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High temperature resins based on allylamine/bismaleimides

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Synthesis, curing, and physical/mechanical properties of 4,4′-bismaleimidodiphenylmethane (BDM), 4,4′-bismaleimidodiphenylether (BDE), 3,3′-bismaleimidodiphenylsulfone (3-BDS), and 4,4′-bismaleimidodiphenylsulfone (4-BDS) adducted with various amount of allylamines were investigated and compared with each other. BDM was reacted with allylamines exclusively through the Michael addition reaction, whereas 3-BDS and 4-BDS were reacted with allylamines by amidation along with the cleavage of an imide-ring C–N bond. Only BDE underwent both reactions to yield BDE/allylamine adducts. Three types of curing reactions might occur depending on the amount of adducted allylamines: (1) thermal homopolymerization through the maleimide double bonds; (2) accelerated homopolymerization by allylamines; and (3) polymerization of the cleaved allylamines by themselves or with the maleimido groups. Of all the BMIs/allylamines adducts under study, the cured BDM/50 mol% allylamine and BDE/50 mol% allylamine adducts have superior mechanical properties. In addition, the former resin has a glass transition temperature (T_g) of 335°C and a degradation temperature (T_d) of 471°C, whereas the latter has a T_g of 349°C and a T_d of 436°C. Copyright © 1996 Elsevier Science Ltd.

(Keywords: bismaleimides; allylamines; high temperature resins)

INTRODUCTION

Bismaleimide (BMI) resins have been developed most rapidly among the polyimides during the past two decades. The main aim of the development was to offer high temperature performance, high toughness, low cost, and maintain the epoxy-like processing. According to the recent review paper by Pater[1], BMIs have been modified by five different methods: (1) synthesis of BMIs with flexible or long segments in the backbone[2,3]; (2) use of aromatic diamine as a chain extender to react with BMIs through the Michael addition reaction[4-6]; (3) blending of BMIs with epoxies[7-9]; (4) copolymerization of BMIs with olefinic compounds via the Diels–Alder reaction[10-12]; and (5) use of aromatic dicyanate esters to blend with BMIs[13,14]. However, the first three methods have the disadvantage of lowering the glass transition temperature (T_g) of the cured resins. Although the fourth and fifth methods have less adverse effects on the high temperature properties and processability, BMIs have a tendency to recrystallize from the mixture with aging[15] and the prepared resin systems often show inconsistent properties in different batch.

Recently, we suggested a novel method to modify the BMI resins by reacting with various amounts of allylamine[16,17]. The prepared BMI/allylamine (BMI/A) adducts have a much lower degree of crystallinity and possess good mechanical properties. Their T_g can be as high as 340°C if the proper type of BMI and amount of allylamine are used. However, by carefully examining the reaction paths between the BMI and allylamine, we found that they are strongly dependent on the type of BMI resin. For example, 4,4′-bismaleimidodiphenylmethane (BDM) reacts with allylamine through the Michael addition reaction, whereas 3,3′-bismaleimidodiphenylsulfone (3-BDS) reacts with allylamine by amidation through the cleavage of an imide-ring C–N bond[18].

To further investigate the reaction paths between BMI and allylamine, we have chosen 4,4′-bismaleimidodiphenylether (BDE) and 4,4′-bismaleimidodiphenylsulfone (4-BDS) in addition to BDM and 3-BDS, to react with various amounts of allylamine. The cure, mechanical and high temperature properties of the prepared BMI/A adducts will be compared.

EXPERIMENTAL

Preparation of BMI monomers

BDM, BDE, 3-BDS and 4-BDS were prepared from maleic anhydride (Janssen Chimica) and 4,4′-diaminodiphenylmethane (Janssen Chimica), 4,4′-diaminodiphenylether (Tokyo Kasei), 3,3′-diaminodiphenylsulfone (Tokyo Kasei), and 4,4′-diaminodiphenylsulfone (Tokyo Kasei), respectively, by the methods described in ref. 16 with some modifications. In general, a solution of diamine (1 mol) in acetone was added dropwise into a flask which had been already charged with a solution of maleic anhydride (2 mol) in acetone. The addition was performed at ice-temperature under a nitrogen atmosphere, and then the flask was stirred overnight at room temperature. The resulting insoluble amic acid was filtered,

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washed with acetone, and dried under vacuum. Cyclization of the amic acid (0.5 mol) to prepare the BDM and BDE was carried out in an acetone solution containing acetic anhydride (1 mol), triethylamine (0.3 mol), and nickel(II) acetate tetrahydrate (0.03 mol) at room temperature for ≈50 h until the product precipitated. Cyclization to prepare the 3-BDS and 4-BDS was carried out in an acetone solution containing amic acid (0.5 mol), acetic anhydride (1 mol), and sodium acetate (0.3 mol) at 50°C overnight until they precipitated. All the precipitates were collected and washed with a sodium bicarbonate solution until free from acetic acid. Finally, the BDM and BDE products were recrystallized from $CHCl_3$/MeOH (1:1 by volume) solution, whereas the 3-BDS and 4-BDS were recrystallized from methanol.

Preparation of N-*phenylmaleimide (PMI) model compound*

PMI model compound was prepared from maleic anhydride and aniline (Hayashi Pure Chemical) based on a method outlined in US Patent 2,444,536[19]. A solution of aniline (1 mol) in ethyl ether was added dropwise to the flask which had been already charged with a solution of maleic anhydride (1 mol) in ethyl ether. The addition was performed at ice-bath temperature under a nitrogen atmosphere. Afterwards, the flask was stirred for 1 h at room temperature and then cooled to 15–20°C. The resulting insoluble maleanilic acid was filtered, washed with ethyl ether and dried under vacuum. Cyclization of the maleanilic acid (1 mol) was carried out in acetic anhydride (350 ml) containing 33 g of sodium acetate at 100°C. After the maleanilic acid had completely dissolved, the reaction mixture was cooled to room temperature and then poured into 700 ml of ice-water. The precipitated product was collected and washed three times with 300 ml ice-water and once with 300 ml petroleum ether. After being dried, the PMI product was recrystallized from cyclohexane.

