl absorption is further shifted to lower frequency at 3411 cm^{-1} due the H-bonding. H-bonding is expected to facilitate a homogeneous phase in the IPN or co-reacted matrices.

3.3. Resin compatibility and SEM analysis

Morphologies of 1/1 blends of Bz-A/BMI and Bz-allyl/BMI were investigated by SEM. Since Bz-allyl/BMI blend formed predominantly a co-reacted network it is expected to show a homogeneous morphology and the same is evident in Fig. 9a. But, the morphology of Bz-A/BMI blend (Fig. 9b) is quite different. As no co-reaction is expected, the degree of intermixing of two polymers is mainly affected by the compatibility of the components, the relative rate of network formation, the composition and degree of cross-linking. However, complete compatibility is not essential to achieve absolute phase mixing, since the permanent entanglements can effectively limit the extent of phase separation. It is believed that the phase separation is kinetically hindered by the simultaneous polymerisation and gelation of two networks i.e. the chain entanglements and cross-linking associated in simultaneous polymerisation would be expected to restrict phase sep-



Scheme 2. Likely cure – reactions in the blend of allyl-functionalised benzoxazine and bismaleimide.

aration. Fig. 9b shows the SEM picture of the Bz-A/BMI blend. It shows the dual phase morphology indicating apparent micro phase separation. The domains are not well-defined indicating phase continuity. The small domains indicate the compatibility and miscibility of the system. The miscibility is promoted by the similar backbone structure and the H-bonding of the two resins. Though no gross phase separation was observed, the milky white appearance is indicative of a minor phase segregation. These observations imply existence of more homogeneous structure in the blend with a micro level phase separation.

3.4. Dynamic mechanical thermal analysis

Fig. 10 illustrates the damping factor, tan δ, for the cured blends (1/1) of Bz-allyl/BMI and Bz-A/BMI. The T_g of cured BMI and cured Bz-allyl are 307 °C and 298 °C, respectively. The Bz-allyl/BMI system demonstrated a single T_g at 274 °C owing to the formation of co-reacted network (Fig. 10a). Two distinct peaks in tan δ at 145 °C and 267 °C are seen for the Bz-A/BMI system (Fig. 10b). This is due to some micro level phase separation as seen in SEM analysis. The Bz-A/BMI IPN resulted in a higher T_g. The lower T_g is attributed to the phase

