

# Bismaleimide-Modified Methyl-Di(phenylethynyl)silane Blends and Composites: Cure Characteristics, Thermal Stability, and Mechanical Property

Quan Zhou, LiZhong Ni

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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**ABSTRACT:** Reactive blends of organic-inorganic hybrid monomer, methyl-di(phenylethynyl)silane (MDPES) and a modified bismaleimide resin (BMI/DBA) have been prepared. The thermal and oxidative stabilities of MDPES-BMI/DBA blends were characterized by thermogravimetric analysis, derivative thermogravimetry, differential thermal analysis, dynamic mechanical analysis, and flexural strength retention at 240°C. Scanning electron microscopy was employed to study the surface morphology of MDPES-BMI/DBA composite after thermal oxidative treat-

ment. With the increase of concentration of BMI/DBA, flexural strength of composites increased from 78 to 331 MPa. The results showed that MDPES-BMI/DBA blends exhibited excellent thermal and thermal oxidative properties, and the interface between MDPES and glass fiber was improved by the incorporation of BMI/DBA. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3721–3727, 2009

**Key words:** thermal stability; high temperature materials; blends; MDPES; composites

## INTRODUCTION

Rapid progress in modern technologies has created a significant demand for processable materials that can be converted into shaped components having high thermal and oxidative stabilities. Current commercial organic-based polymers are limited to use temperatures below 300°C.<sup>1,2</sup> Introduction of the inorganic nanomaterials into polymer matrix can lead to substantially enhanced thermal and mechanical properties of the polymer material, due to the mini-size effect, surface, and interface effects of the nanocomposites.<sup>3–5</sup> In recent years, a number of organosilicon-acetylenic hybrid polymers composed by  $-\text{SiR}_2-\text{C}\equiv\text{C}-$  ( $\text{R} = \text{alkyl, aryl}$ ) have been developed. Corriu and coworkers<sup>6,7</sup> reported that organosilicon polymers containing a  $\pi$ -electron system, in which a regular alternating arrangement of a silylene unit and a diacetylene group  $[-(\text{SiR}_1\text{R}_2)_m-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-]_n$  ( $\text{R}_1 = \text{R}_2 = \text{alkyl, aryl}$ ,  $m = 1, 2$ ) were synthesized by coupling reaction involving the use of the dilithiobutadiyne and various dihalosi-

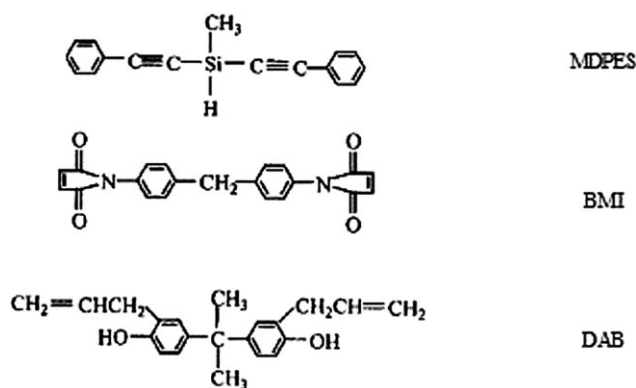
lanes. The pyrolysis of  $[-\text{Si}(\text{CH}_3)_2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-]_n$  under a stream of argon to 1400°C gave a  $\beta$ -SiC containing ceramic in high yield (84%). Itoh and coworkers<sup>8,9</sup> also found that nine new kinds of thermosetting polymers with the  $\text{Si}(\text{H})-\text{C}\equiv\text{C}$  unit were synthesized by dehydrogenative polycondensation reactions between hydrosilanes and diethynyl compounds in the presence of a magnesia catalyst.

Previous work in our group<sup>10–13</sup> has focused on approach to synthesize methyl-di(phenylethynyl)silane (MDPES) and methyl-tri(phenylethynyl)silane (MTPES) by lithium phenylacetylide with methyl-dichlorosilane and methyltrichlorosilane. Thermosets exhibit excellent thermal properties and thermogravimetric analysis (TGA) curves show the temperature of 5% weight loss ( $T_{d5}$ ) in nitrogen was 615 and 695°C for MDPES and MTPES, respectively. The pyrolysis of cured MTPES under a stream of argon to 1450°C gave a ceramic in high yield (81%). The results of thermal conversion of polymer to ceramic showed that pyrolytic products were made up of  $\beta$ -SiC, graphite, and glassy carbon. Therefore, organosilicon-acetylenic hybrid polymers are one class of ideal candidates of high temperature matrix and ceramic precursors. However, unfavorable mechanical properties corresponding to poor adhesive force between MDPES and glass fibers limited the application as high performance matrix resin. To our knowledge, most of the published literatures referred to synthesis, reaction mechanism, kinetics,

Correspondence to: L. Ni (nilizhong@online.sh.cn).