Preparation of BMI/A adducts

All of the BDM/A, BDE/A, 3-BDS/A, and 4-BDS/A adducts were prepared by the same procedure. In general, various amounts of allylamine (Tokyo Kasei) in chloroform were added dropwise into a flask which had been charged with a slurry of BMI (0.2 mol) in chloroform. The reaction was carried out at 40°C for ≈5 h under a nitrogen atmosphere until the BMI was completely dissolved and a clear solution obtained. The solution was washed with distilled water and solid products obtained by removing the chloroform under vacuum at 90°C. To name the BMI/A adduct prepared with different molar percentages of allylamine, we designated the product of BMI reacting with 10 mol% allylamine as a BMI/10% adduct, and so on. The molar percentage is calculated by dividing the moles of allylamine by the moles of BMI.

Preparation of PMI/allylamine (PMI/A) adduct

A solution of allylamine (1 mol) in chloroform was added dropwise into a flask which had been already charged with PMI (1 mol) in chloroform solution. The reaction was performed at 40°C under a nitrogen atmosphere for 2 h. The precipitated product was then collected and washed with chloroform before being dried under vacuum.

Curing of BMI/A adducts

Curing of the various BMI/A adducts was conducted in a hot press under 1.38×10^7 Pa pressure for 2 h at 180°C plus 5 h at 220°C.

Sample characterization

I.r. spectra of the samples were recorded on a Hitachi 270-30 Model IR with KBr pellets. ^1H and ^{13}C n.m.r. spectra were recorded on a Bruker AM-300WB Model NMR spectrometer with dimethyl sulfoxide-d_6 (DMSO-d_6) or $CDCl_3$ as solvent. Mass spectra were recorded on a Finnigan Mat TSQ-46C Model mass spectrometer. Differential scanning calorimetry (d.s.c.) was performed in a Du Pont 9900-910 Model DSC. Dynamic mechanical analysis (d.m.a.) was performed in a Du Pont model 9900-983 DMA. Thermogravimetric analysis (t.g.a.) was conducted in a Du Pont Model 9900-954 TGA. All the thermal analyses were run under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. The flexural properties of cured samples were measured by the three-point bending test according to ASTM-D-790. Tests were run in an Instron TM tensile tester at a crosshead speed of 0.5 cm min^{-1}.

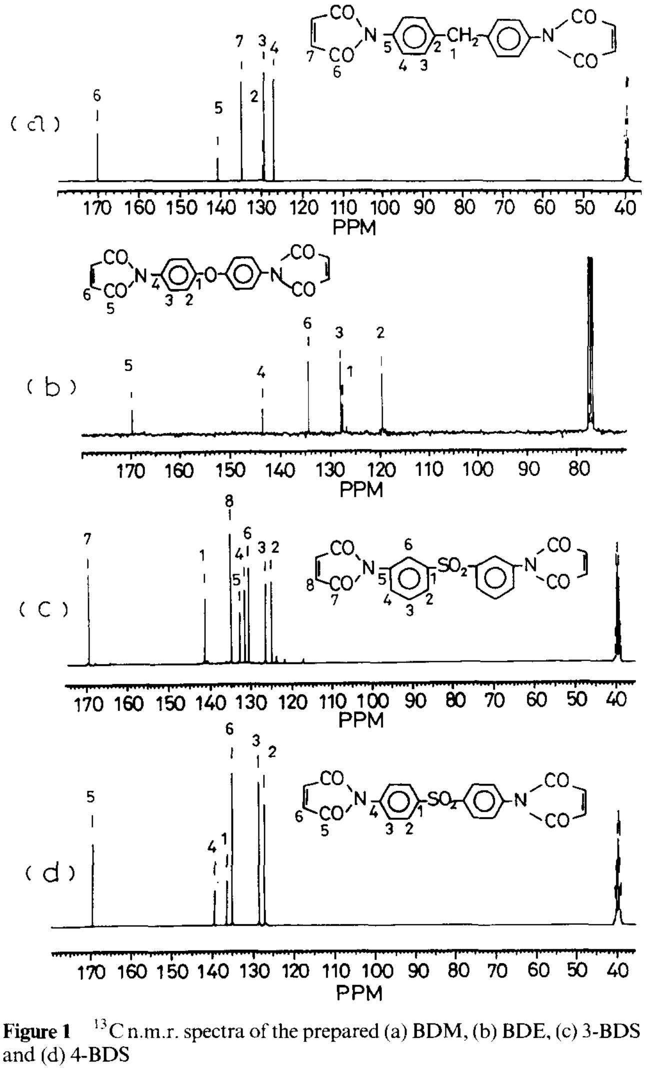


Figure 1 ^{13}C n.m.r. spectra of the prepared (a) BDM, (b) BDE, (c) 3-BDS and (d) 4-BDS

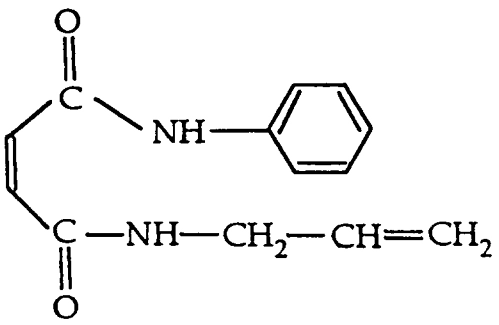
RESULTS AND DISCUSSION

Characterization of BMIs and BMI/A adducts

^{13}C n.m.r. spectra of the prepared BDM, BDE, 3-BDS, and 4-BDS are shown in *Figure 1*, along with the assignments of each carbon. Their d.s.c. spectra shown in *Figure 2* indicated that they are crystalline solids with melting points at 158, 177, 207 and 248°C, respectively. The curing peaks of BDM and BDE are broad, both appearing at 220°C. They have been associated with the thermal homopolymerization of the resins[16,19]. In addition, the thermal polymerization of 3-BDS and 4-BDS resins took place at 211 and 253°C, immediately after they had become molten.

