

Investigation on bismaleimide bearing polysiloxane (BPS) toughening of 4,4'-bismaleimido diphenylmethane (BMI) matrix—synthesis, characterization and toughness

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N-(4-Hydroxyphenyl) maleimide was synthesized via two synthesizing procedures, and a new bismaleimide bearing polysiloxane (BPS) was prepared by reacting *N*-(4-hydroxyphenyl) maleimide with dichlorodimethyl silane at first, then the adduct was reacted with polysiloxane terminated by hydroxyl groups. The products were characterized by i.r., n.m.r. and elemental analysis, respectively. The molecular weight of BPS was determined by g.p.c. and its curing behaviour and cured resin thermal stability were investigated by d.s.c. and t.g.a. The toughening effect of BPS was investigated by introducing it into 4,4'-bismaleimido diphenylmethane (BMI) cured matrix. The results indicated that adding 20 wt% BPS into the BMI matrix could increase the impact strength 3.7 times as much as that of the pure BMI matrix. The toughening mechanism of the matrix was elucidated by the glass transition temperature, determined by d.s.c., and the fracture surface morphology was observed by s.e.m. Copyright © 1996 Elsevier Science Ltd.

(Keywords: bismaleimide; polysiloxane; toughness)

INTRODUCTION

Bismaleimides are widely used as high performance composite matrices. As compared with other thermosetting polyimides, bismaleimides display both excellent high performance and low cost; thus they have been selected as attractive candidates for advanced composite matrices¹. Their major disadvantage of brittleness leads to very low impact strength at break and such matrices cannot be matched successfully with high performance fibres.

From the point of view of molecular design, introducing flexible linkage or chains into bismaleimides can effectively improve the toughness of the matrix². Siloxanes are a type of polymer chain which gives both flexibility and thermal stability due to their high bond energy and the low rotation barrier energy of the Si-O bond³; thus, introducing a siloxane chain rather than an oxyalkylene linkage⁴ into bismaleimides can be employed to give the matrix good toughness without sacrificing thermal stability. Most past investigations⁵⁻⁹ on silicone containing bismaleimides mainly focused on extending bismaleimides by a silicone monomer, i.e. diphenylsilanediol. These studies dealt with preparing silicone-modified bismaleimide⁵, processing of resins and composites⁶⁻⁸, properties of composites^{5,8} and

morphology of the cured resin⁹. Such resin systems would be expected to create many microcavities in the matrix as a result of the combination of liquid state silicone additives and emission of volatile products during the cure⁹. It was demonstrated that the microcavities in the matrix could induce intrinsic brittleness and reduce impact strength¹⁰. To overcome the disadvantages, it seems to be desirable to develop monomers of polysiloxanes terminated by addition polymerization functional groups, especially bismaleimides bearing polysiloxane (BPS). We thought that the investigation on BPS merited further attention. In particular, investigations of polymer transitions and their role in the toughness of BPS/4,4'-bismaleimido diphenylmethane (BMI) copolymers merited study. The present work describes an investigation of the synthesis, characterization and toughening behaviour of new BPSs.

EXPERIMENTAL

Materials

Maleic anhydride was recrystallized from acetic anhydride, and 4-aminophenol was recrystallized from ethanol. Dichlorodimethyl silane was purified by treatment with formamide, and then distilled. Polysiloxane terminated by hydroxyl groups was purchased from Chengdu Silicone Applied Research Centre and used as received. *N,N*-Dimethyl formamide (DMF) was refluxed

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in the presence of calcium hydride and then distilled under reduced pressure. Pyridine was treated in the same manner. BMI was an industrial product, and was recrystallized twice from toluene before use.

Synthesis

Preparation of *N*-(4-hydroxyphenyl) maleamic acid. A flask equipped with a mechanical stirrer and a reflux condenser was charged with maleic anhydride (0.22 mol, 21.6 g) dissolved in acetone (200 ml). 4-Aminophenol (0.2 mol, 21.8 g) was added in portions over 30 min at ambient temperature, and the solution turned into a yellow slurry. The mixture was allowed to react at ambient temperature for 1.5 h, and the slurry was isolated by filtration. The precipitate was washed with acetone, then dried at 50°C in a vacuum oven. *N*-(4-Hydroxyphenyl) maleamic acid was obtained as a yellow powder in a high yield of 93.6%. I.r. (KBr), cm^{-1} : 3482 (–OH); 2700–3300 (–COOH); 1699 (C=O in –COOH); 1627 (C=O in amide carbonyl group); 1608 (C=C); 1507 (aromatic backbone).