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Scheme 1 Chemical structure of MDPES, BMI, and DAB.

and thermal stability of organosilicon-acetylenic hybrid polymers. Information concerning on the modification or blends remains vacant except Dai's research. Dai et al.<sup>14,15</sup> reported that the interface properties between MDPES and glass fiber were improved by di[(*N*-*m*-acetonylphenyl)phthalimide]ether belonging to one kind of polyimide. However, because of its chain rigidity and strong interchain interaction, most polyimides were insoluble in common organic solvents and intractable in their imide forms. Therefore, further applications of MDPES by modification of polyimide were limited because of its poor processability and solubility. It is highly desirable to exploit a new approach to modify MDPES resin, which involved the formation of homogenous blends and was expected to have high temperature resistance, good mechanical properties, and processability.

Bismaleimide resins (BMIs) are a leading class of thermosetting materials based on low molecular weight building blocks and terminated by reactive groups which undergo polymerization by thermal or catalytic means. BMIs have the advantages of good thermal stability, high cross-linking ability, superior specific strength and specific modulus, good retention of mechanical properties, and low water absorption. However, unmodified BMI resins suffer from brittleness and poor processability because of high cross-linking density after curing, poor solubility in ordinary solvents and narrow processing window. Previous studies showed that 2, 2'-diallyl bisphenol A (DAB) was one of the most effective modifiers of BMI to improve toughness and processability although maintaining other good properties.<sup>16</sup>

In this article, continuing our research on MDPES, a novel homogeneous blends containing MDPES and 2, 2'-diallyl bisphenol A modified 4,4'-bismaleimido-diphenylmethane resin (BMI/DBA) have been prepared. Cure behavior of MDPES-BMI/DBA was monitored by DSC. Thermal and thermal oxidative properties were systematically investigated by TGA,

differential thermal analysis (DTA), derivative thermogravimetry (DTG), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM). The mechanical properties of MDPES-BMI/DBA composites were investigated as a function of their composition. Moreover, dielectric property, moisture absorption, and phase morphology will be reported in other literatures.

## EXPERIMENTAL

### Materials

MDPES was prepared according to the literatures.<sup>10,11</sup> 4,4'-bismaleimidodiphenylmethane (BMI) was purchased from HongHu Chemicals (China) and used as received. 2, 2'-diallyl bisphenol A (DAB) was purchased from SiChuan JiangYou Chemical Factory (China) and used without further purification. Plain-weave, silane treated E-glass fabric (0.18 mm, ZheJiang JuShi Glass Fiber Co.) (China) was used without any treatment. The chemical structures of MDPES, BMI, and DBA are presented in Scheme 1.

### Preparation of MDPES prepolymer

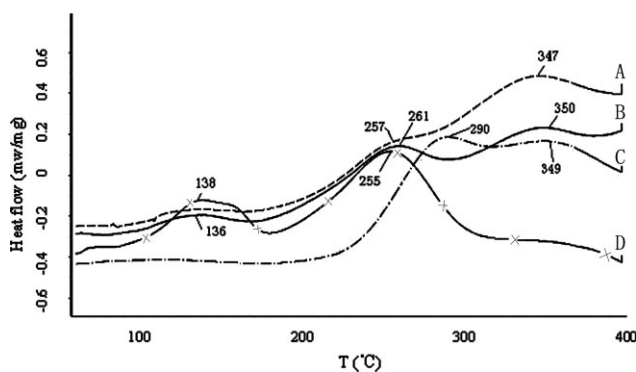
MDPES was placed in four-neck flask with a mechanical stirrer, thermometer, and reflux condenser under nitrogen atmosphere. Prepolymer was obtained by thermal polymerization at 300°C for 2 h.