Various BMI resins were reacted with 10, 50 and 200 mol% allylamine to yield a series of BMI/A adducts and changes in their i.r. spectra with the amount of allylamine are shown in *Figure 3*. Interestingly, by comparison between four different types of BMI/A adducts, we found the BDM/A adducts were formed exclusively by the Michael addition reaction; the peaks at 3140 cm^{-1} contributed by the double bonds of the maleimido groups disappeared when BDM was reacted with 200 mol% allylamine. Also, the intensity of the peaks at 920 and 3300 cm^{-1} contributed by the allyl groups and secondary amino groups gradually increased with the amount of allylamine. On the other hand, 3-BDS/A and 4-BDS/A adducts did not undergo Michael addition reactions as indicated by insignificant change of the peaks at 3140 cm^{-1}. The imido peaks at 1720 and 1780 cm^{-1} completely disappeared and were replaced by the amido peaks at 1640 cm^{-1} when BDS reacted with 200 mol% allylamine. The peak at 1395 cm^{-1} (ν_{C-N-C}) also disappeared, indicating that the imido ring had opened. When BDE reacted with 200 mol% allylamine, the imido rings were not completely opened as indicated by the i.r. spectra (*Figure 3*). It is believed that small amount of allylamine still participated in the Michael addition reactions.

Michael addition reactions between BMIs and aromatic amine have been well studied and documented[4–6]. However, how the allylamine opened the imido ring was not understood until we used PMI as a model compound to react with allylamine in another study[18]. It has been shown that the amino group of allylamine attacked one of the carbonyl groups of maleimido ring, and yielded two amido groups along with the cleavage of imide-ring C–N bond. The chemical structure of the PMI/A adduct was suggested to be as follows:



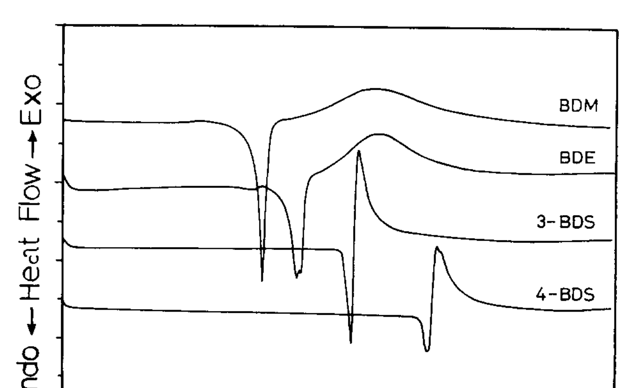


Figure 2 D.s.c. spectra of the prepared BDM, BDE, 3-BDS and 4-BDS

The presence of two amido groups in the PMI/A adduct has been verified by the ^{1}H n.m.r. spectrum, for the NH's are exchangeable with D_2O[18]. In this study we confirmed the chemical structure by 2D n.m.r. shown in *Figures 4* and *5*. The 2D representation is the line-to-line correspondence between ^{1}H and ^{13}C splitting. Using this method, the chemical structure of the PMI/A adduct can be easily determined from the 2D ^{1}H–^{13}C correlated spectroscopy (COSY) shown in *Figure 4*. For example, the NH peak at 8.6 ppm of the ^{1}H n.m.r. spectrum was correlated with the peaks of two neighbouring carbons at 41.1 and 163.3 ppm of the ^{13}C n.m.r. spectrum, whereas the NH peak at 10.4 ppm was correlated with those at 119.3 and 162.2 ppm of the ^{13}C n.m.r. spectrum. Thus, two amido groups in the PMI/A molecule can be determined. Further verification was obtained from the distortionless enhancement by polarization transfer (DEPT) experiment, in which the carbon peaks contributed by CH_2 reversed their direction and the carbons without any proton attached did not appear in the DEPT ^{13}C n.m.r. spectrum (see *Figure 5*). Thus, the carbon peaks in the ^{13}C n.m.r. spectrum of the PMI/A adduct were assigned from the 2D n.m.r. The i.r. spectrum of PMI/A has been reported in *Figure 6*[18]. The peaks at 1650 and 3290 cm^{-1} contributed by the amido groups are similar to those in the i.r. spectrum of BDS/200%A adducts (see *Figure 3*). Therefore, it is clear that the amino group of allylamine has opened the imido ring of BDS/A adducts by amidation during the adduction reaction.

So far, two reaction paths between the allylamine and BMI have been found; one is the Michael addition reaction and the other is the amidation through the cleavage of an imide-ring C–N bond. Michael addition reaction found for BDM reacting with allylamine might be associated with the electron donor characteristic of a methylene group inbetween two phenyl rings, which deactivates the imido-ring opening reaction and favours the Michael addition reaction. On the other hand, the sulfone group of BDS is an electron acceptor which activates the imido-ring opening reaction.

Curing of BMI/A adducts

Figure 7 shows the d.s.c. spectra of various BMIs adducted with 10, 50 and 200 mol% allylamine. It can be seen that the addition of 10 mol% allylamine significantly reduced or completely erased the crystallinity of the BMIs. The initial cure temperature also shifted to