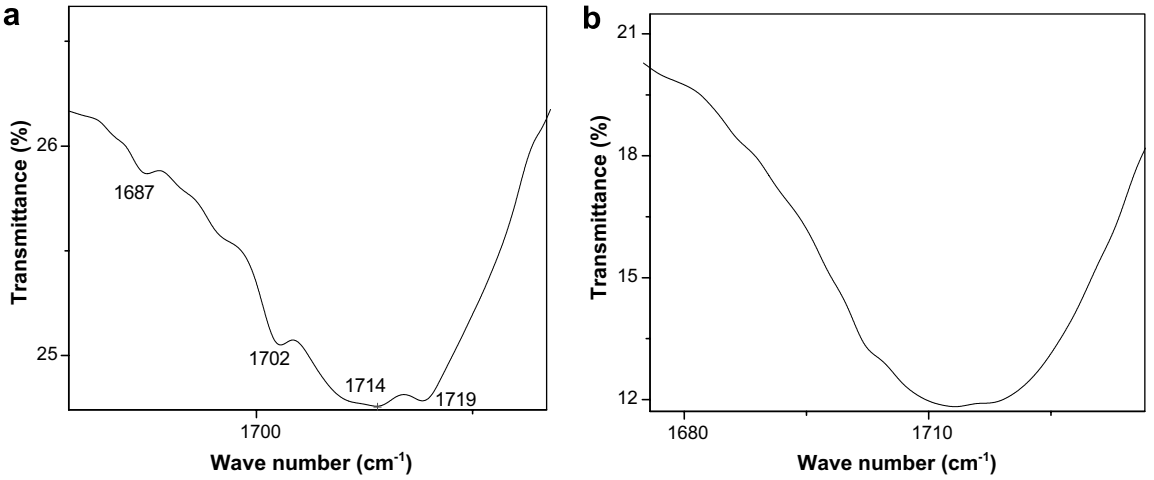
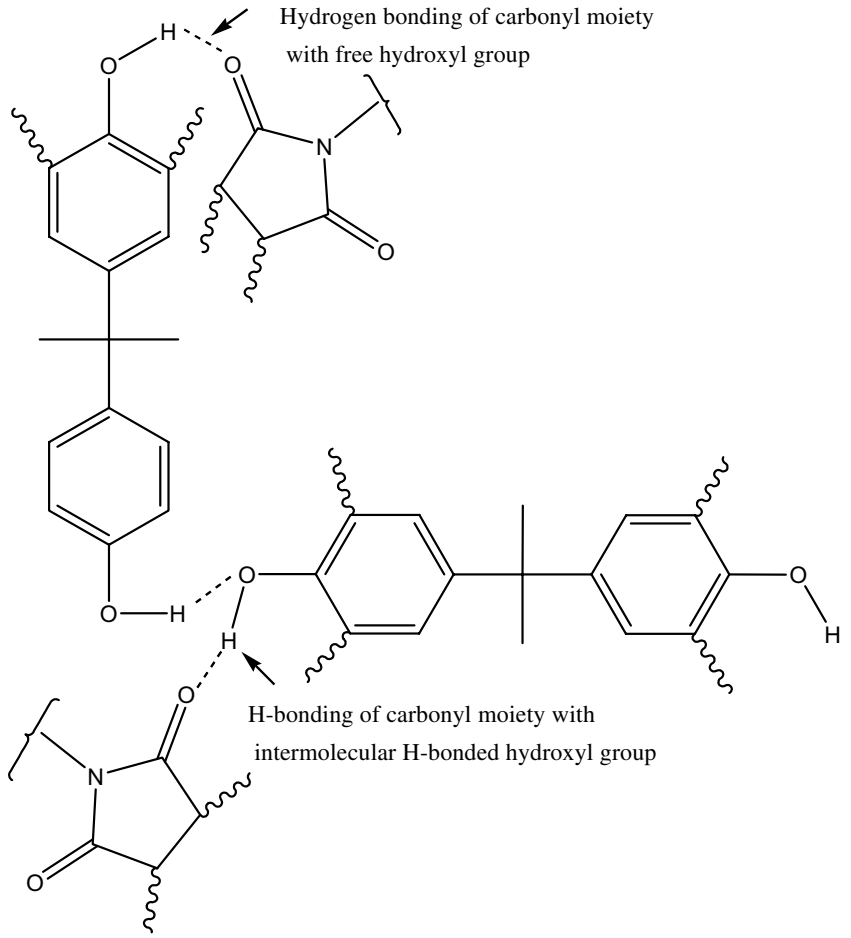


Fig. 7. FTIR spectra of carbonyl region of (a) cured blend of Bz-A/BMI (1/1) (b) cured BMI.



Scheme 3. H-bonded carbonyl groups in polybenzoxazine/bismaleimide (Bz-A/BMI) blend.

separated polybenzoxazine segments. The tan δ profile corresponding to the IPN is broad (180–290 °C). Reduced tan peak height in Bz-allyl/BMI system compared to Bz-A/BMI is associated with a lower

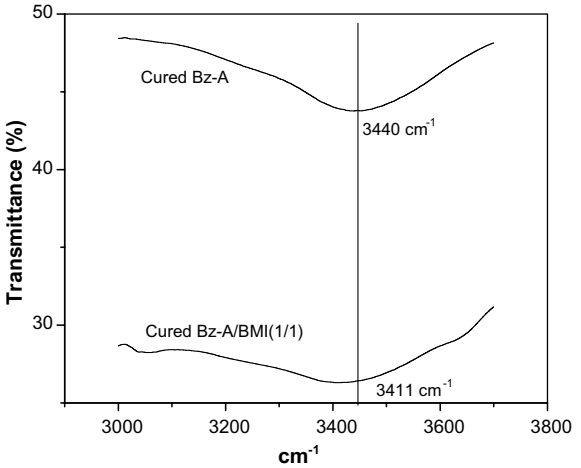


Fig. 8. Shift in hydroxyl absorption due to H-bonding with carbonyl groups in the cured Bz-A and cured Bz-A/BMI.