### Preparation of MDPES-BMI/DBA blends

The weight percentage ratio of BMI and DBA was kept at 57 : 43 (1 : 0.85M ratio). The mixture was placed in a flask equipped with a mechanical stirrer, thermometer, and reflux condenser. The mixture was heated to 140°C and maintained for 25 min to obtain a transparent brown liquid. When the mixture was cooled to 70°C, acetone was added to the flask to give a solution with 50% resin content. After then, the preweight amount of MDPES prepolymer was added into the above mixture with stirring to obtain a brown-red homogenous liquid. Table I listed the formulations of different weight ratio of MDPES-BMI/DBA.

TABLE I  
Formulations of MDPES-BMI/DBA Blends

| Resin system | Weight percentage ratio |
|--------------|-------------------------|
| BM-15        | BMI/DBA : MDPES = 1 : 5 |
| BM-25        | BMI/DBA : MDPES = 2 : 5 |
| BM-35        | BMI/DBA : MDPES = 3 : 5 |
| BM-45        | BMI/DBA : MDPES = 4 : 5 |
| BM-55        | BMI/DBA : MDPES = 5 : 5 |



**Figure 1** DSC curves of MDPES-BMI/DBA with different weight ratios (A : BM-15; B : BM-35; C : MDPES; and D : BMI/DBA).

### Preparation of MDPES-BMI/DBA thermosets

MDPES-BMI/DBA thermosets were prepared by curing the molten blends in glass sheet molds applying a silicone mold release agent. The molten blends were degassed under vacuum at 150°C. The following cure schedule was used in air 200°C/2 h → 220°C/2 h → 240°C/4 h → 260°C/2 h → 280°C/2 h → 300°C/4 h (Heating rate: 1°C/min). The thermosets were cooled to the ambient temperature at a rate of 2°C/min.

### Preparation of MDPES-BMI/DBA laminates

MDPES-BMI/DBA blends (38% by weight) were dissolved into acetone to form homogeneous solution. The prepregs were made by dipping the fabric into above solution. The prepregs were dried at room temperature for 12 h and further heated in the vacuum oven at 70°C until no weight loss. The prepregs were stacked and molded between thick metallic plates to achieve a proper number of piles and thickness. The pressure of 6 Mpa was applied for com-

paction of the piles immediately after the system attained 200°C. Cure schedule was as follows: 200°C/2 h → 220°C/2 h → 240°C/4 h → 260°C/2 h → 280°C/2 h → 300°C/4 h (Heating rate: 1°C/min).

## Characterizations

### DSC measurements

DSC measurement was performed with a Perkin-Elmer DSC-7. The DSC was calibrated with high purity indium. Sample (8–10 mg) was weighed into small DSC aluminum pans, sealed with holed aluminum lid and experiment was conducted under a nitrogen flow of 20 cm<sup>3</sup>/min. In the dynamic analysis, the sample was scanned at 10°C/min.

### TGA, DTG, and DTA measurements

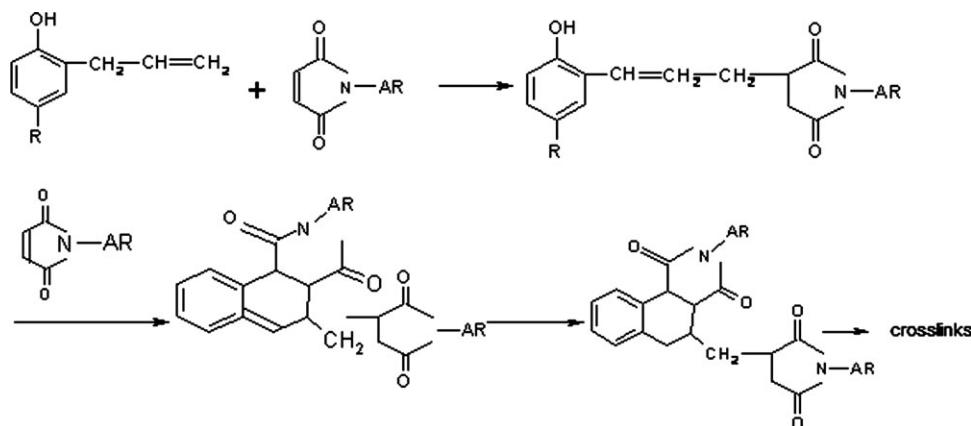
TGA, DTG, and DTA were performed on a Perkin-Elmer Pyris Diamond. The thermosets were heated from room temperature to 1200°C at heating rate of 10°C/min at the atmosphere of nitrogen and air. The gas flow rate was 60 mL/min.

