

Syntheses of an Aromatic Nitrile Ether Diamine and the Bismaleimide Bearing the Diamine and the Properties of Their Copolymers with 4,4'-Bismaleimidodiphenylmethane (BMDPM)

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ABSTRACT: A new chain-extension modifier for bismaleimide (BMI), 2,6-di-(4-amino-phenoxy)benzotrile (DAPB), was synthesized through nucleophilic substitution of 2,6-dichlorobenzotrile by 4-aminophenol using anhydrous sodium carbonate as an acid acceptor, toluene as a dehydrating agent, and *N,N'*-dimethylacetamide (DMAC) as a dipolar aprotic solvent. Based on the diamine, another modifier for bismaleimide, 2,6-bis(4-maleimidophenoxy)benzotrile (BMPB), was also synthesized, first by the reaction of DAPB with maleic anhydride and then by dehydration. DAPB and BMPB were used to modify a popular commercial BMI, 4,4'-bismaleimidodiphenylmethane (BMDPM), for improving the shear strength of the resin. The results showed that the shear strength of the DAPB-modified BMDPM resin was superior to that of either neat BMDPM or the 4,4'-diaminodiphenylmethane (DADPM)-modified BMDPM (a commercial modified BMDPM resin system). In addition, the heat resistance of the cured DAPB-modified BMDPM resin was higher than that of the cured DADPM-modified BMDPM resin. The excellent properties were also found in the BMPB-modified BMDPM resin. It was found that the BMPB-modified BMDPM resin was superior to neat BMDPM in both shear strength and heat resistance. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1317–1327, 2002

Key words: polyimides; modifications; additives

INTRODUCTION

Bismaleimide (BMI) resins are one of the most important thermosetting polymers because of their high thermal stability, nonvolatility, and

low cost.^{1,2} Some examples of applications include multilayer-printed boards for large-scale computers, encapsulation resin and passivation layers for IC dies, advanced carbon fiber composites for the aerospace industry, and structural adhesives.³ However, the brittleness of the pure resins is a major hazard in their applications. Therefore, in the past 30 years, many investigations focused on improvement of the toughness of the resins. As results, many additives have been found and well studied, including polyetherimide, polysiloxane-

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imide, allyl-terminated copolymers, and reactive rubbers,^{1,2,4-12} which are able to effectively enhance the toughness of the bismaleimides.

Poor shear strength is another disadvantage of neat BMI resins.^{2,12} However, a few reports focusing on overcoming this disadvantage can be found in the literature.^{2,12-18} Furthermore, some studies were not practical because of the use of expensive additives or complex processing procedures.¹⁴⁻¹⁸ In some cases, some modifiers, such as rubber and some thermoplastic polymers, could strongly decrease the heat resistance.^{2,12}

From the point of view of molecular design, introducing strong polar linkage or chains into BMI can improve the adhesion properties of the resins with the substrates.^{12,13} On the other hand, introducing aromatic heterocyclic groups into the resins can prevent strongly decreasing the heat resistance of the cured resins.¹ It is well known that the cyano group is "strongly polar"¹² and phenyl rings are "heat-resistant."¹ Hence, theoretically, the coreaction between BMI resins and the modifiers, containing cyano groups and aromatic rings, could give good shear strength and thermal stability to the cured resins.

Based on the assumption mentioned above, we attempted to add a class of additives containing cyano groups and aromatic rings to BMI. The results showed that the additives could greatly increase the shear strength of the resin without strongly decreasing the heat resistance of BMI.¹³

For purposes of further studying the properties of the additive derivatives containing cyano groups and aromatic rings, especially the properties of the additive-modified BMI resins, two monomers, 2,6-di-(4-aminophenoxy)benzotrile (DAPB) and a bismaleimide bearing the diamine, 2,6-bis(4-maleimidophenoxy)benzotrile (BMPB), were prepared in our laboratory. In this article, we report on the syntheses of DAPB and BMPB and the properties of their copolymers with a popular commercial BMI resin, 4,4'-bismaleimidodiphenylmethane (BMDPM).

EXPERIMENTAL

Materials

The 2,6-dichlorobenzotrile (DCBN) used was an industrial product and purified first by sublimation and then by recrystallization from ethyl alcohol. 4-Aminophenol was recrystallized from an-

hydrous ethyl alcohol under a N₂ atmosphere and dried under a vacuum. BMDPM was also an industrial product and was recrystallized twice from toluene before use. Other materials were used as received. AR-grade solvents were used.

Instrumentation and Test Methods

The melting point was measured by the capillary method and uncorrected. FTIR spectra were recorded on a Nicolet 20SDX-IR spectrophotometer using KCl pellets. ¹H-NMR and ¹³C-NMR were carried out on a Bruker ACP-300 spectrometer (300 MHz), using DMSO-*d*₆ (or CDCl₃) as the solvent and TMS as the internal standard. Curing behaviors of the prepolymers of BMDPM with DAPB [4,4'-diaminodiphenylmethane (DADPM) or BMPB] were studied using a DuPont DSC2910 differential scanning calorimeter at a heating rate 10°C/min under nitrogen. The thermal stability of the cured resins was determined on a DuPont TGA2950 thermogravimetric analyzer at a heating rate 10°C/min under air. The shear tests were carried out using a tension tester according to China State Standard GB1450.1-83.