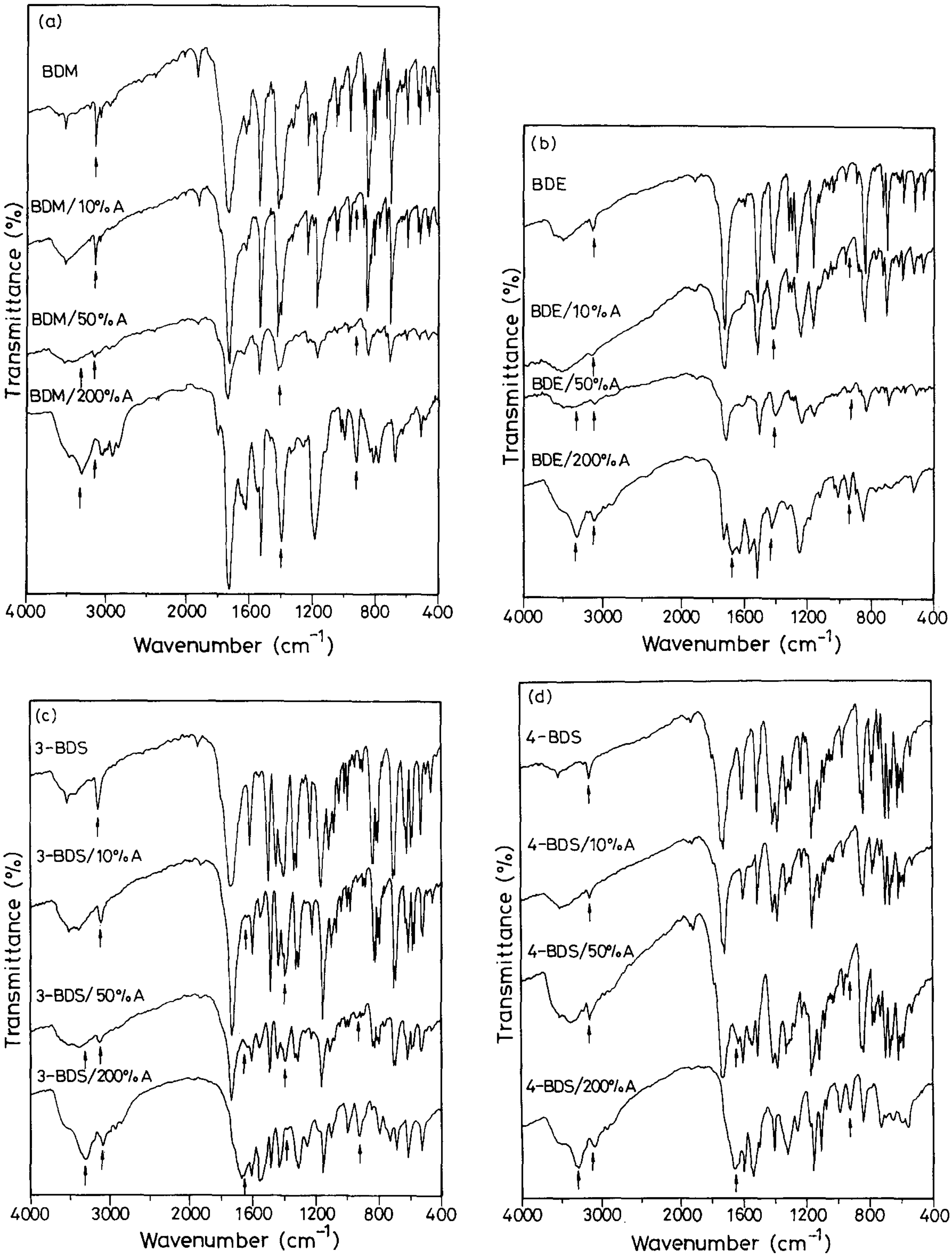


Figure 3 I.r. spectra of (a) BDM, (b) BDE, (c) 3-BDS and (d) 4-BDS, and their adducts with 10, 50 and 200% allylamines

lower temperature (compared to *Figure 2*). Except for the 4-BDS/A adducts, the accelerated cure reactions of BDM/10%A, BDE/10%A and 3-BDS/10%A were due to the accelerated homopolymerization of BDM, BDE, and 3-BDS portions under the influence of the adducted allylamines. Homopolymerization was consistent with the mass spectra recorded. For instance, a mass spectrum of cured BDM/10%A adduct has a base peak at m/z 358, equivalent to the molecular weight of BDM (see *Figure 8*). In this experiment, the specimens were inserted directly into the mass spectrometer and the pyrolysis was performed close to the ion source. Thus, the appearance of the peak at m/z 358 is consistent with depolymerization in the pyrolytic stage and indicative of the incorporation of this unit in the polymer. Similar peaks were also found in the mass spectra of the homopolymerized BMI[18]. The accelerated effects of adducted allylamine on the polymerization of BDM were believed to be attributable to the 'charge transfer complex' effect[20] in view of the fact that the allyl groups from the adducted allylamine is an electron-rich olefin and the double bonds of the maleimido groups are an electron poor olefin.