Preparation of *N*-(4-hydroxyphenyl) maleimide. Procedure 1: A three-necked flask equipped with a mechanical stirrer and a reflux condenser was charged with *N*-(4-hydroxyphenyl) maleamic acid (0.2 mol, 41.4 g), acetic anhydride (0.76 mol, 77.6 g) and sodium acetate (0.068 mol, 5.6 g). The mixture was reacted at 87°C for 1 h, then quenched. The mixture was poured into a large amount of water, and the precipitate was collected by filtration, washed with dilute sodium bicarbonate solution, then with water and finally recrystallized twice from ethanol. *N*-(4-acetoxyphenyl) maleimide was obtained as pale yellow crystalline needle in a yield of 87.2%, m.p. 164–165°C. I.r. (KBr), cm^{-1} : 2960 (–CH₃); 1707 and 733 (imide structure); 1589 (C=C); 1507 (aromatic ring); 1472 (–CH₃ asymmetric deformation); 1365 (–CH₃ symmetric deformation). Anal. Calc.: C, 62.34%; H, 3.90%; N, 6.06%. Found: C, 62.19%; H, 3.48%; N, 6.07%.

A three-necked flask equipped with a mechanical stirrer, a water segregator, a thermometer and a reflux condenser was charged with *N*-(4-acetoxyphenyl) maleimide (0.2 mol, 42.6 g), 200 ml of methanol, 4-toluenesulfonic acid (5.8×10^{-5} mol, 0.01 g). The mixture was refluxed at 62.5°C until the temperature rose to 65°C indicating that the methanol–methylacetate azeotrope had distilled. The methanol was evaporated, and a crude product with melting range 135–175°C was obtained. After recrystallizing from isopropyl alcohol, the *N*-(4-hydroxyphenyl) maleimide was obtained as orange yellow crystalline needles in a yield of 56.3%, m.p. 181–182°C. I.r. (KBr), cm^{-1} : 3482 (–OH); 1778, 1702 and 717 (imide structure); 1603 (C=C); 1522 (aromatic ring). Anal. Calc.: C, 63.49%; H, 3.70%; N, 7.41%. Found: C, 63.52%; H, 3.18%; N, 7.33%.

Procedure 2: A three-necked flask fitted with a water segregator, a thermometer and a mechanical stirrer was charged with *N*-(4-hydroxyphenyl) maleamic acid (0.2 mol, 41.4 g), 4-toluenesulfonic acid (0.016 mol, 2.8 g), dimethylformamide (21 ml) and toluene (300 ml). The mixture was refluxed for 6 h until the stoichiometric amount of water from the cyclodehydration reaction was completely segregated and the slurry then turned

into a clear orange yellow solution. The toluene was evaporated, and the residue of black liquid was poured into a large amount of water. The precipitate was collected by filtration, washed with dilute sodium bicarbonate solution (5 wt%), then with water. After recrystallizing from a mixed solvent of water–isopropyl alcohol (1 : 1 v/v), orange yellow crystalline needles were obtained in a yield of 62.6%, m.p. 181–182°C. I.r. (KBr), cm^{-1} : 3482 (–OH); 1778, 1702, 717 (imide structure); 1603 (C=C); 1522 (aromatic ring). Anal. Calc.: C, 63.49%; H, 3.07%; N, 7.41%. Found: C, 63.50%; H, 3.70%; N, 7.36%.

Preparation of bismaleimide bearing polysiloxane (BPS). A three-necked flask was fitted with a reflux condenser, a dropping funnel and mechanical stirrer. The apparatus was thoroughly flame dried and purged with dry N₂. The flask was charged with a solution of dichlorodimethyl silane (0.1 mol, 12.9 g) diluted with DMF (50 ml). A mixture of *N*-(4-hydroxyphenyl) maleimide (0.1 mol, 18.9 g) dissolved in DMF (50 ml) and pyridine (0.1 mol, 7.9 g) was added dropwise to the vigorously stirred solution in the flask at 0°C under dry N₂. The mixture was then stirred for 4 h at ambient temperature, and the mixture gradually turned dark brown. Polysiloxane terminated by hydroxyl groups (0.05 mol, 34 g) was dissolved in DMF (50 ml) and pyridine (0.1 mol, 7.9 g), then was added dropwise to the reaction mixture at 0°C under dry N₂. Stirring of the mixture was continued at 40°C for another 4 h, and the solution turned dark red. The mixture was allowed to stand overnight, and the product was isolated by pouring the reacting mixture on to crushed ice. The precipitate was collected by filtration, washed with dilute sodium bicarbonate solution, then with water. The product was dried at 50°C in a vacuum oven for 10 h. BPS was obtained as yellow red powder in a yield of 89.4%. I.r. (KBr), cm^{-1} : 2964 (–CH₃); 1780, 1710, 695 (imide structure); 1609 (C=C); 1518 (aromatic ring); 1098 and 1022 (Si–O–C and Si–O–Si stretching). ¹H n.m.r. (dimethylsulfoxide-*d*₆), δ (ppm): 7.17–6.65 (*m*, 8H, aromatic and 4H, olefinic); 0.25 (*bs*, 12H, Si–CH₃ linked to phenoxy); 0.01 (*s*, the other Si–CH₃ in polysiloxane chain).