Synthesis of DAPB

To a 1000-mL four-necked round-bottom flask, fitted with a condenser, nitrogen inlet, Dean-Stark trap, a thermometer, and a mechanical stirrer, DCBN (53 g, 0.31 mol), 4-aminophenol (77.0 g, 0.71 mol, 15% excess to DCBN) and DMAC (400 mL) were charged. Then, anhydrous Na₂CO₃ (75.0 g, 0.71 mol) and toluene (300 mL) were charged to the flask. The reaction mixture was stirred under the purge of N₂ and heated to reflux (about 120°C) and maintained at this temperature for 4 h. Then, the toluene was removed and the temperature was increased to 140°C for 30 h. After cooling to 50°C, the reaction mixture was poured into 2 L of ice water. The precipitate was filtered and washed with both a cold dilute sodium hydroxide solution (5 wt %) and water. The precipitate was dissolved in acetone, reprecipitated to remove unreacted 4-aminophenol and any trapped salts, filtered, and dried. After recrystallization from a mixture of solvents of CH₃OCH₂CH₂OH and water (2:1, v/v), DAPB was obtained as amber crystal needles: 68.5 g, mp 210–212°C; yield 70%.

ANAL. Calcd for C₁₉H₁₅N₃O₂: C, 71.92%; H, 4.76%; N, 13.25%. Found: C, 72.21%; H, 4.80%; N, 13.25%

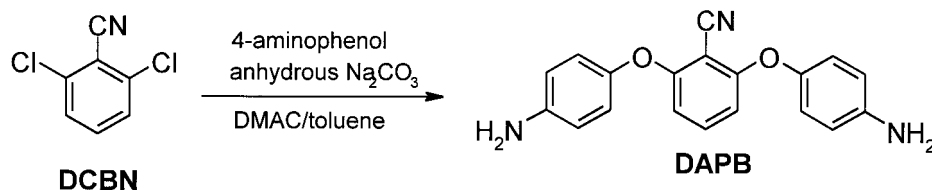


Figure 1 Procedure for preparation of DAPB.

FTIR (Fig. 2), cm^{-1} : 3469, 3410, 3333 ($-\text{NH}_2$), 1627, 1595 (aromatic ring), 1206, 1026 ($-\text{C}-\text{O}-\text{C}-$), 2223 ($-\text{CN}$). Mass spectrum (EI, Fig. 3), 317 (M^+ , base peak). The $^1\text{H-NMR}$ data are shown in Figure 4.

Synthesis of BMPB

A 500-mL three-necked flask equipped with a thermometer and a mechanical stirrer was charged with maleic anhydride (39.2 g, 0.4 mol) dissolved in tetrahydrofuran (200 mL). DAPB (31.7 g, 0.1 mol) was added in portions over 0.5 h at ambient temperature, and the solution slowly turned into a pale yellow slurry. The reaction was maintained at ambient temperature for 5 h, and the slurry was isolated by filtration. The precipitate was washed with acetone, then dried at 50°C under a vacuum. Bismaleamic acid bearing DAPB was obtained as a pale yellow powder in a yield of 90%.

FTIR (Fig. 7), cm^{-1} : 3309 ($-\text{COOH}$); 2233 ($-\text{CN}$); 1712 ($\text{C}=\text{O}$); 1650 (aromatic ring). The data of $^1\text{H-NMR}$ is shown in Figure 8.

The bismaleamic acid (24 g, 0.05 mol), dioxane (100 mL), sodium acetate (0.82 g, 0.01 mol), and acetic anhydride (20.4 g, 0.2 mol) were charged to

a 250-mL three-necked flask, equipped with a condenser, thermometer, and a magnetic stirring bar. The mixture was stirred at room temperature for 0.5 h and then allowed to react at 60°C for 20 h. After cooling, the solution was poured into 250 mL cold water. The precipitate was collected by filtration, washed with a dilute sodium bicarbonate solution, then with water, and finally recrystallized from a mixture of methyl alcohol and chloroform (3:1, v/v); BMPB was obtained as yellow crystals in a yield of 81.2%; mp $230-231^\circ\text{C}$.

FTIR (Fig. 7), cm^{-1} : 3076 ($-\text{CH}=\text{CH}-$ in the imide ring); 2233 ($-\text{CN}$); 1712, 1750, 690 (imide ring); 1650 (aromatic ring).

ANAL. Calcd for $\text{C}_{27}\text{H}_{15}\text{N}_3\text{O}_6$: C, 67.93%; H, 3.17%; N, 8.80%. Found: C, 67.81%; H, 3.26%; N, 8.61%.

Prepolymerization of BMDPM with DAPB (BMPB or DADPM) and Curing of the Prepolymers

Prepolymerization of BMDPM with DAPB (BMPB or DADPM) in certain compositions was done in a solution using methyl isobutyl ketone (MIBK) as a solvent. Refluxing BMDPM with DAPB (BMPB or DADPM) in the MIBK solution yielded a homogeneous solution after 4–5 h. The solvent was re-

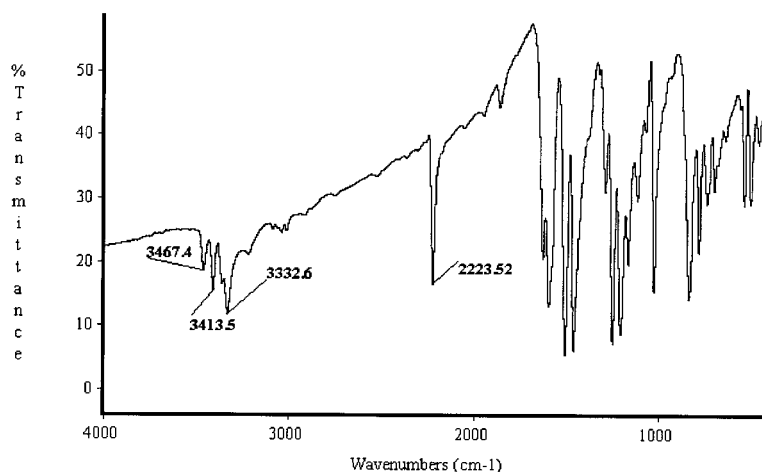


Figure 2 FTIR spectrum of DAPB.