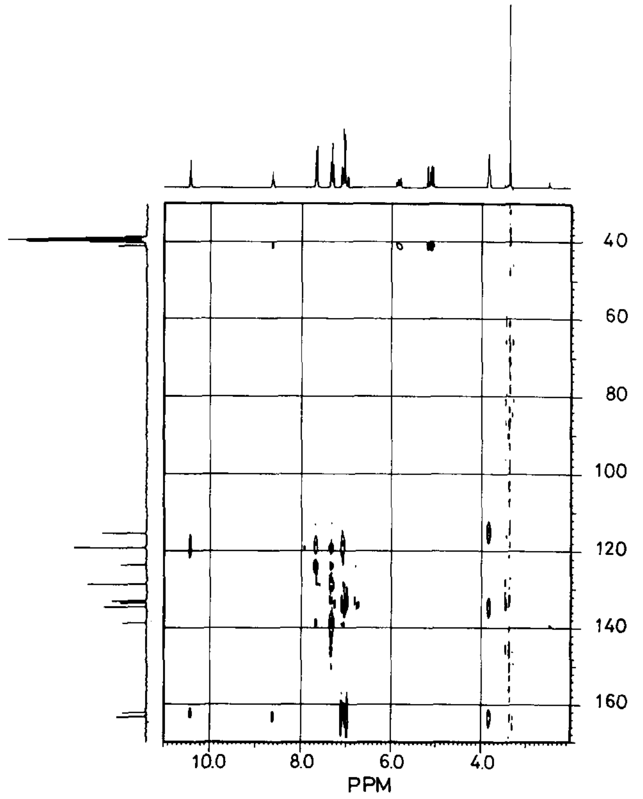


Figure 4 2D ^1H–^{13}C correlated spectrum (COSY) of the prepared PMI/A adduct

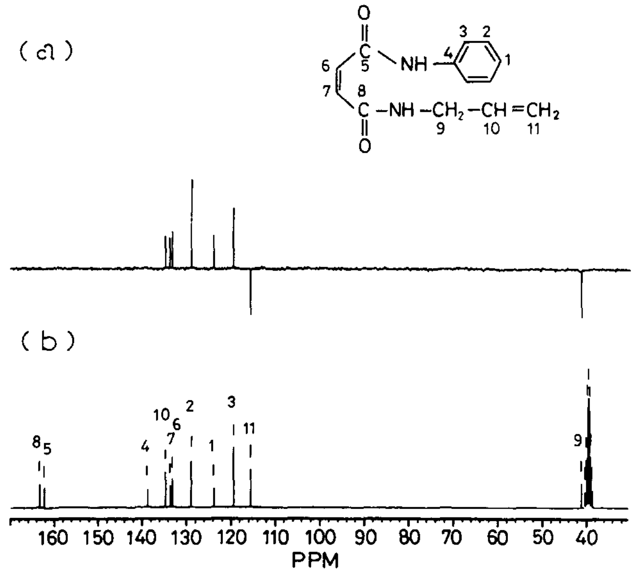


Figure 5 (a) DEPT and (b) ^{13}C n.m.r. spectra of the prepared PMI/A adduct

However, this would not be the case for 3-BDS/10%A adducts, because the adducted allylamines were prone to cleavage from the 3-BDS/A adducts at 170–180°C as indicated by their t.g.a. and i.r. spectra.

A small drop in the weight of 3-BDS/10%A adduct was observed as shown in *Figure 9a*, indicating that some degradation took place at a temperature slightly lower than the cure temperature. I.r. spectra of the 3-BDS/200%A adduct after heating at 180°C for 30 min revealed that the degradation was due to the cleavage of allylamine groups along with the recovery of the maleimido groups (see *Figure 10*). The peaks at 1720 and 1420 cm^{-1} contributed by the imido ring reappeared, whilst the peaks at 1660 cm^{-1} contributed by the amido groups and at 920 cm^{-1} contributed by the allyl groups were reduced in their intensity. Since the cleaved allylamino groups have chances to possess free radicals and/or ionic charges, they might initiate the homopolymerization of 3-BDS in the 3-BDS/10%A adduct at lower temperature. Due to the similarity of the chemical structure between the 3-BDS and 4-BDS, the allylamino groups of 4-BDS/10%A adducts were also cleaved prior to the cure temperature. The cure peak of 4-BDS/10%A adduct was barely found at ≈190°C but grew larger as the amount of adducted allylamine was increased. The cleaved allylamines are not able to initiate the homopolymerization of 4-BDS, because the double bonds of 4-BDS are quite unreactive as indicated by their polymerization at much higher temperature (≈250°C). Thus, the cleaved allylamines might react with each other through double bonds of the allyl groups and contributed to the cure peaks at 170–190°C.

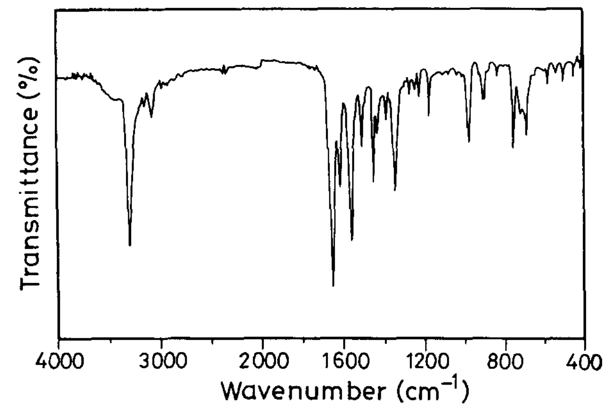


Figure 6 I.r. spectrum of the prepared PMI/A adduct[18]

When the amount of allylamine to adduct BDM was increased to 50 mol%, the melting peak further shifted to lower temperature and the curing peak became broader. However, the heat of exotherm is 200 Jg^{-1} similar to that of BDM/10%A, indicating that the allyl groups also participated in the curing reactions through the 'charge transfer complex' mechanism. When the amount of allylamine was increased to 200 mol%, the initial curing peak was significantly reduced. However, the other peak, which appeared at ≈245°C, was believed to be associated with the reactions of cleaved allylamines, because the adducted allylamines were cleaved at a similar temperature to that seen in their t.g.a. thermogram shown in *Figure 9b*. On the other hand, for the 3-BDS/A adducts, the allylamino groups were cleaved along with the recovery of imido ring of 3-BDS at 170°C, prior to the cure reactions. When it is in small quantity ($\leq$ 50 mol%), the cleaved allylamine will accelerate the homopolymerization of 3-BDS through the maleimide double bonds. When the cleaved allylamines are plentiful, they have more chance to encounter each other and polymerize by themselves. As a result, the initial cure peak was still strong and appeared at a lower temperature when the allylamine was increased to 200 mol%. Since the cleaved