Curing of bismaleimide bearing polysiloxane (BPS)

A solution of BPS in DMF was introduced into a glass dish in an oven. The solvent was evaporated at 160°C, and the temperature was subsequently raised and maintained at 240°C for 2 h, then at 280°C for 10 h. The cured BPS was obtained as a dark brown resin.

Blending, copolymerization and impact test

BMI and BPS in a certain composition was first ground in a glass mortar, then thoroughly mixed using a vibrating mixer. The blend was sieved with a 180 mesh cm^{-2} sieve. Fine solid powder of blend (3 g) was then placed in an aluminium mould with dimensions of 5 cm \times 0.7 cm \times 0.3 cm, which was placed in an oven at 160°C. The temperature was maintained for 30 min so that the BPS dissolved in the BMI. After 6.5 h, the liquid mixture had turned completely solid consistent with copolymerization of BMI and BPS. The temperature was then elevated and kept at 180°C for 6 h, 200°C for 1 h and 240°C for 3 h to complete cure. The impact

specimens of the blends were obtained thus. The impact test was carried out using a Charpy impact tester.

Characterization methods

I.r. spectra were recorded on a Nicolet DX V4 spectrometer as KBr pellets. ^1H n.m.r. spectra were obtained using a Varian FT-80 spectrometer at 80 MHz. D.s.c. and t.g.a. traces were recorded using a Perkin-Elmer 7 thermal analyser system. D.t.a. traces were performed on a Beijing LCT-1 d.t.a. The curing behaviour and glass transition determined by d.t.a. and d.s.c. were performed at a heating rate of $20^\circ\text{C min}^{-1}$ in atmospheres of N_2 , and the thermal stability determined by t.g.a. was performed at a heating rate of $10^\circ\text{C min}^{-1}$ in an atmosphere of air. Molecular weight and molecular

weight distribution were analysed by a Waters Model 150CL g.p.c. using tetrahydrofuran as mobile phase and polystyrene standards. The measuring temperature was 25°C . Impact fracture surfaces were observed using a S520 scanning electron microscope.

RESULTS AND DISCUSSION

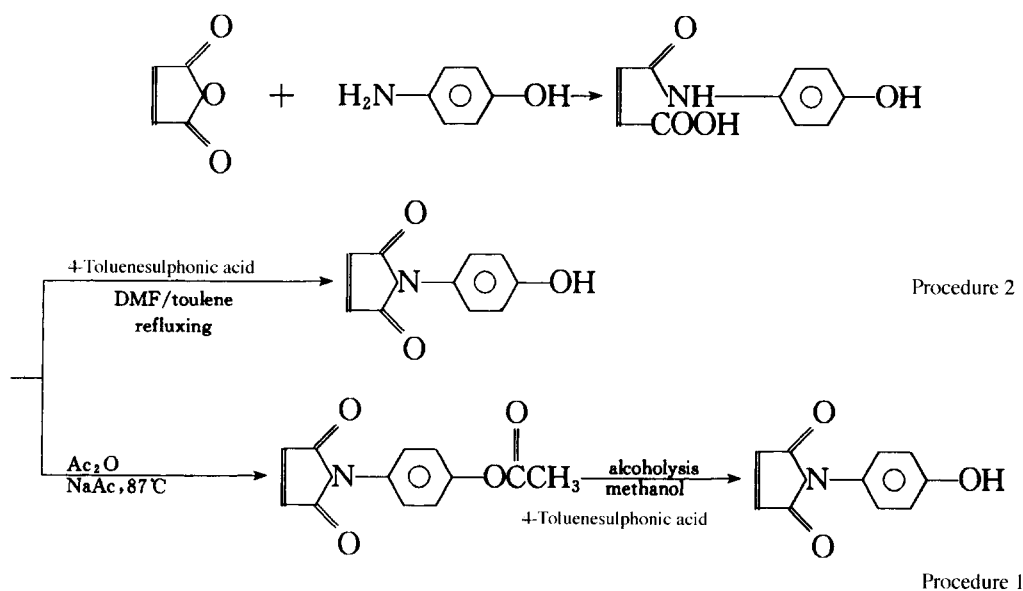
Synthesis of *N*-(4-hydroxyphenyl) maleimide and bismaleimide bearing polysiloxane (BPS)

Two procedures were adopted to synthesize *N*-(4-hydroxyphenyl) maleimide (see *Scheme 1*). Procedure 1 was described by Towney¹¹ and involves synthesis of *N*-(4-hydroxyphenyl) maleamic acid, cyclodehydration of *N*-(4-hydroxyphenyl) maleamic acid, and alcoholysis of *N*-(4-acetoxyphenyl) maleimide. This procedure gives *N*-(4-acetoxyphenyl) maleimide during cyclodehydration because acetic anhydride is used as dehydrating agent; thus, alcoholysis is required to obtain the target product. Procedure 2 uses 4-toluenesulfonic acid as the dehydrating agent and is a simpler procedure. *Table 1* outlines the comparison of two procedures.