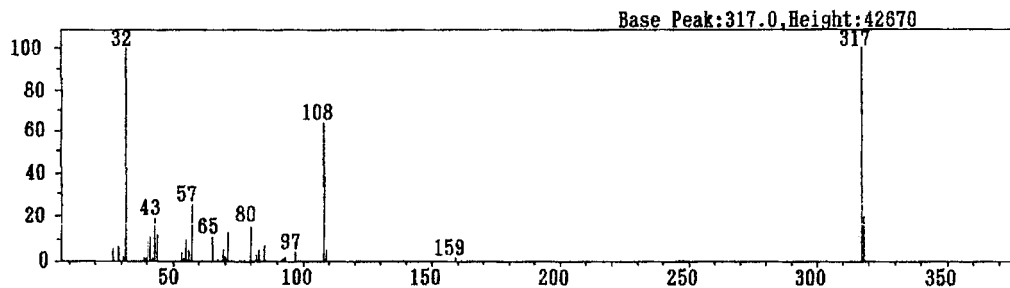


Figure 3 Mass spectrum of DAPB.

moved by using a rotary evaporator and a red brown solid of the prepolymers was obtained.

Curing of the Prepolymers (Under Air)

The prepolymers were ground in a glass mortar and the fine solid powder was introduced into an aluminum dish in an oven at 160°C. The temperature was kept at the temperature for 6 h. Then, the temperature was elevated and kept at 180°C for 4 h, 200°C for 2 h, 220°C for 5 h, and 240°C for 5 h.

Preparation of the Shear Strength Test Specimens

The fine prepolymer powder of BMDPM with DAPB (DADPM or BMPB) mentioned above (6.0 g) was placed on a metal plate with a temperature controller. The temperature on the surface of the plate was maintained at $160 \pm 2^\circ\text{C}$. After melting, the prepolymers were applied quickly to two pre-

heated (at 160°C) aluminum slices (the dimension of both the slices was $7.02 \times 2.02 \times 0.20$ cm, and the applied area of the prepolymer was 2.02×2.02 cm). The applied area of aluminum slices was quickly overlapped according to a general manner and moved to an oven at 160°C under air. The temperature was maintained at 160°C for 6 h. Then, the temperature was elevated and kept at 180°C for 4 h, 200°C for 2 h, 220°C for 5 h, and 240°C for 5 h. Thus, the specimens for testing the shear strength were obtained.

RESULTS AND DISCUSSION

Syntheses and Characterizations of DAPB and BMPB

The synthesis of DAPB was studied by several researchers.^{19–21} In summary, DAPB was pre-

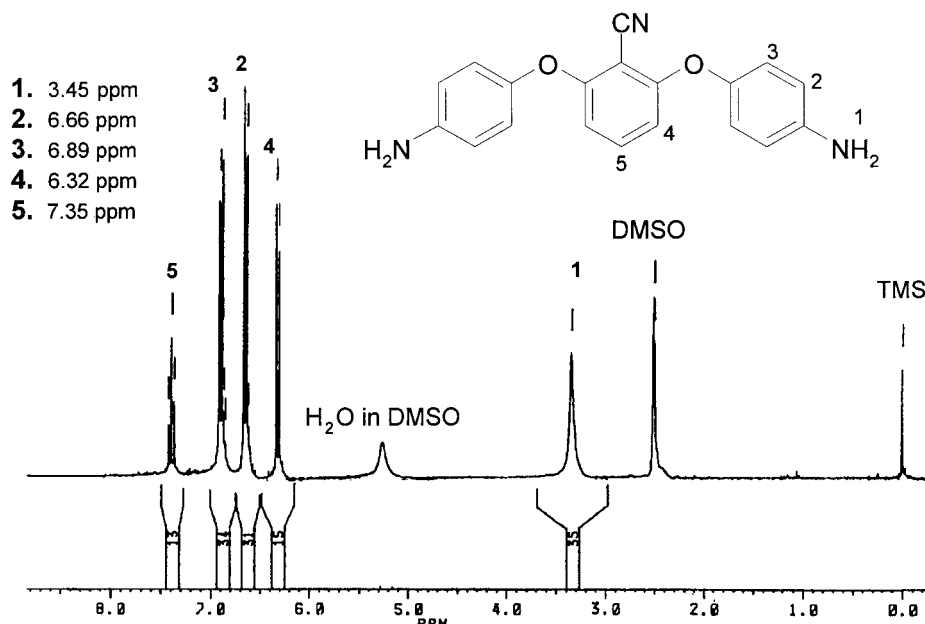


Figure 4 ¹H-NMR spectrum of DAPB (300 MHz, DMSO-*d*₆, 25°C).