### DMA measurements

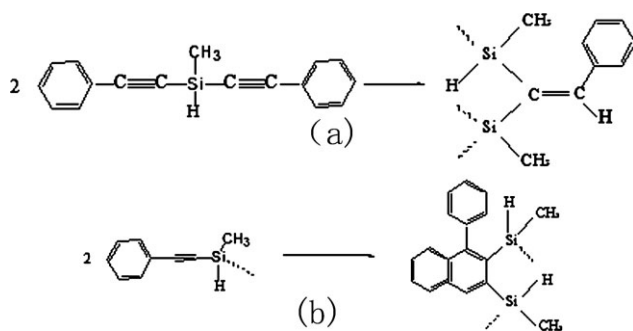
DMA was performed with a Rheogel-4000 and the storage modulus  $E'$  and  $\tan \delta$  were determined as the sample was subjected to temperature scan mode at a programmed heating rate of 5°C/min from ambient to 350°C at a frequency of 11 Hz in the atmosphere of nitrogen. A sample 30 × 8 × 3 mm was used. The test method was carried out by a flexural mode.

### Flexural strength analysis

The flexural strength was measured on XinSanSi (China) testing machine, model CMT 4204. The dimension of the sample was 80 × 15 × 3 mm. The span length was set to 50 mm. A crosshead speed of



**Figure 2** Reactions of BMI and DAB.



**Figure 3** Reactions of MDPES (a) Si-H addition reaction and (b) Diels-Alder reaction.

10 mm/min was used during determining flexural strength.

#### Scanning electron microscope

The surface morphology of MDPES-BMI/DBA composite was studied with a JEOL, JSM-6360LV scanning electron microscope. The surface was coated with platinum prior to imaging.

## RESULTS AND DISCUSSIONS

### Cure characterization

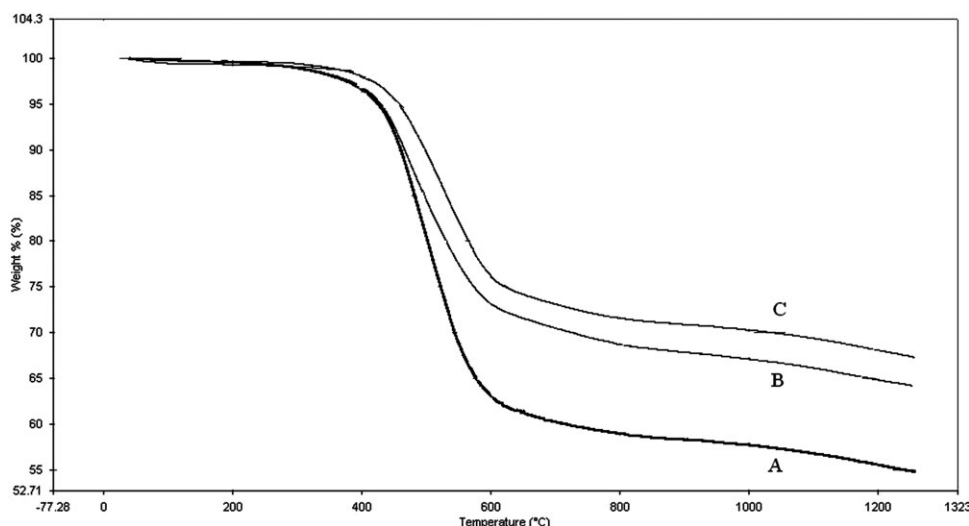
Figure 1 showed the overlay of the DSC curves of BM-15, BM-35, MDPES, and BMI/DBA at a heating rate of 10°C/min from room temperature to 400°C in nitrogen. It can be seen that BMI/DBA has two exothermic peaks, one peak at higher temperature (around 255°C), which was attributed to "Diels-Alder" reaction with the formation of high cross-linking density structure, the other peak at lower temperature (around 138°C) corresponding to "Ene"

**TABLE II**  
Flexural Strength for Composites at Room Temperature and 240°C

| Resin system | Flexural strength $\sigma_f$ /MPa |       | Retention at 240°C (%) |
|--------------|-----------------------------------|-------|------------------------|
|              | Room temperature                  | 240°C |                        |
| BM-15        | 78                                | 65    | 91.5                   |
| BM-25        | 180                               | 146   | 81.5                   |
| BM-35        | 234                               | 187   | 80.3                   |
| BM-45        | 276                               | 215   | 78.8                   |
| BM-55        | 331                               | 245   | 73.8                   |

reaction between C=C (BMI) and allyl (DBA) with the formation of 1 : 1 intermediate (Fig. 2).