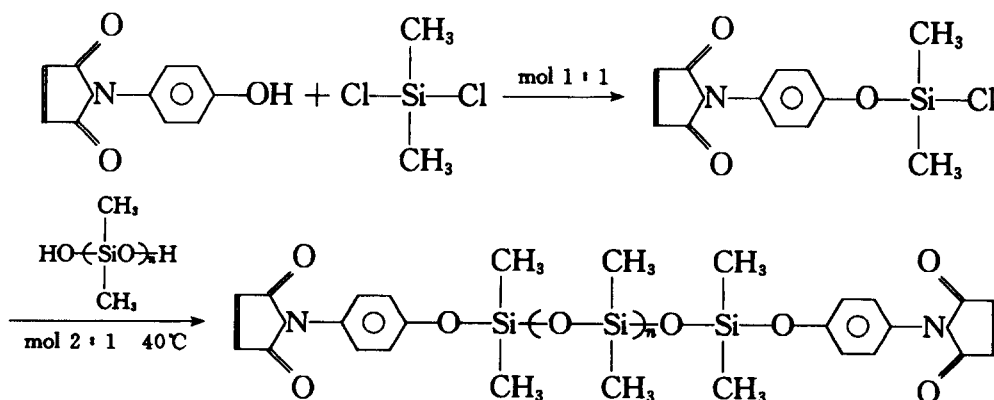
Scheme 2 presents the synthesizing procedure for BPS, which is the same as the route of Mikroyannidis

Table 1 Comparison of procedures for synthesizing *N*-(4-hydroxyphenyl) maleimide

| Item | Procedure 1 | Procedure 2 |
|------------------------------------|-------------|-------------|
| Synthesizing steps | 3 | 2 |
| Overall yield (%) | 45.3 | 58.2 |
| Overall synthesizing time (h) | 17–18 | 8–9 |
| Melting point ($^\circ\text{C}$) | 181–182 | 181–182 |



Scheme 1 Synthesis of *N*-(4-hydroxyphenyl) maleimide



Scheme 2 Synthesis of bismaleimide bearing polysiloxane (BPS)

Table 2 G.p.c. data of BPS and polysiloxane terminated by hydroxyl groups

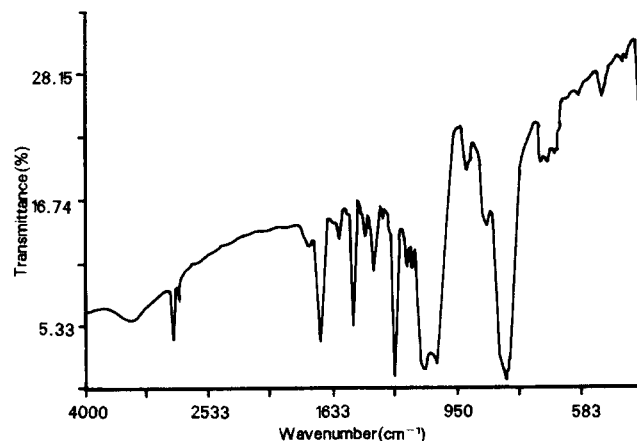
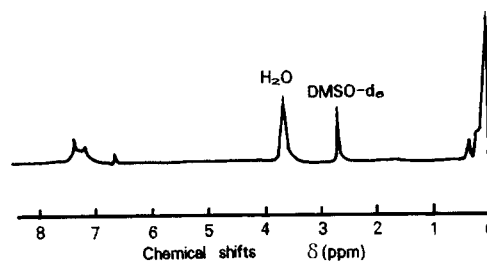
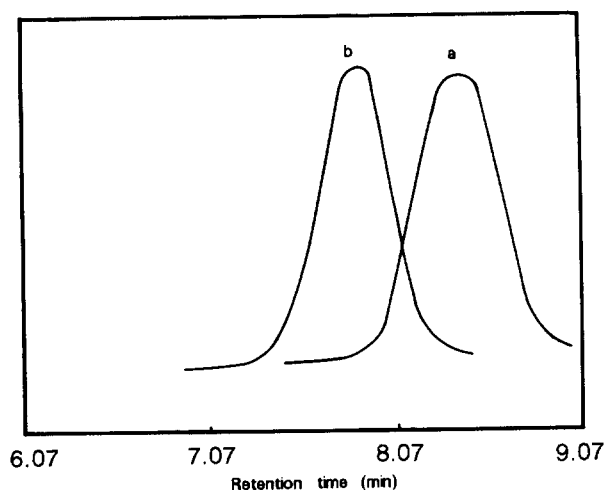
| | BPS | | | | | Polysiloxane terminated by hydroxyl groups | | | | |
|-------------------|-------------|-------------|-------------|----------------|-----------------------|--|-------------|-------------|----------------|-----------------------|
| | \bar{M}_n | \bar{M}_w | \bar{M}_z | \bar{M}_η | \bar{M}_w/\bar{M}_n | \bar{M}_n | \bar{M}_w | \bar{M}_z | \bar{M}_η | \bar{M}_w/\bar{M}_n |
| Experimental data | 1402 | 2065 | 3587 | 2065 | 1.47 | 758 | 1092 | 2666 | 1092 | 1.44 |
| Calibrated data | 1249 | 1840 | 3196 | 1840 | 1.47 | 700 | 1008 | 2461 | 1008 | 1.44 |