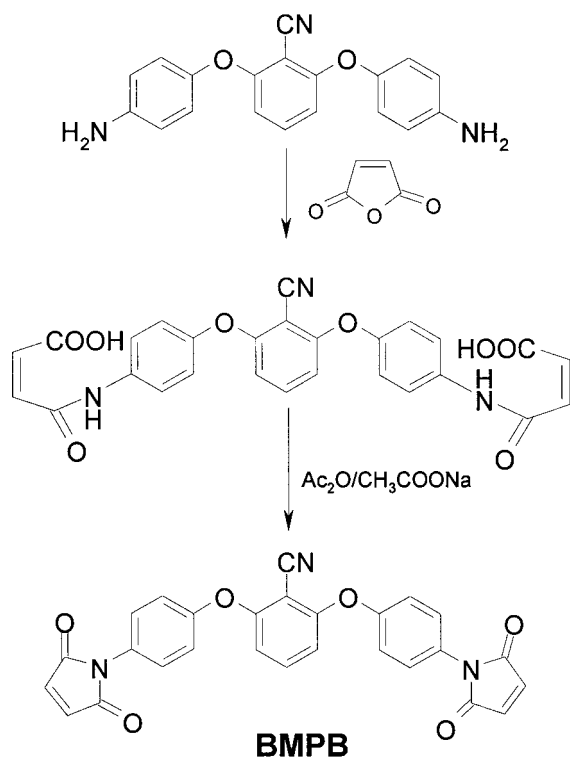


Figure 5 Procedure for preparation of BMPB.

pared by reacting 2,6-difluorobenzonitrile with 4-aminophenol in a dipolar aprotic solvent in the presence of some inorganic bases. However, the procedure was not practicable due to a complex pretreatment procedure for solvents and the use of an expensive raw material, 2,6-difluorobenzonitrile.¹⁹⁻²¹ In this work, we report a different procedure: A cheaper raw material, DCBN, was

used and the solvent, DMAC, was directly used without any pretreating procedure. In this route, the water contained in the solvent and formed by the reaction of 4-aminophenol with Na_2CO_3 was removed by the toluene-water azeotropic mixture. The procedure is shown in Figure 1.

It has been found in our work that two factors, the reaction time and the amount of oxygen in the reaction system, were more important for the preparation of DAPB. It was very necessary to keep the reaction system in the absence of oxygen by continuously introducing N_2 to the reaction system. Contrarily, a dark solution was formed in the initial stages of the reaction and the yield of DAPB was strongly decreased due to the forming oxide of 4-aminophenol. For increasing the yield of DAPB, it was also important to carry out the reaction for a longer time (more than 24 h). We attempted to synthesize DAPB in a short period (6 h), but the yield of DAPB was very low and the main product was 2-(4-aminophenoxy)-6-chlorobenzonitrile (pale yellow crystal needles, mp 121–122°C

ANAL. Calcd. for $\text{C}_{13}\text{H}_9\text{ClN}_2\text{O}$: Cl, 14.49%. Found: Cl, 14.27%.

The results mean that the nucleophilic substitution of DCBN by 4-aminophenolate was done step by step.

The chemical structure of DAPB was characterized by FTIR, the mass spectrum, and the $^1\text{H-NMR}$ spectrum. Figure 2 is the FTIR spectrum of DAPB. Characteristic absorption peaks appear at 2223 cm^{-1} due to the resonance of the $-\text{CN}$ group in DAPB, and characteristic absorptions at 1206 and 1026 cm^{-1} are assigned to $-\text{C}-\text{O}-\text{C}-$

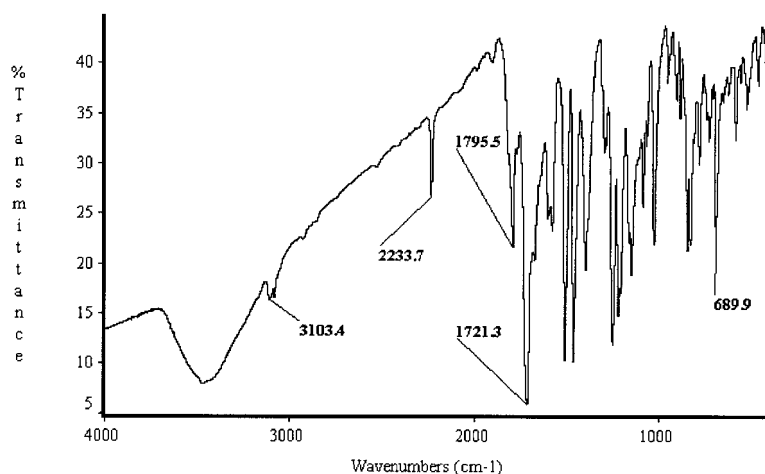


Figure 6 FTIR spectrum of *iso*-BMPB.

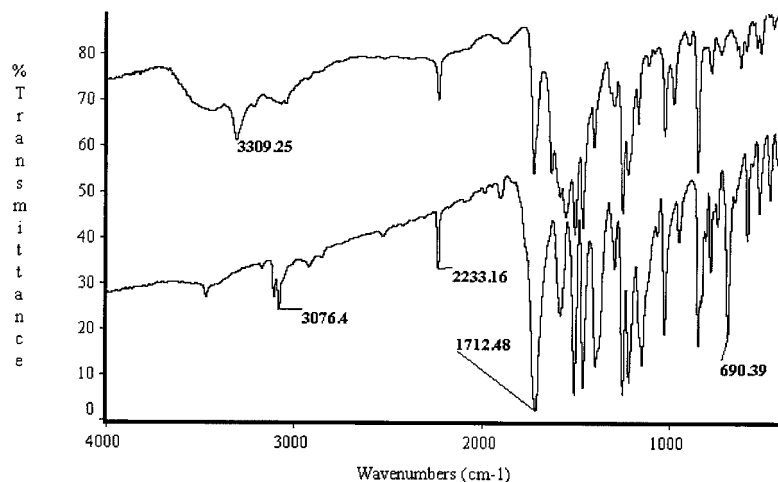


Figure 7 FTIR spectrum of BMPB: (top) bismaleamic acid; (bottom) BMPB.