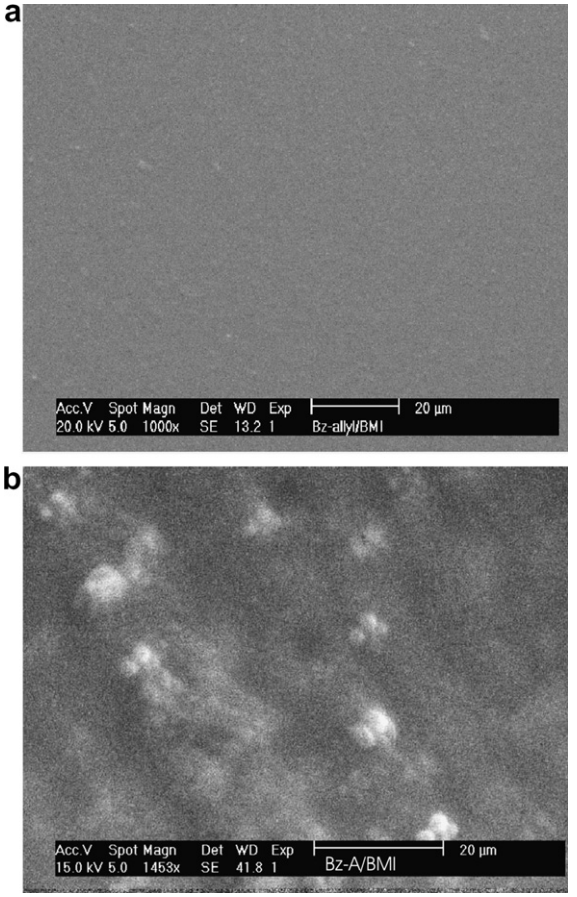


Fig. 9. (a) Homogeneous morphology of cured Bz-allyl/BMI blend (1/1) (b) small level microphase separation in cured Bz-A/BMI system (1/1).

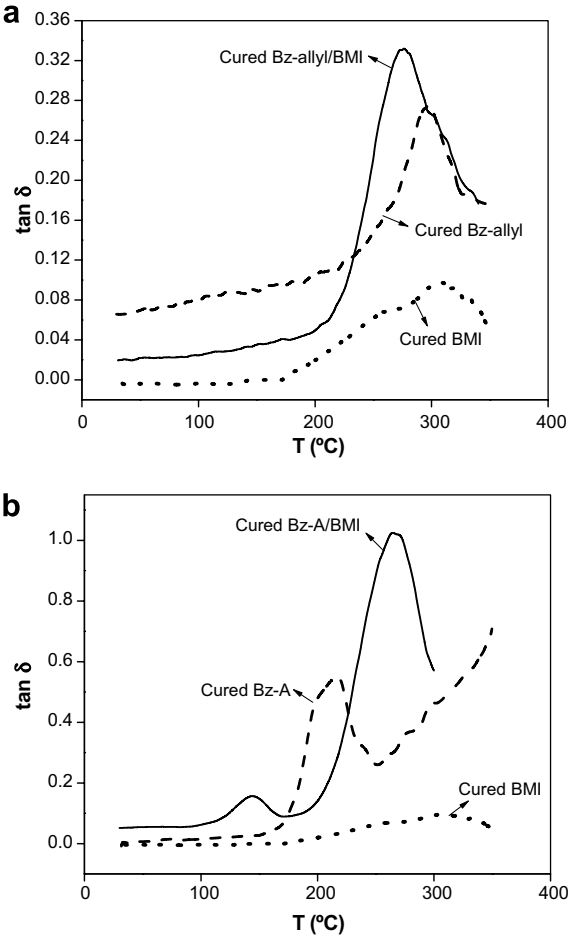


Fig. 10. tan δ behavior of (a) cured Bz-allyl/BMI (1/1) and (b) cured Bz-A/BMI (1/1).

segmental mobility and a higher degree of cross-linking in the former case. Based on DSC and DMTA it can be concluded that Bz-A/BMI forms mainly an IPN with minor phase separated polybenzoxazine domains.