*et al.*¹². The only difference is that synthesis of BPS needs more reacting time and higher reacting temperature (40°C) in the second stage than that the literature report.

Characterization of BPS

The chemical structure of BPS was characterized by i.r. and ¹H n.m.r. spectroscopy. Figure 1 is the i.r. spectrum of BPS. Characteristic absorption peaks appear at 1770, 1720 and 720 cm⁻¹ due to an imide structure, and characteristic absorption near 1100 cm⁻¹ are assigned to Si-O-C and Si-O-Si stretching. The absorption bands at 2964, 1609 and 1518 are assigned to -CH₃, olefinic bond and aromatic ring backbone stretching, respectively. Figure 2 is the ¹H n.m.r. spectrum of BPS. The spectrum shows a singlet around 6.65 ppm associated with olefinic protons; this confirms the presence of the maleimide groups. There is also a multiplet around 7.17–6.90 ppm assigned to aromatic protons. The methyl protons of Si-CH₃ groups linked to the phenoxy show a downfield shift compared with that of the other methyls protons of Si-CH₃. This behaviour is due to the deshielding effect of the aromatic ring.

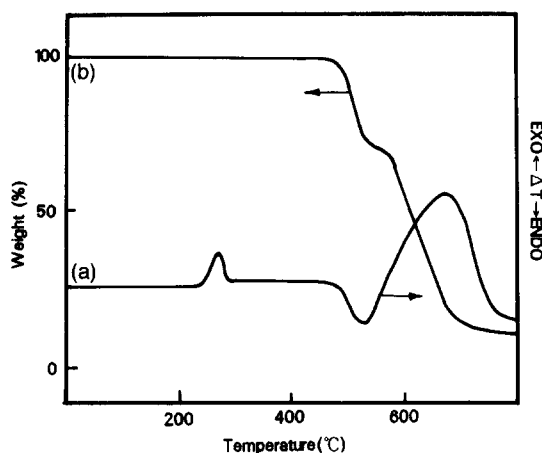
The molecular weight and molecular weight distribution were determined by gel permeation chromatography (g.p.c.) Figure 3 shows the g.p.c. traces of BPS and polysiloxane terminated by hydroxyl groups. Polystyrene standards were used so the g.p.c. results needed calibration. Comparing the results of g.p.c. with the molecular weight of polysiloxane terminated by hydroxyl groups as measured by terminal group analysis using ¹H n.m.r. spectroscopy it was found that the number-average molecular weight (\bar{M}_n) was 699.6 by n.m.r. while the g.p.c. determining datum was 758.1. The conversion coefficient of g.p.c. calculated by dividing two data is 1.08 for polysiloxane terminated by hydroxyl groups. The same calibration has been done for BPS and the conversion coefficient for g.p.c. for BPS was determined as 1.12. The difference of two conversion coefficients suggests that BPS should have better solubility in the g.p.c. solvent tetrahydrofuran (THF) than the polysiloxane terminated by hydroxyl groups, and it results in the BPS elution curve shifting to a lower retention time. Further, the solubility parameter calculation for BPS and polysiloxane terminated by hydroxyl groups following Fedors *et al.*¹³ revealed that BPS has a higher solubility parameter (21.7) due to introducing maleimide and aromatic rings into the molecular backbone; polysiloxane terminated by hydroxyl groups has a lower solubility parameter (16.8). The solubility parameter for THF was determined as 19.6 according to Burrell¹⁴, and the solubility parameter for BPS being nearer to that of THF is consistent with our experimental observations (see above). Table 2 records the experimental and calibrated data for g.p.c. The real \bar{M}_n weight of BPS is 1249, which corresponds to an average of approximately 12.0 dimethylsiloxane units