stretching. The absorption bands at 3469, 3410, and 3333 cm^{-1} are assigned to —NH_2 . Characteristic absorptions at 1627 and 1595 cm^{-1} are assigned to aromatic ring backbone stretching. The mass spectrum of DAPB in Figure 3 confirms the structure proposed (M^+ 317, relative intensity 97.2%). The $^1\text{H-NMR}$ spectrum of DAPB in Figure 4 shows five different proton signals, as expected. The relationship between the positions

of the signals and the chemical structure of DAPB is given in Figure 4.

Figure 5 presents the procedure for the preparation of BMPB, which is the same as that of the general BMIs.^{7,22} The only difference is that the synthesis of BMPB needs more reaction time. It is interesting that isoimide, an isomer of BMPB, was found in the preparation of BMPB, when the dehydrating reaction time of the bismaleamic

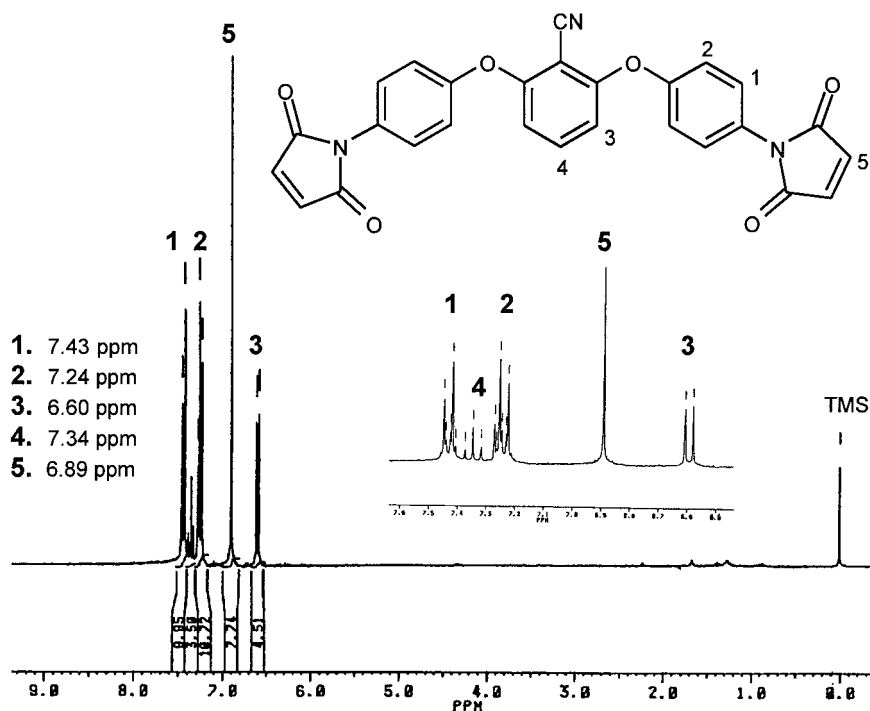


Figure 8 $^1\text{H-NMR}$ spectrum of BMPB (300 MHz, CDCl_3 , 25°C).

Table I Comparison of Shear Strength Between Neat BMDPM Resin and the Modified BMDPM Resins

| Polymers | Shear Strength (MPa) |
|---|----------------------|
| $n(\text{BMDPM})/n(\text{DAPB}) = 3.7:1$ | 7.01 |
| $n(\text{BMDPM})/n(\text{DADPM}) = 3.7:1$ | 5.10 |
| BMDPM | 2.65 |

acid was less than 5 h. Figure 6 shows the FTIR spectrum of the isomer. The characteristic absorption peaks that appeared at 1795, 1721, and 690 cm^{-1} prove the formation of the isoimide in the reaction system.²³ It was found in our work that the isomer was a sticky yellow substance when it was just separated from the reaction mixture by pouring the mixture into cool water. However, the sticky yellow substance slowly solidified after removing the water and the maleamic acid. The solidified substance had a broad range of melting temperatures (from 110 to ca. 140°C , measured by the capillary method) and was dissolvable in the common organic solvents. It was also observed that the concentration of the isomer was slowly decreased and the amount of BMPB increased with an increasing reaction time in the reaction system. Therefore, a longer reaction period (ca. 20 h) is very necessary for obtaining a higher yield of BMPB.

The chemical structure of BMPB was also characterized by FTIR and the $^1\text{H-NMR}$ spectrum. The FTIR spectrum in Figure 7 shows that the characteristic absorption of the $-\text{CN}$ group in BMPB appears at 2223 cm^{-1} and the characteristic absorptions of the imide rings in BMPB appear at 690, 1712, and 1750 cm^{-1} . The $^1\text{H-NMR}$ spectrum of BMPB in Figure 8 shows five different proton signals, as expected. The relationship between the positions of the signals and the chemical structure of DAPB is marked in Figure 8.