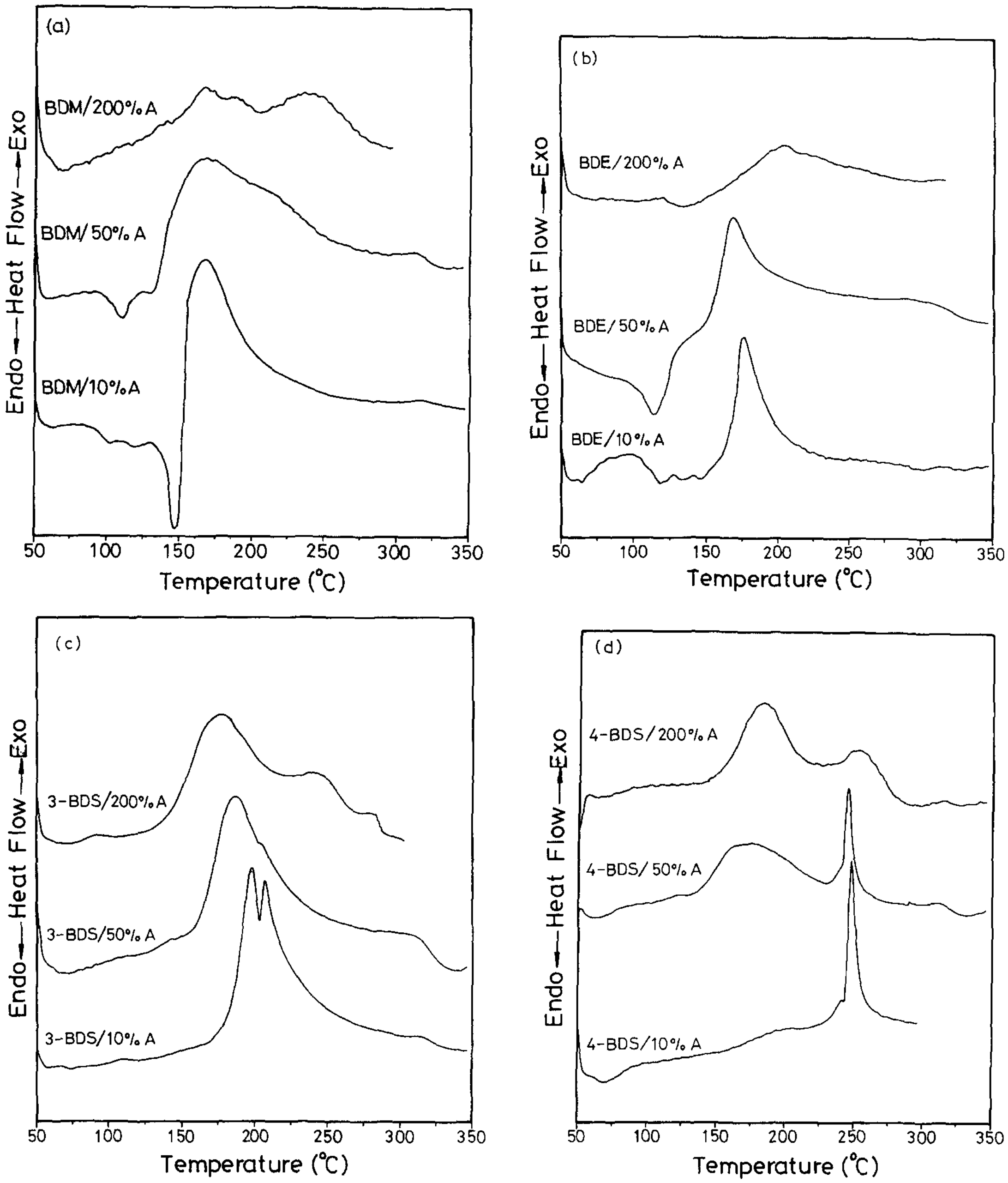


Figure 7 D.s.c. spectra of (a) BDM/A, (b) BDE/A, (c) 3-BDS/A and (d) 4-BDS/A adducts with 10, 50 and 200 mol% allylamines

allylamines had a better chance to react with each other, they did not vaporize off at the cure temperature range as indicated in the t.g.a. thermogram of the 3-BDS/200%A adduct (*Figure 9a*).

In the case of BDE/A adducts, their cure peak became extremely broad when BDE was adducted with 200 mol% allylamine (*Figure 7b*). Similar to the BDM/200%A adduct, the previous cure peak at 170–180°C was reduced and the major cure peak, which appeared at 200°C, was believed to be associated with the reactions of cleaved allylamine. Since the allylamino groups of BDE/A adducts were partly from a Michael addition reaction and partly from amidation, their cleavage temperature is presumably higher than that of the BDS/A adducts but lower than BDM/A adducts.

Properties of the cured BMI/A adducts

Although the BMI resins are able to undergo thermal

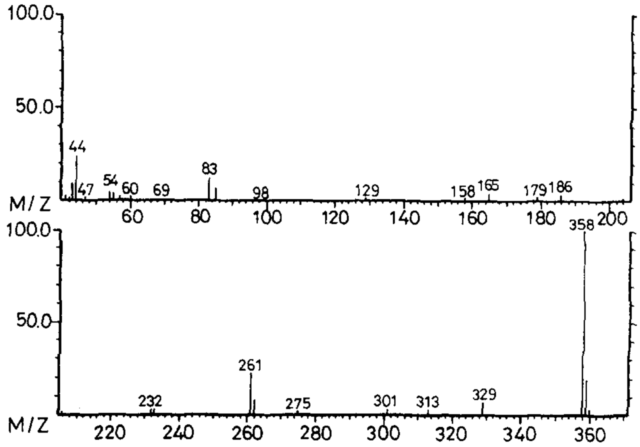


Figure 8 A typical mass spectrum of cured BDM/10%A[16]

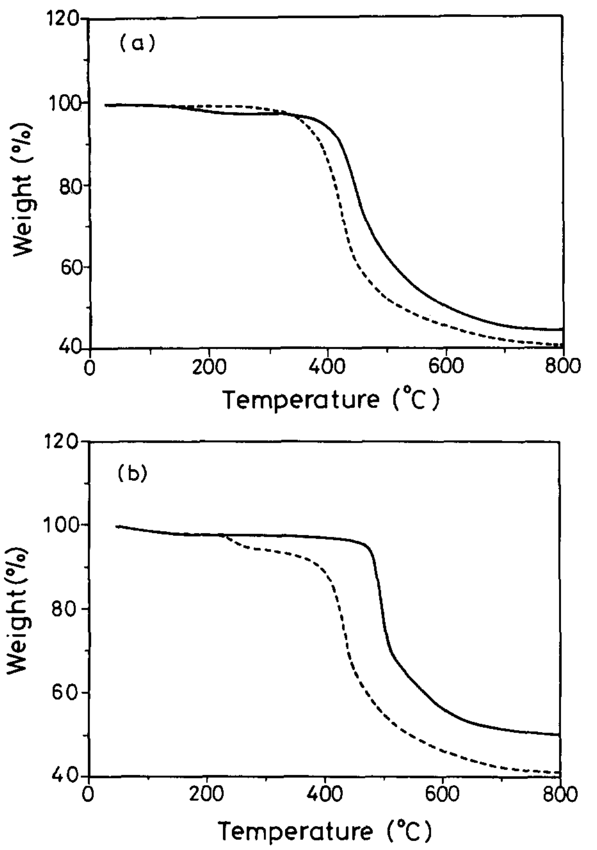


Figure 9 T.g.a. thermograms of the allylamine-adducted (a) 3-BDS and (b) BDM, both adducted with (——) 10 mol% and (- - -) 200 mol% allylamines