**Figure 1** i.r. spectra of BPS**Figure 2** ¹H n.m.r. spectra of BPS**Figure 3** G.p.c. traces for (a) polysiloxane terminated by hydroxyl groups and (b) BPS

per molecule. It was found that the calibrated \bar{M}_n of BPS was slightly higher than the calculated \bar{M}_n (1190) of BPS based on the calibrated \bar{M}_n of polysiloxane terminated by hydroxyl groups. This may be due to the loss of the low molecular weight product during isolation. Thus, the

Table 3 D.s.c. results of BPS/BMI copolymer

| Composition of BMI/BPS copolymers in weightness | Glass transition temperatures (°C) | | |
|---|------------------------------------|-----------------|-------------|
| | Siloxane phase | Copolymer phase | Imide phase |
| 100/0 | — | — | — |
| 90/10 | — | 200 | — |
| 80/20 | — | 198 | — |
| 70/30 | 76 | 190 | 330 |
| 50/50 | 76 | 186 | 323 |
| 0/100 | 62 | — | 301 |

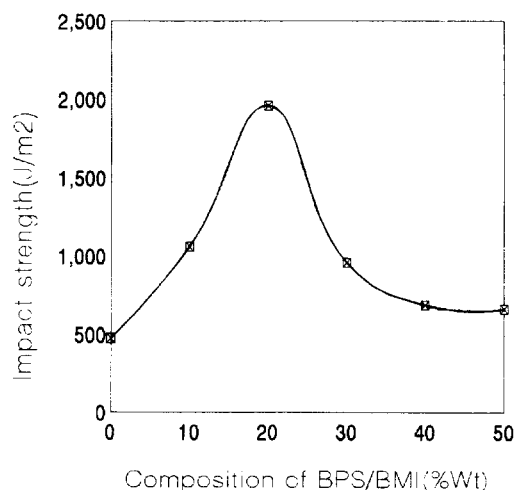
**Figure 4** (a) D.t.a. trace for BPS and (b) t.g.a. trace for its cured resin

molecular weight distribution of BPS is compatible with that of polysiloxane terminated by hydroxyl groups.

The curing behaviour of BPS and the thermal stability of its cured resin were investigated by d.t.a. and t.g.a. *Figure 4* presents the d.t.a. trace for BPS and t.g.a. trace for its cured resin. The d.t.a. spectra showed two exotherm peaks; one appeared in the temperature range 231–315°C assigned to the curing reaction of BPS, the other was located in the temperature range 544–770°C and is attributed to decomposition of the polymer chain. As compared with bismaleimides containing oxyalkylene linkages^{2,4}, the main chain of BPS consists of maleimide rings, aromatic rings and a high bond energy Si–O covalent bond; such molecular design provides the cured resin of BPS with good thermal stability. The t.g.a. trace for BPS cured resin indicates that it shows onsets of degradation at 482°C, which is higher than that of bismaleimides containing oxyalkylene linkages⁴, and the decomposition of the cured BPS exhibits two-step weight loss. Considering the weight loss steps for cured BPS, the first step is probably assigned to decomposition of maleimido and aromatic rings, while the other is may be due to that of the polysiloxane chain.

Toughening behaviour of BPS blended and copolymerized with BMI

BPS was expected to toughen the BMI matrix as a result of including the polysiloxane chain. *Figure 5* shows the impact strength depending on the composition of BPS/BMI copolymers by weight. It is found that the curve shows a maximum in impact strength at the composition of 20 wt% BPS in the copolymer. As

**Figure 5** Impact strength vs. composition (wt%) of BPS/BMI blends

compared with the pure BMI matrix, the copolymer matrix can attain 3.7 times the impact strength at most, and all copolymers show higher impact strength assigned to BPS toughening. It is worthy of note that the impact strength decreases dramatically when the composition of BPS exceeds 20 wt%, and afterwards the variation of impact strength tends to become slight and then levels off with the weight percentage of BPS. Thus, introducing BPS into a BMI matrix can give the matrix greater toughness, and such toughening behaviour is related to the network structure of the cured resins.

Table 3 shows the d.s.c. results for BPS/BMI copolymers at various weight compositions. It is found that pure BMI cured resin shows no glass transition temperature, while pure BPS cured resin shows two glass transition temperatures; one appears at 62°C attributed to the siloxane phase and the other appears at 301°C assigned to the imide phase. The glass transition temperature of the siloxane phase seems to be inconsistent with previously reported values¹⁵; this should be due to the crosslink of BPS, which restrains the segment motion of siloxane chains. As compared with BMI cured resin, BPS cured resin exhibits a glass transition temperature at 301°C attributed to the imide phase. Because the two maleimide groups are connected by a stiff linkage consisting of an aromatic ring and methylene for BMI while it is joined by a flexible siloxane chain for BPS, the introduction of polysiloxane has resulted in a network in which polymaleimide is dispersed in flexible siloxane chains, thus enhancing the segment motion of polymaleimide in the cured BPS network and resulting in

the appearance of a glass transition temperature for imide phase.