Mechanical Properties of the DAPB (BMPB)-modified BMDPM Resins

Until now, no report about introducing DAPB (or BMPB) to BMDPM has been found in the literature. However, it is well known that a commercial diamine, DADPM (4,4-diaminodiphenylmethane), was used to modify BMDPM and the modified resins are popular in industry.¹² The reaction of BMDPM with DADPM is more complicated and in-

cludes the Michael addition reaction between the diamine (DADPM) and the couple bonds of BMDPM and the homopolymerization reaction of BMDPM.¹² To compare the strength of DAPB-modified BMDPM resin with that of the DADPM-modified BMDPM resin, in this work, the molar ratio between DAPB and BMDPM was controlled at 1:3.7, which was the same as the optimum ratio used usually in the DADPM-modified BMDPM resin system.⁶ The results are listed in Table I. It was found that DAPB can effectively improve the shear strength of the BMDPM resin. In addition, the shear strength of the DAPB-modified BMDPM resin is also superior to that of the DADPM-modified BMDPM resin, which means that introducing DAPB to BMDPM can give the matrix good adhesion properties.

Similarly, BMPB-modified BMDPM resins give good results. Figure 9 shows the shear strength depending on the composition of BMPB/BMDPM copolymers by weight. It was found that the curve shows the maximum in shear strength when the ratio of BMPB/BMDPM in the copolymer is 30 wt %. As compared with the neat BMDPM matrix, the copolymer matrix can attain 1.6 times the shear strength.

Thermal Analyses of the DAPB (BMPB)-modified BMDPM Resins

Curing Reaction of the DAPB (BMPB)-modified BMDPM Resins

In Figure 10, the endothermic peaks correlated with the DAPB/BMDPM prepolymer and the DADPM/BMDPM prepolymer are also observed

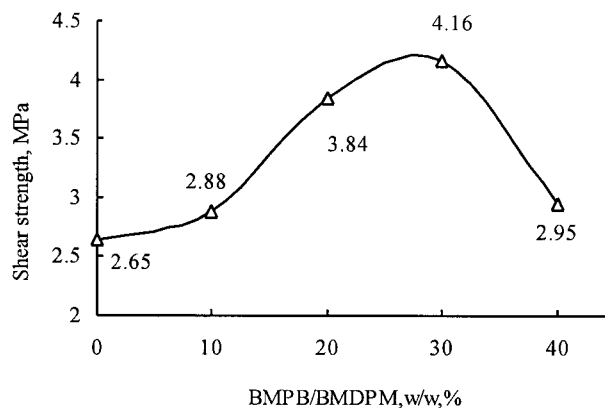


Figure 9 Relationship between shear strength of the BMPB-modified BMDPM resin and the BMPB/BMDPM ratio (w/w, %).

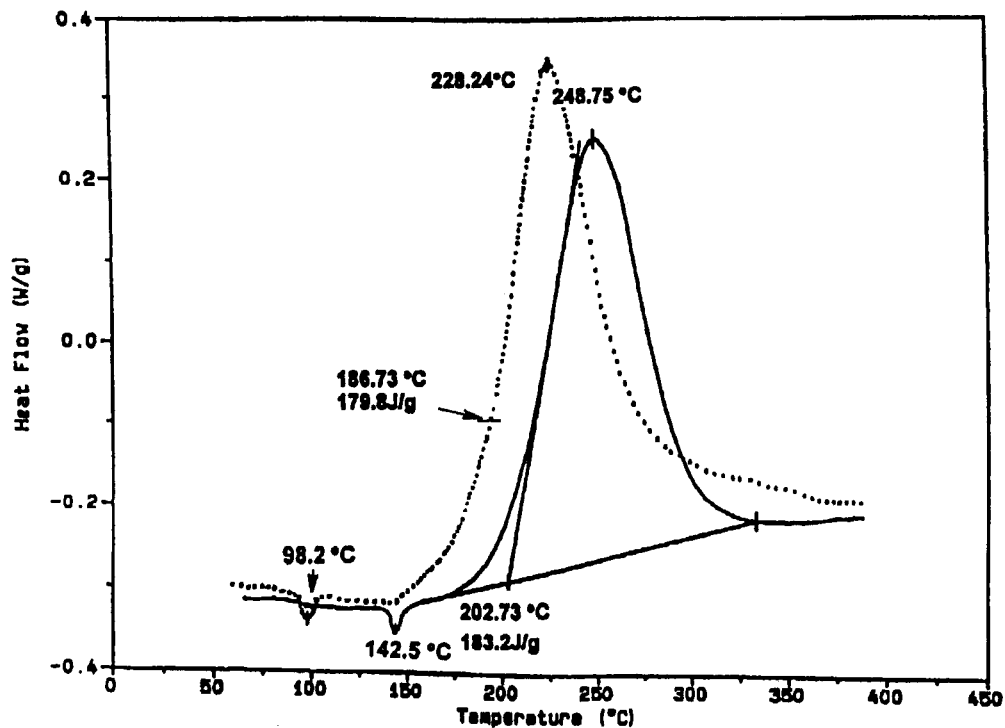


Figure 10 DSC traces of (—) DAPB-modified BMDPM resin and (.....) DADPM-modified BMDPM resin.

at 98 and 142°C, respectively. This means that the melting temperature of the prepolymers is lower than that of BMDPM. Figure 11 shows DSC traces of BMPB on heating. The endothermic peak at 231°C is attributed to the melting of BMPB. The exothermic peak at 299°C shows that

the thermohomopolymerization of BMPB is completed at a very high temperature. However, it is interesting that an endothermic peak is observed at 154°C [Fig. 12(b)] for the BMPB/BMDPM prepolymer (30%, w/w), which indicates that a BMPB/BMDPM comelting substance with a melt-