3.5. Thermal stability of the blends

Fig. 11 depicts the thermogravimetric analysis of the cured (1/1) Bz-A/BMI blend along with those of the cured components. The 5% and 10% weight loss temperatures (T_5 and T_{10}) of the blend are 335 °C and 385 °C, respectively, which are higher than those of pure polybenzoxazine (i.e. 275 °C and 335 °C, respectively). The char yields at 800 °C in nitrogen are 35.6%, 43.4% and 43.2% for cured Bz-A, cured BMI and cured Bz-A/BMI, respectively. The T_5 and T_{10} are improved in comparison

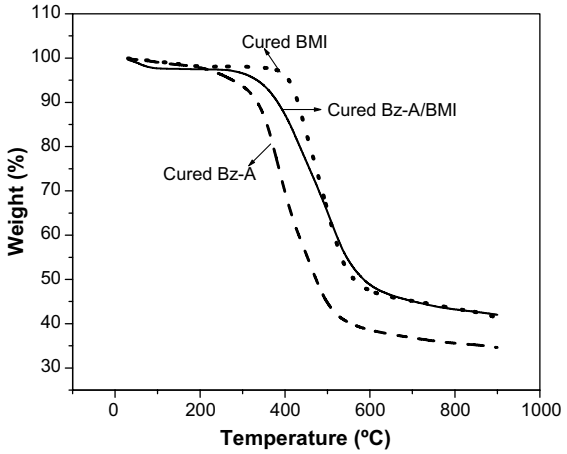


Fig. 11. TGA of cured BMI, cured Bz-A and cured Bz-A/BMI blend (1/1).

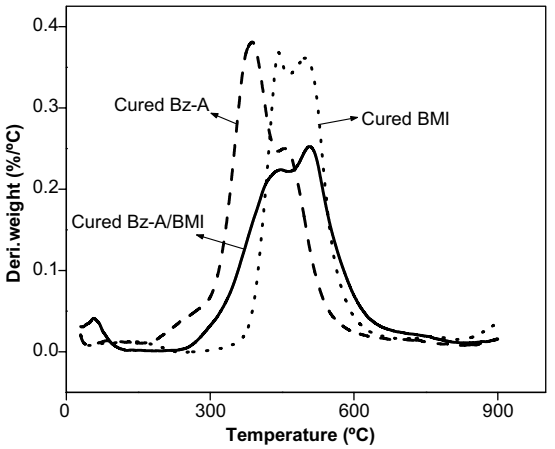


Fig. 12. Derivative weight loss vs. temperature shows the change in mechanism of degradation in cured Bz-A, BMI and Bz-A/BMI blends.

to polybenzoxazine homopolymer. The char yield of the blend is significantly improved over the polybenzoxazine and is at par with that of the cured BMI. The results are complied in Table 2.

Fig. 12 shows the DTA patterns of the Bz-A/BMI (1/1) IPN system. Derivative mass-loss shows the rapidity of decomposition reactions in a polymer. In polybenzoxazines, decomposition below 300 °C is attributed to the amine evaporation and the phenolic degradation occurs at around 400 °C. However, there are two dominant thermal decomposition mechanisms. A major mass-loss event occurs at approximately 390 °C and a minor one at 460 °C. In the blend, the major mass-loss event (degradation of Mannich bridge) merged with the phenolics degradation and both were shifted to a higher temperature (*ca.* 440 °C). This decomposition pattern arises from the presence of cross-linked bismaleimide–polybenzoxazine IPN structures, which imparts thermal stability to the blend.

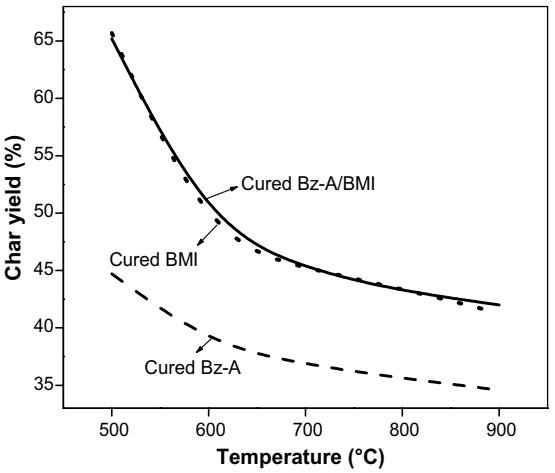


Fig. 13. Char yields at different temperatures of cured Bz-A, cured BMI and cured Bz-A/ BMI blend (1/1).