In the case of MDPES, the exothermic peak temperatures of the thermally initiated homopolymerization occurred at 290 and 349°C. An previous report<sup>10</sup> that the lower temperature was attributed to addition reaction between Si-H and C≡C and higher temperature corresponding to "Diels-Alder" reaction between C≡C (Fig. 3). The lower exothermic temperatures of BMI/DBA implied a higher reactivity than that of MDPES. As seen in Figure 1, MDPES-BMI/DBA blends take place at a temperature similar to or slightly higher than that of pure MDPES and BMI/DBA. An increase of concentration of BMI/DBA in blends lead to an increase of the height of first exothermic peak in the lower temperature range. Meanwhile, the last exothermic peak still remained unchanged which was attributed to the reaction between Si-H and C≡C. Therefore, it was assumed that MDPES-BMI/DBA mixtures were attributed to physical blends and the cure reaction for MDPES and BMI/DBA could take place independently.



**Figure 4** TGA curves for MDPES-BMI/DBA blends in nitrogen (heating rate: 10°C/min) (A) BM-55, (B) BM-35, and (C) BM-15.



**TABLE III**  
**Thermal Property Data for MDPES-BMI/DBA Blends in Nitrogen**

| Resin system | Td <sub>5</sub> /°C | Td <sub>10</sub> /°C | T <sub>max</sub> /°C | 800°C Char residue/% | 1000°C Char residue/% | 1200°C Char residue/% |
|--------------|---------------------|----------------------|----------------------|----------------------|-----------------------|-----------------------|
| BM-15        | 457                 | 498                  | 530                  | 71.6                 | 70.3                  | 68.1                  |
| BM-35        | 429                 | 464                  | 471                  | 68.7                 | 67.1                  | 64.8                  |
| BM-55        | 426                 | 459                  | 465                  | 58.9                 | 57.7                  | 55.5                  |

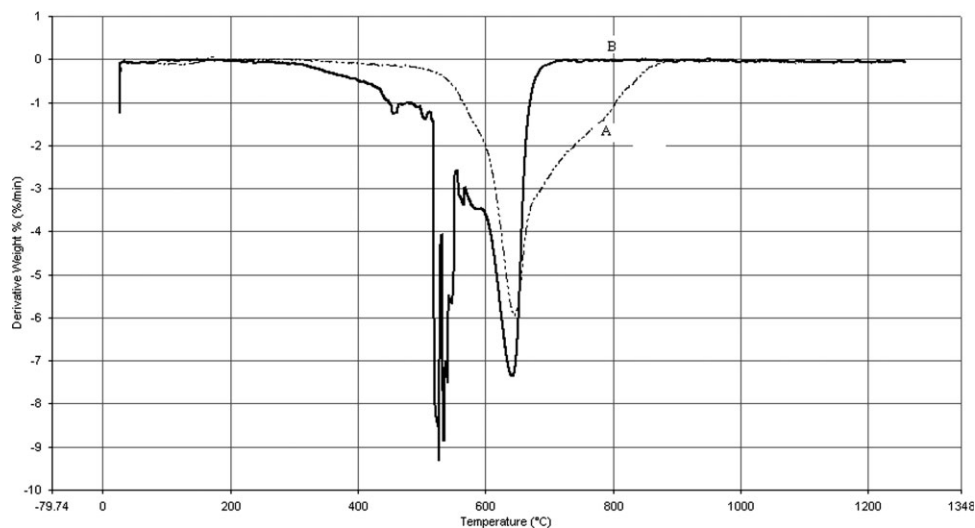
### Mechanical property

In this work, the mechanical properties of the glass laminated composites, cured under identical conditions were investigated. The composition effect on flexural strength at room temperature was summarized in Table II. From Table II, it can be clearly seen that flexural strength of the composites increased from 78 to 331 MPa with the increase of amount of BMI/DBA. This could be probably correlated to the cured structure of BMI/DBA. The curing reactions between BMI and DBA were proposed to take place through reactions between allyl groups of DBA and maleimide groups of BMI, in which some portion of BMI self-polymerization occurred simultaneously. All these reactions that occurred during curing belonged to the addition reaction and no byproducts of low-molecular weight were generated. The fiber wetting was promoted by the more polar and viscous BMI/DBA. Therefore, the cured resin structure in the final composites was more compact and had fewer defects. Additionally, many aromatic and heteroatom rings existed in the cured resin structure after curing. The blends resulted in stronger interface. All these features of the composite could be responsible for the improvement of flexural strength. However, it was noted that high temperature performance was adversely affected as evident from