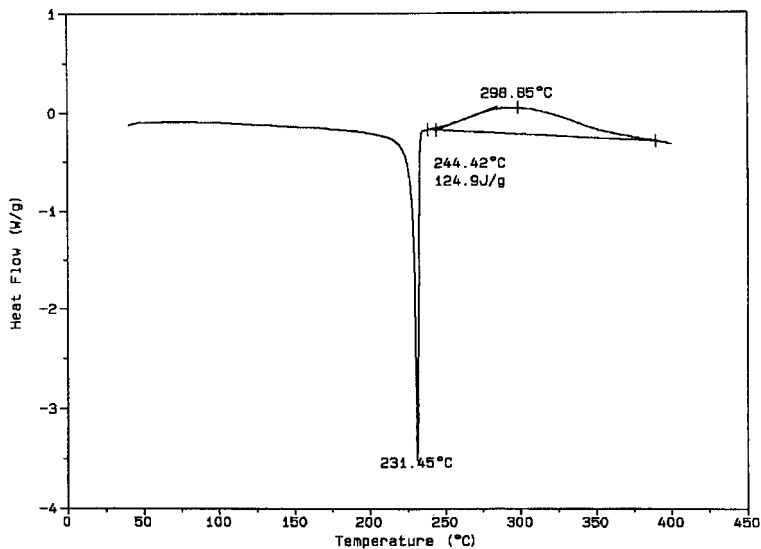


Figure 11 DSC traces of BMPB.

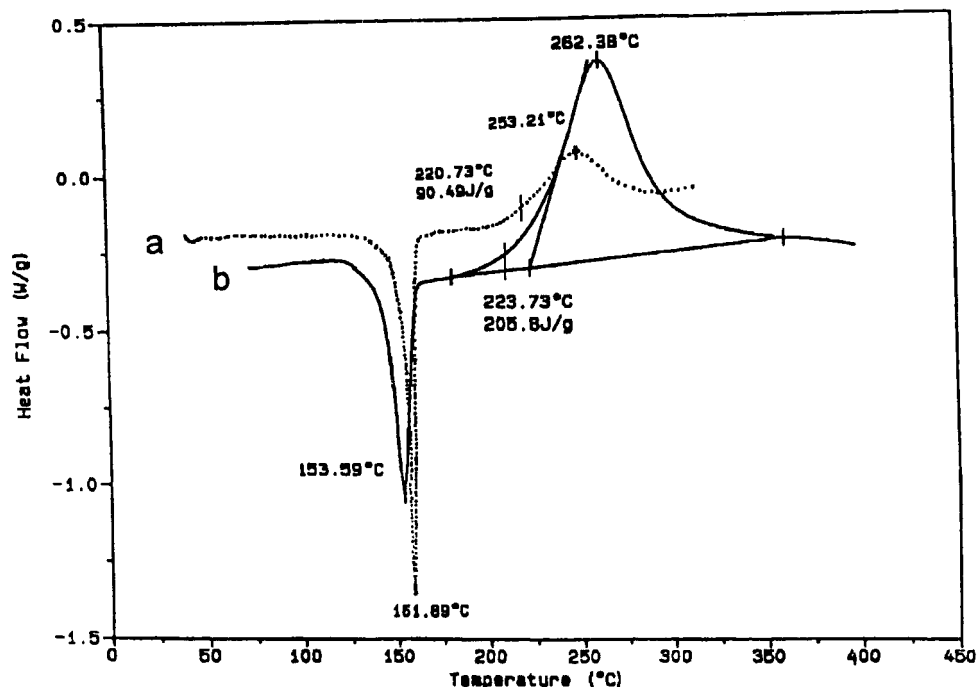


Figure 12 DSC traces of (a) neat BMDPM resin and (b) BMPB-modified BMDPM resin.

ing point of 154°C is formed. It is also interesting that the melting point of the comelting substance is also lower than that of BMDPM [162°C; see Fig. 12(a).]

In Figures 10–12, exothermic transitions of the curing of the prepolymers are observed in the temperature range of 200–350°C. The heat of the curing reaction (ΔH), fusion temperature of the prepolymers (T_m), onset temperature of the curing reaction, and exothermal peak position (T_{exo}) are determined from the DSC traces and are listed in Table II. It is interesting that the change

of the ΔH value of the curing resin is consistent with the change of molecular weight of the monomers added to the resins. This could be explained by the dimension of the ΔH value in the DSC. Because the DSC curves give the heat of reaction in J/g, the ΔH value would be parallel with the molecular weight of the monomers added to the resins. For example, the molecular weight of DADPM (198) is less than that of DAPB (317); therefore, the ΔH value of the DADPM/BMDPM resin (179.8 J/g) is less than that of DAPB/BMDPM (183.2 J/g). Analogously, the ΔH value

Table II Comparison of Thermal Characteristics Between Neat BMDPM Resin and the Modified BMDPM Resins

| Polymers | T_m (°C) | Onset Temperature (°C) | T_{exo} (°C) | ΔH (J/g) |
|--|---------------|---------------------------|--------------------------|---------------------|
| BMDPM | 162 | 221 | 253 | 90.5 |
| BMPB | 232 | 244 | 299 | 124.9 |
| BMPB/BMDPM (30%, w/w) | 154 | 223 | 262 | 205.8 |
| $n(\text{DAPB})/n(\text{BMDPM})$ = 1:3.7 | 142 | 203 | 249 | 183.2 |
| $n(\text{DADPM})/n(\text{BMDPM})$ = 1:3.7 | 98 | 187 | 228 | 179.8 |