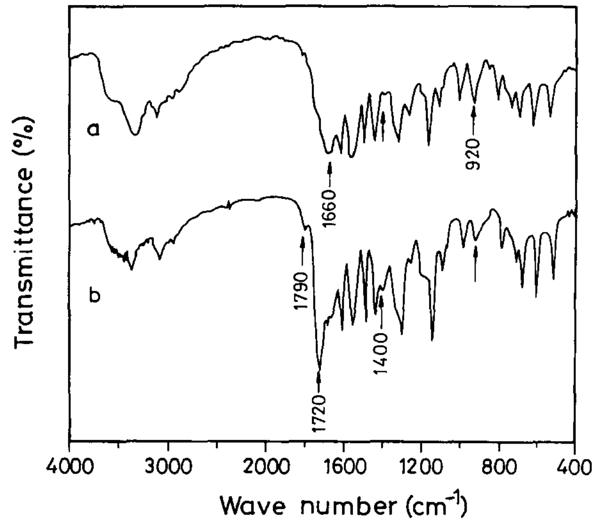


Figure 10 I.r. spectra of the 3-BDS/200%A adducts: (a) without cure and (b) cured at 180°C for 30 min

homopolymerization, they are too brittle to be moulded as a specimen for mechanical tests. Moreover, 3-BDS/200%A and 4-BDS/200%A adducts could not be moulded either, because part of the cleaved allylamines which did not participate in the curing reactions would create voids. Excluding the above, the T_g of cured (or moulded) BMI/A adducts under study, defined by the loss modulus peak of d.m.a. spectra, is measured and shown in *Figure 11*. Apart from the cured 3-BDS/A adducts, the BMI adducted with 10 mol% allylamine

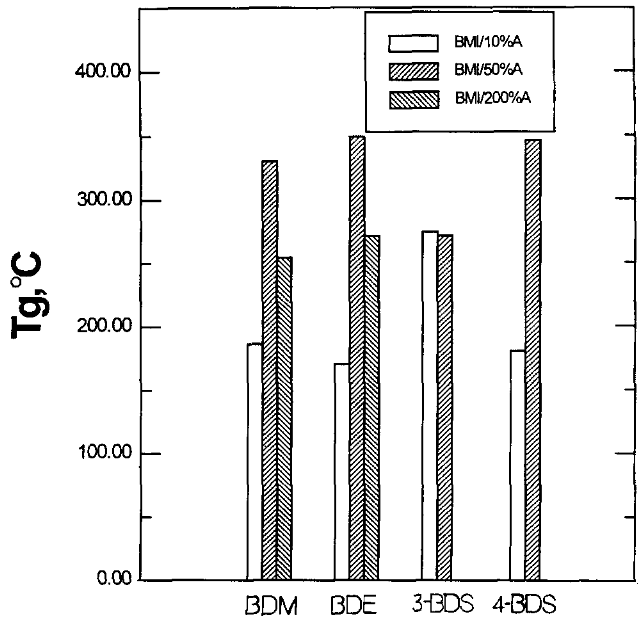


Figure 11 T_g of the cured BDM/A, BDE/A, 3-BDS/A, and 4-BDS/A adducts with 10, 50 and 200 mol% allylamines

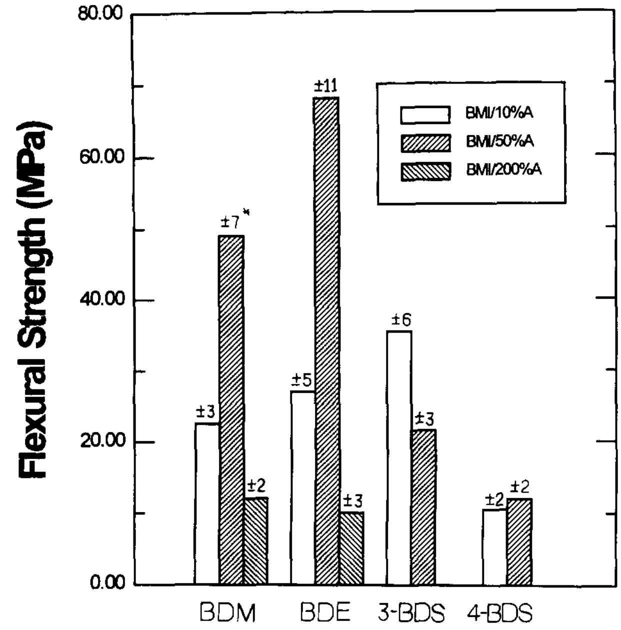


Figure 12 Flexural strength of the cured BDM/A, BDE/A, 3-BDS/A and 4-BDS/A adducts with 10, 50 and 200 mol% allylamines

have the lowest T_g. However, when the amount of adducted allylamine was increased to 50%, the T_g reached its highest value, more than 330°C (except for cured 3-BDS/A adduct). When it was further increased to 200%, the T_g of BDM/200%A and BDE/200%A adducts was reduced because of the lesser amount of curing (*Figure 7*). A similar trend was also found for the flexural strength of cured BMI/A adducts (except for cured 3-BDS/A adduct), where that of the cured BMI/50%A adducts was the highest (as shown in *Figure 12*). Although the similar heat exotherm during cure was found between BDM/10%A (and BDE/10%A) and BDM/50%A (and BDE/50%A), their T_g and flexural strength differ tremendously. It seems that the adducted