Fig. 13 depicts the char yield of the Bz-A/BMI blend (1/1) at different temperatures. At 700 °C in nitrogen, the char yields of the cured Bz-A and the blend are 36.8% and 45%, respectively. The char

Table 2
Thermal stability of cured monomers and Bz-allay /BMI and Bz-A/BMI blends

Cured samples	T_5 (°C)	T_{10} (°C)	Char yield (%) at 800 °C
Bz-allyl	395	422	44.0
Bz-allyl/BMI (1/0.5)	350	397	36.0
Bz-allyl/BMI (1/1)	387	418	39.0
Bz-allyl/BMI (1/1.75)	373	412	38.5
Bz-allyl/BMI (1/2.5)	385	418	39.0
BMI	410	430	43.4
Bz-A	275	335	35.6
Bz-A/BMI (1/1)	335	385	43.2

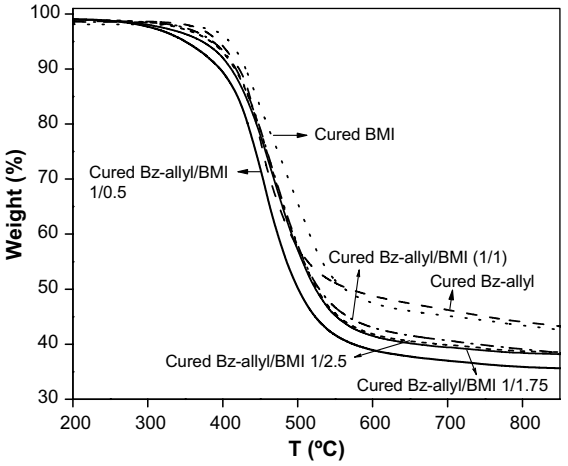


Fig. 14. TGA thermograms of Bz-allyl/BMI blends.

yield of the Bz-A/BMI was also improved in comparison to that of the cured bismaleimide resin. This improvement in thermal features implies that formation of IPN with bismaleimide strengthens the network of polybenzoxazine.

Thermal stability of the co-reacted blend (Bz-allyl/BMI) was also studied by using TGA (Fig. 14). The initial decomposition temperature and char yield (about 39%) remained unaffected by composition. As molar ratio of BMI increases, both the T_5 and T_{10} increase marginally. In fact, co-reaction with BMI marginally decreased the initial thermal stability of the blend compared to that of neat cured Bz-allyl. When the bismaleimide is in deficit, the presence of unsaturated groups from ene-reaction is conducive to the reduced initial decomposition temperature and char yield. Similar observations have been reported previously in Alder-ene resin systems [37,39]. As the bismaleimide composition increases, more of Diels–Alder products result, as a consequence of which, the thermal stability increases. The effect of BMI on thermal stability is evident from the data given in Table 2.

4. Conclusions

The present article deals with the investigations on curing and thermal properties of blends of benzoxazines with a bismaleimide resin. Bz-A/BMI blend manifested an apparent single cure profile. BMI cure was accelerated by Bz-A. The cured blend of Bz-A with BMI exhibited intermolecular H-bonding as evidenced from IR studies. DMTA and SEM analyses conclude the formation of a SIPN of BMI and Bz-A with minor phase separated polybenzoxazine domains. The thermal stability and T_g of the Bz-A/BMI were significantly increased relative to polybenzoxazine, attributed to cross H-bonding and network interpenetration. The curing of allyl-functionalised benzoxazine and bismaleimide blends (Bz-allyl/BMI) indicated the co-reaction between the two by Alder-ene type reaction forming a single-phase system. The processing temperature was lowered on blending. The T_g of the IPN was significantly improved over that of polybenzoxazine (Bz-A). However, the co-reaction resulted in a marginal decrease in the T_g of the system in comparison to the polybenzoxazine (Bz-allyl). The results showed that blending resulted in easier processing and higher thermal stability.

Acknowledgements

Permission of VSSC to publish this paper is gratefully acknowledged. One of the authors (KS Santhosh Kumar) is thankful to University Grants Commission for providing a fellowship.

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