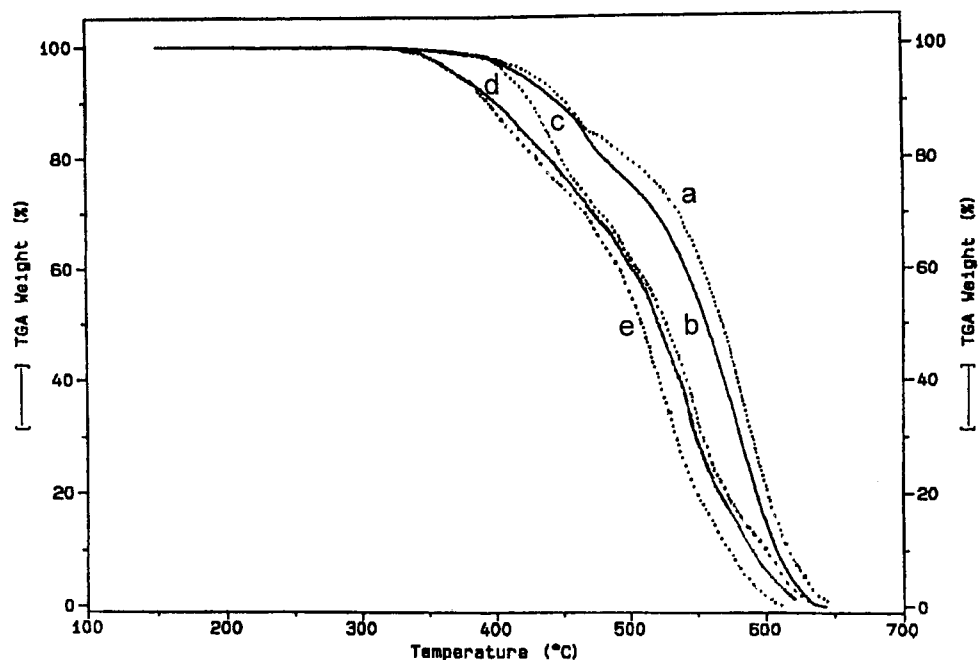


Figure 13 TGA curves of the BMPB (DAPB)-modified BMDPM resins: (a) BMPB; (b) BMPB/BMDPM; (c) BMDPM; (d) DAPB/BMDPM; (e) DADPM/BMDPM).

of BMPB (124.9 J/g) is more than that of BMDPM (90.5 J/g), just because the molecular weight of BMPB (477) is more than that of BMDPM (358).

There was a doubt in our work whether —CN groups participated in the polymerization reaction of the DAPB (BMPB)/BMDPM resin. By using FTIR spectra, it was found that the characteristic absorption of —CN groups in the cured resin appeared at 2233 (2228) cm^{-1} . This means

that —CN groups did not participate in the polymerization reaction.

Thermal Oxidative Stability of the DAPB (BMPB)-modified BMDPM Resins

The relative thermal stability for the cured modified BMDPM resins was evaluated by thermogravimetric analyses. The results are given in Figure 13 and Table III. The high heat-resistant

Table III TGA Data of Neat BMDPM Resin and the Modified BMDPM Resins

| Polymers | Weight Loss Temperature ($^{\circ}\text{C}$) | | | | | | | |
|--|--|----------|----------|----------|----------|-------------------|-------------------|-------|
| | T_5 | T_{10} | T_{15} | T_{30} | T_{50} | $T_{\text{max}1}$ | $T_{\text{max}2}$ | T_i |
| BMDPM | 395 | 415 | 428 | 465 | 516 | 432 | 542 | 214 |
| BMPB | 431 | 452 | 469 | 534 | 567 | 453 | 583 | 241 |
| BMPB/BMDPM (30%, w/w) | 421 | 448 | 466 | 520 | 557 | 468 | 580 | 235 |
| $n(\text{DAPB})/n(\text{BMDPM})$ = 1:3.7 | 370 | 398 | 418 | 478 | 525 | 409 | 539 | 213 |
| $n(\text{DADPM})/n(\text{BMDPM})$ = 1:3.7 | 367 | 391 | 409 | 464 | 511 | 412 | 533 | 208 |

T_5 , T_{10} , T_{15} , T_{30} , and T_{50} are the temperatures when weight loss was 5, 10, 15, 30, and 50%, respectively. $T_{\text{max}1}$ and $T_{\text{max}2}$ are the decomposition peak temperature. T_i is the heat-resistant temperature index calculated according to $T_i = 0.49[T_5 + 0.60(T_{30} - T_5)]$.

index (T_i) indicates that the BMPB-modified BMDPM resin has a higher level of thermal oxidative stability than that of neat BMDPM resin. It was also found that the thermal oxidative stability of the DAPB-modified BMDPM resin is superior to that of the DADPM-modified BMDPM resin. Therefore, it is obvious that introducing DAPB (or BMPB) to the BMDPM resin not only improves shear strength of the resin, but also gives good heat resistance to the resin.

CONCLUSIONS

The following conclusions can be given based on this work:

1. DAPB was synthesized through a convenient procedure using a cheap raw material, 2,6-dichlorobezonitrile. The bismaleimide bearing DAPB (BAPB) was also prepared.
2. DAPB can effectively improve the shear strength of BMDPM, and the strength of the DAPB-modified BMDPM resin is superior to that of the popular commercial DADPM-modified BMDPM resin system. Furthermore, the heat resistance of the DAPB-modified BMDPM resin is higher than that of the DADPM-modified BMDPM resin.
3. BMPB not only improved the shear strength of the BMDPM resin, but also increased the heat resistance of the resin.

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