As indicated in Table 3, all copolymers of BPS/BMI show glass transition temperatures in the range 186–200°C, which did not appear in either cured BMIs or cured BPSs, and these glass transition temperatures decrease as BPS compositions increase. In contrast to the network of BMI, which has no observable glass transition temperature, introducing BPS has enhanced flexibility of the network and permitted a certain extent of motion for the segments in the network, accounting for the appearance of glass transition temperatures. As compared with the network of BPS, which has two glass transition temperatures assigned to the imide and siloxane phases, respectively, the BPS/BMI copolymer has only one glass transition temperature when the BPS loading is below 20 wt%, and this glass transition temperature is attributed to neither of the phases in the cured BPS network. The appearance of this single glass transition temperature indicates that a compatible network of BMI and BPS has been formed, which seems to be a homogeneous phase. At least these copolymer networks exhibit no phase separation which is detectable by means of d.s.c. Seris *et al.*¹⁶ had investigated the influence of siloxane rubber on the thermal polymerization process of BMI. Their conclusions demonstrate that

methyl groups linked to silicon atoms can give $-CH_2\cdot$ radicals which result in grafting of the siloxane rubber to the BMI chain, making the rubber compatible with the BMI polymer. Such a situation probably also occurred in the BPS/BMI system, which led to formation of a compatible network and accounts for the appearance of one glass transition within the 186–200°C range. The above discussion suggests that the BPS/BMI copolymer should be a homogeneous phase when the BPS loading is less than 20 wt%.

It is interesting to note that glass transition temperatures attributed to the siloxane and imide phases appear again in BPS/BMI copolymers when the BPS composition passes 20 wt%. This confirms the phase separation of BPS from the matrix. When the BPS composition is higher than 20 wt%, grafting BPS to BMI chains does not occur for every BPS monomer. Meanwhile the BPS radical polymerization at 160°C needs a long period for completion because its initial polymerization temperature by d.t.o. is up to 231°C; thus, the excess BPS has enough time to aggregate and form a BPS dispersed phase. It can be deduced that phase separation is probably the dominant step for non-grafting of BPS as a result of competition between radical polymerization and phase separation above 160°C, and this results in appearance of a BPS dispersed phase.