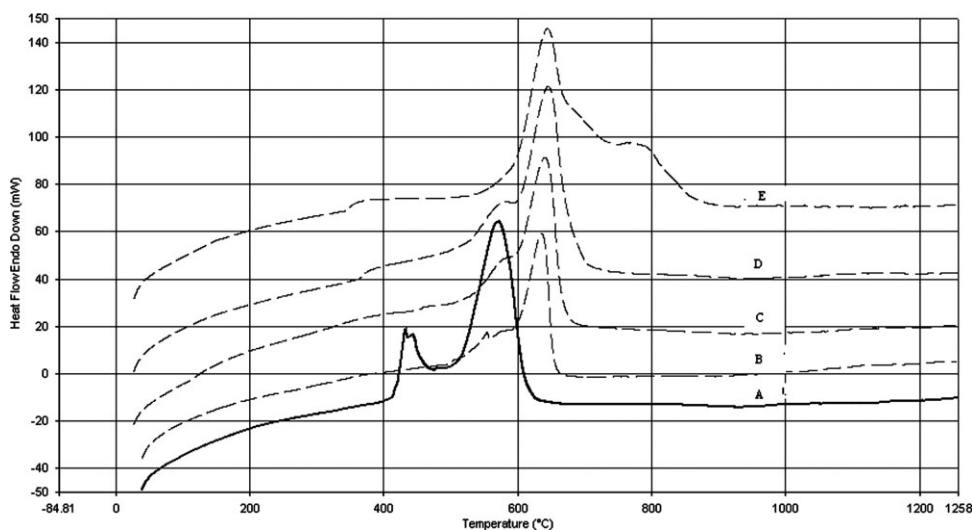
decrease in flexural strength at 240°C. The retention of flexural strength at this temperature varied from 91.5% to 73.8% with the proportional to the content of BMI/DBA, which was attributed to relative lower thermal stability compared with MDPES. Even then, MDPES-BMI/DBA blends still exhibited excellent thermal property.

### Thermal and thermal oxidative properties

The thermal stability of MDPES-BMI/DBA thermosets was characterized by TGA in nitrogen atmosphere. Figure 4 showed the overlay curves of weight loss as a function of temperature from room temperature to 1200°C. From Figure 4, it can be seen that MDPES-BMI/DBA blends showed a similar degradation pattern. The data of thermal stability was listed in Table III. With the increase of amount of BMI/DBA, Td<sub>5</sub> and T<sub>max</sub> (temperature of maximum degradation rate) were in the range from 457°C to 426°C, from 530°C to 465°C, respectively, the char residue at 1200°C was in the range from 68.1% to 55.5%. This phenomenon could be explained by the formation of succinimide functionality between BMI and DBA, which involved chain extension through "Ene" addition reaction at lower temperature followed by cross-linking via "Diels-Alder" reaction,



**Figure 5** DTG curves of MDPES and MDPES-BMI/DBA blends in air (A) MDPES and (B) BM-35.



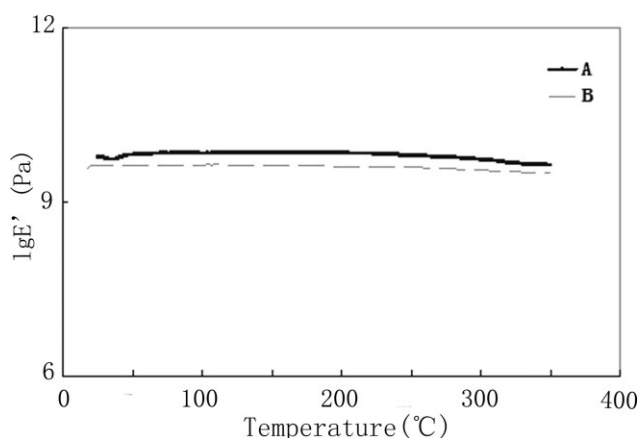
**Figure 6** DTA curves for MDPES-BMI/DBA blends in air. (A) BMI/DBA, (E) MDPES, (B) BM-55, (C) BM-35, and (D) BM-15.