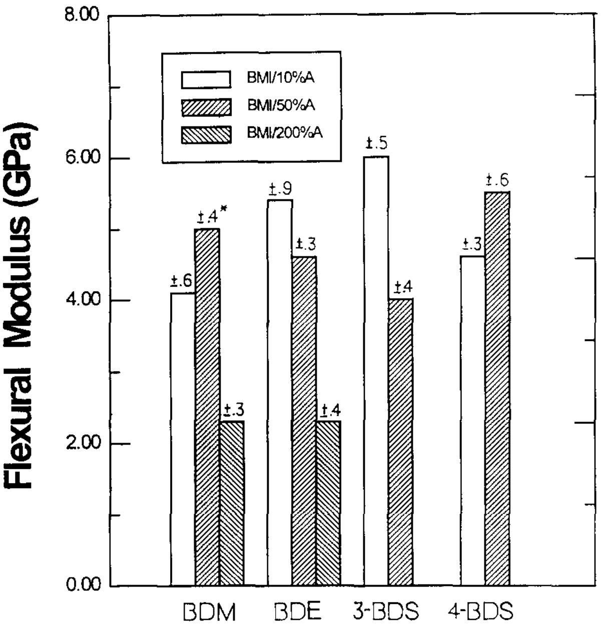


Figure 13 Flexural moduli of the cured BDM/A, BDE/A, 3-BDS/A and 4-BDS/A adducts with 10, 50 and 200 mol% allylamines

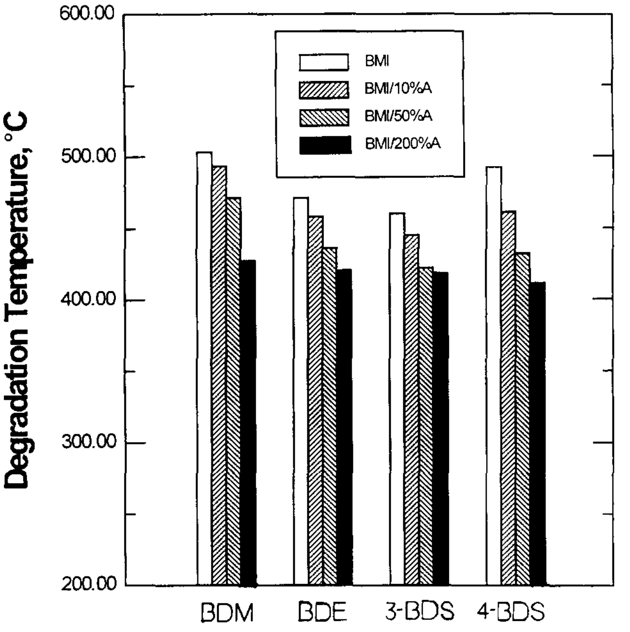


Figure 14 Degradation temperatures of BDM, BDE, 3-BDS and 4-BDS, and their adducts with 10, 50 and 200 mol% allylamines

allylamines in the BMI/50%A adducts were able to act as a cross-linker to increase the crosslinking density. On the other hand, all the cured BMI/A adducts are of a brittle material, as indicated by their high flexural moduli shown in *Figure 13*. The lowest flexural moduli found for the cured BDM/200%A and BDE/200%A might be a result of the low extent of cure and the possession of large quantity of unreacted allylamino groups.

The degradation temperature (T_d) of a series of BMI resins and their BMI/A adducts measured by t.g.a. at the maximum degradation rate is shown in *Figure 14*. The BDM resin has the highest T_d of 503°C. When it was adducted with 50% allylamine, the T_d only dropped to 471°C. The T_d of the BDE resin was 471°C. When it was adducted with 50% allylamine, the T_d dropped to 436°C. In spite of this, the cured BDE/50%A adduct has the highest T_g and flexural strength among all the BMI/A adducts. Although the cured 4-BDS/50%A adduct has a rather high T_g of 346°C and a T_d of 432°C, its flexural strength is extremely low (see *Figure 12*). Therefore, comparing the thermal and mechanical properties of all the cured BMI/A adducts under study, BDM/50%A and BDE/50%A adducts are superior and have the potential to be used as high temperature resin in aerospace, electronic, and other high-technology applications.

CONCLUSIONS

BDM, 3-BDS, and 4-BDS adducted with various amount of allylamines were synthesized by one of the following two reaction paths: Michael addition reaction for BDM reacting with allylamine, or amidation along with the cleavage of an imide-ring C–N bond, found for 3-BDS and 4-BDS reacting with allylamine. Only synthesis of the BDE/A adducts underwent both reaction paths. The allylamino groups adducted by the Michael addition reaction are more stable (cleavage at 245°C), whereas those by amidation, cleaved at 170°C prior to the cure reactions. Three types of reaction paths for curing of various BMIs and their BMI/A adducts probably occurred: (1) thermal homopolymerization of various BMI resins through the maleimide double bonds; (2) accelerated homopolymerization of the BMI portions by the adducted or then-cleaved allylamino groups; and (3) polymerization of the already cleaved allylamines from BMI/A adducts (especially for BDS/A adducts) through the double bonds of allyl groups or with the recovered maleimido groups.

As to the properties of BMIs and their BMI/A adducts, BMI resins, 3-BDS/200%A and 4-BDS/200%A are too brittle to be moulded. Except for 3-BDS/A adducts, the BMI/10%A adducts have the lowest T_g and flexural strength, whereas those of the BMI/50%A adducts are the highest. However, with a further increase the amount of adducted allylamine to 200 mol%, both the T_g and flexural strength were reduced owing to the lesser amount of curing. On the other hand, the T_d of BMI/A adducts decreased with the amount of adducted allylamine. However, the cured BDM/50%A and BDE/50%A adducts still had T_d of 471 and 436°C, respectively. With $T_g > 330°C$ and high flexural strength, they are believed to have a great potential for high temperature applications.

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