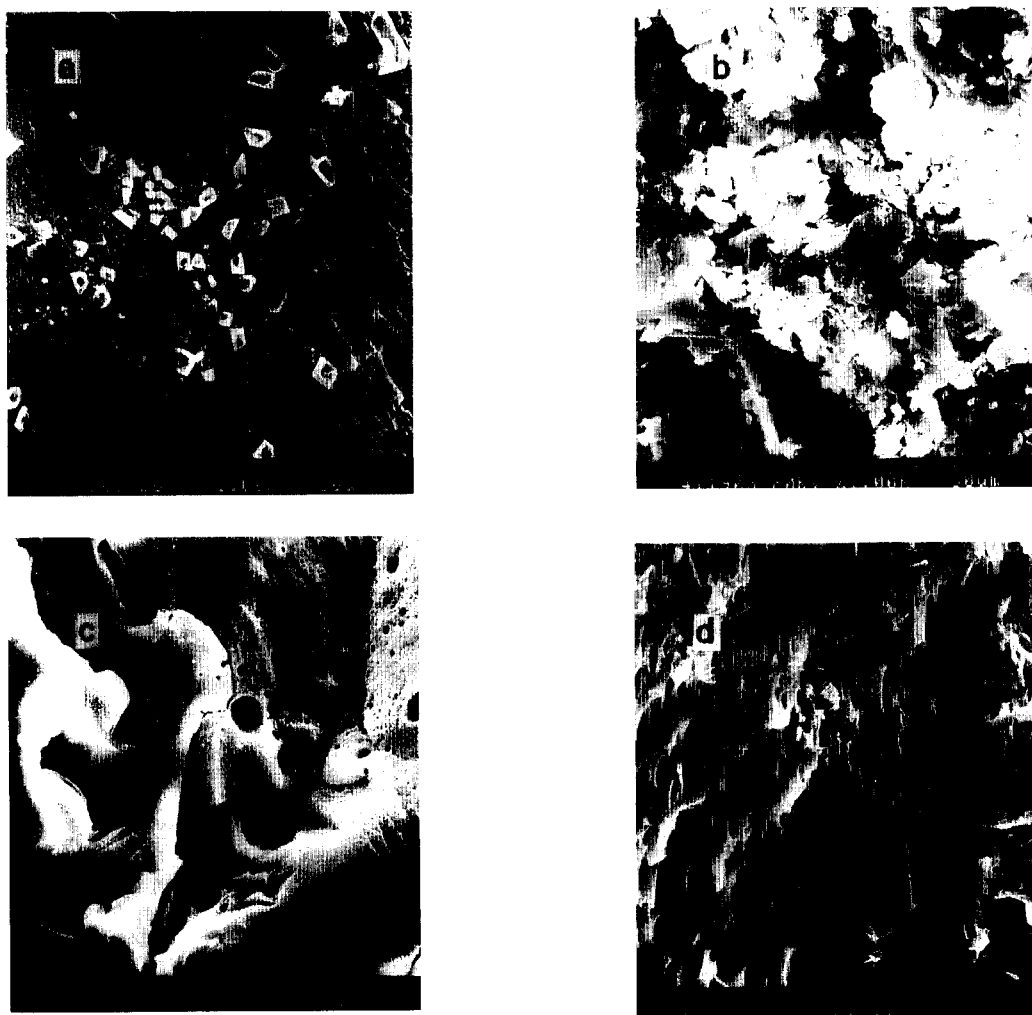


Figure 6 Fracture surface of BPS/BMI blends by SEM for compositions of (a) 0:100 w/w; (b) 1:4 w/w; (c) 3:7 w/w; (d) 1:1 w/w

Figure 6 is the SEM observation of fracture morphology for BPS/BMI copolymers at various compositions. It can be seen that the pure BMI matrix shows a smooth fracture surface, and represents a typical brittle break, while copolymers of BPS/BMI with compositions lower than 20 wt% show irregular fracture surfaces and represent typical ductile failure. As discussed before, introducing BPS into BMI results in the appearance of a new glass transition temperature for a compatible copolymer phase forming derived from grafting BPS to BMI chains, and such glass transition temperatures may be the main cause of increased toughness of the matrix. When BPS is less than 20 wt%, BPS/BMI cured resins exhibit a homogeneous phase; introduction of BPS allows the network more flexibility and permits the copolymer to create plastic deformation to a certain extent. When an impact load is applied to the matrix, it first creates plastic deformation, then ductile yielding, and at last shows ductile failure. Furthermore, the increasing toughness with BPS loading is due to a decrease in glass transition temperature for increasing siloxane content in the matrix.

When the composition of BPS surpasses 20 wt%, microcavitation appears in the fracture surface with dimensions of *ca* 10 μm , and the fracture morphology of the copolymer containing 30 wt% BPS shows little ductile fracture, while the fracture morphology of a copolymer containing 50% BPS exhibits plastic flow in the impacting direction. The existence of microcavitation created during the fracture process is probably a consequence of BPS dispersed particles being pulled out. It is found that the edge of microcavitation is smooth, which demonstrates that the interfacial adhesion is very weak. The reasons that the two phases have poor adhesion may be due to the low reactivity of BPS at 160°C and different curing shrinkage of BPS and BMI. Low reactivity of BPS monomer at 160°C results in its failure to copolymerize with BMI after phase separation; this results in less chemical bonds connecting the two phases. Meanwhile, the different curing shrinkage of the two monomers also leads to poor interfacial adhesion. It is known that weak interface adhesion causes impact strength reduction^{17,18}, and the same situation has also occurred in BPS/BMI copolymer as the BPS loading passes 20 wt%. It is worthy of note that the matrix also has better toughness than the pure BMI matrix, although increasing toughness of the matrix is not as high as expected. The fact that impact strength varies little with matrix composition changes from 30 wt% BPS to 50 wt% BPS reveals that debonding of the two phases is not dominant for absorbing impact energy, and further demonstrates the poor interfacial adhesion. The fracture observation of the matrix containing 50 wt% BPS show characteristics of shear-yielding morphology, and the toughening mechanism is similar to that of rubber toughened epoxy resin¹⁹, while the fracture observation of the matrix containing 30 wt% BPS exhibits a mixed fracture morphology including either localized ductile yielding or localized shear-yielding features.

CONCLUSIONS

On the basis of molecular design, highly thermally stable

and toughened bismaleimide (BPS) consisting of an aromatic ring, a maleimide ring and a highly thermally stable Si–O bond has been prepared by a new route. Prepared BPS possesses either high thermal stability or toughness to the inclusion of a polysiloxane chain in its molecule structure. It has been demonstrated that cured BPS begins to decompose at 482°C, which is higher than that of bismaleimide containing oxyalkylene linkages. The investigation of toughening behaviour of BPS/BMI copolymer indicates that introducing 20 wt% BPS into BMI can increase the impact strength of the matrix 3.7 times compared with that of the pure BMI matrix, and such toughening behaviour results from creating plastic deformation and ductile yielding in the matrix because a homogeneous copolymer phase has been formed. The difference in shrinkage and reactivity for BPS and BMI during cure results in weak adhesion between two phases of the matrix when the BPS composition is higher than 20 wt%, and leads to a dramatic fall of impact strength for the BPS/BMI matrix.

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