BMI self-polymerization, and further cross-linking at higher temperature. The thermal degradation of BMI resins was overwhelmingly a function of the bridge between the succinimide rings. However, excellent thermal stability of MDPES-BMI/DBA blends was still remained which was attribute to the introducing of inorganic silicon, high cross-linking density, and the existence of large numbers of thermally stable aromatic rings, heteroatom rings.

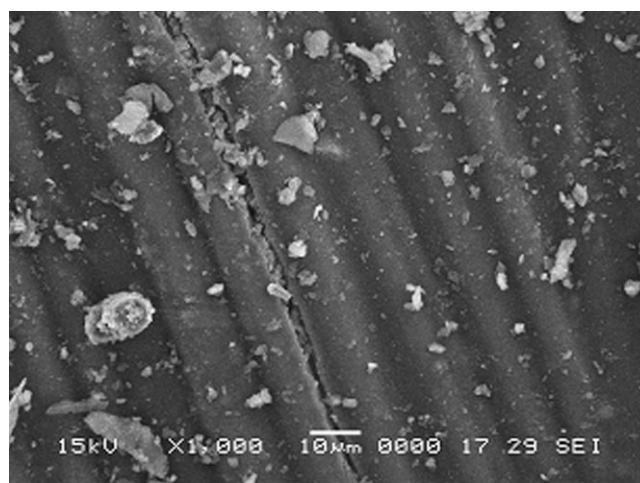
The thermal degradation of MDPES and MDPES-BMI/DBA blends in air were investigated according to DTG curves. As shown in Figure 5, MDPES started to lose weight at around 540°C and showed two stages of weight loss: the first period was between 540 and 700°C and the second stage was between 700 and 850°C. Thermal decomposition rate of first stage was obviously faster than second stage. In the case of MDPES-BMI/DBA blends, three degradation stages were observed and the first two

stages were attributed to BMI/DBA, the degradation initially proceeded from succinimide ring breakdown and was followed by the formation of carbon dioxide, carbon monoxide, aniline, methylaniline corresponding to BMI and phenol derivatives attributed to DBA.

Thermal stability of MDPES, BMI/DBA, and different weight ratio of MDPES-BMI/DBA blends in air were studied by DTA curves. From Figure 6, it can be seen that MDPES had more thermal stable than BMI/DBA in air. Thermal degradation of BMI/DBA and MDPES in air took place between 400 and 620, 550–850°C, respectively. As for MDPES-BMI/DBA blends, accompanying by the increase of concentration of BMI/DBA, initial and maximum



**Figure 7** Effect of amount of BMI/DBA on  $E'$  of MDPES-BMI/DBA composites (A) BM-55 and (B) BM-25.



**Figure 8** SEM of surface of BM-35 composite after treating at 500°C for 7 min in air.

decomposition temperature gradually decreased. These results were in agreement with DTG analysis.

The overlay storage modulus ( $E'$ ) as a function of temperature for MDPES- BMI/DBA composites were plotted in Figure 7. From Figure 7, it can be seen that  $E'$  almost kept straight line from room temperature to 350°C, which proved excellent thermal mechanical stability of MDPES-BMI/DBA blends. No obvious damping peak ( $\tan \delta$ ) was observed, which meant that the glass transition temperature exceeded 350°C.

The surface morphology of BM-35 composite after thermal oxidative treatment at 500°C for 5 min was investigated by SEM. Total weight loss was only 9.1%. Figure 8 showed that surface of composite preserved smooth and compact. Further, it can be seen that glass fibers were strongly bonded by resin without distinct space attributing to good adhesive between resins and glass fiber. Therefore, the interface was improved by blending with BMI/DBA.

### CONCLUSIONS

To improve the bonding force between MDPES and glass fiber, various concentrations of BMI/DBA were blended with MDPES and the properties of the blends were studied. The blends dissolved well in organic solvent and their processability was improved relative to pure MDPES. DSC results revealed that cure reaction for MDPES and BMI/DBA may take place independently and the mixture was ascribed to physical blends. Thermal stability was characterized by TGA, DTA, and DTG. With the increase of amount of BMI/DBA,  $Td_5$  in nitrogen was in the range from 457°C to 426°C. It was obvious that MDPES-BMI/DBA blends exhibited excellent high temperature resistance. Thermal deg-

radation of MDPES-BMI/DBA blends in air took place by two stages. With the increasing of concentration of BMI/DBA, flexural strength of composites increased from 78 to 331 MPa and the interface between MDPES and glass fiber was improved by the incorporation of BMI/DBA.

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