Synthesis and Properties of Bismaleimide Resins Containing Ether Bonds

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Synopsis

New bismaleimides containing ether bonds were prepared. The thermal properties of the bismaleimides were investigated by differential scanning calorimetry (DSC). The effects of structure of the bismaleimides and curing conditions on the thermal and mechanical properties of the cured resins such as initial decomposition temperature (T_d), glass transition temperature (T_g), and flexural strength were studied. The introduction of ether bonds to bismaleimide resins decreased the brittleness of the resins without reductions in their heat-resistant properties.

INTRODUCTION

Polyimides, which are well known as high-temperature-resistant polymers, may be classified into two different groups: condensation-type and addition-type resins. The latter resins are produced from bisimides containing unsaturated end groups that can polymerize without the evolution of volatiles.[1-5]

One of the most important bisimides belongs to bismaleimides. The bismaleimides are crosslinked to yield polyimide resins with high-temperature resistance. The cured resins, however, are extremely brittle because of their high crosslink density.

This paper reports on the preparation and curing of new bismaleimides containing ether bonds. These bismaleimides are expected to have improved handling and processing characteristics, and to yield cured resins with flexibility or reduced brittleness. The effect of structure of these bismaleimides on thermal and mechanical properties of the cured resins was discussed.

EXPERIMENTAL

Materials

1-Fluoro-4-nitrobenzene was prepared from 1-chloro-4-nitrobenzene and potassium fluoride according to the method of Finger.[6]

1,2-Bis(4-aminophenoxy)ethane (1d) and 1,2-bis-[2-(4-aminophenoxy) ethoxy]ethane (1e) were prepared according to the method of Feld et al.[7]
1,2-Bis(4-nitrophenoxy)ethane and 1,2-bis[2-(4-nitrophenoxy)ethoxy]ethane were prepared from 1-fluoro-4-nitrobenzene and appropriate glycols. The nitro derivatives were reduced with a 5% Pd/C catalyst and hydrazine hydrate.

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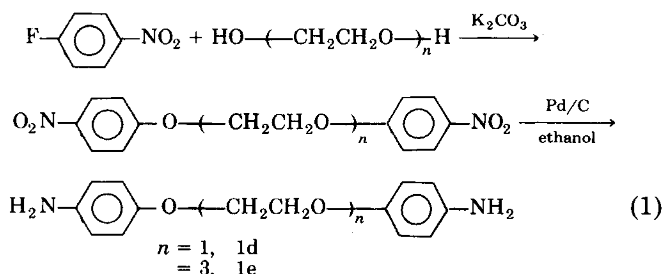


The diamines obtained were recrystallized from ethanol: 1d, yield 58%, mp 176–177°C (lit.[7] 59%, 179–180°C); 1e, yield 51%, mp 94–97°C (lit.[7] 55%, 93–95°C).

2,2-Bis[4-(4-aminophenoxy)phenyl]propane (1a, Wakayama Seika Kogyo), bis[4-(3-aminophenoxy)phenyl]sulfone (1b, Hitachi Chemical), 3,4′-diaminodiphenylether (1c, Wakayama Seika Kogyo), and 1,6-diaminohexane (1f, Wako Pure Seika Kogyo) were commercial materials. The diamines (1a–c) were recrystallized from ethanol or 2-propanol: 1a, mp 128–129°C; 1b, mp 131–132°C; 1c, mp 74–75°C. Diamine 1f was purified by distillation under reduced pressure: bp 102°C/20 mm Hg.

Bismaleimides

Bismaleimides were prepared from corresponding diamines and maleic anhydride by a modification of the method of White et al.[5]

General procedure for the preparation of bismaleimides are as follows. A 1000-mL four-necked flask was charged with maleic anhydride (1.10 mol) and dry acetone (200 mL). A solution of diamine (0.50 mol) in dry acetone (400 mL) was added into the flask over a period of 2 h at ice bath temperature under a nitrogen atmosphere, and the flask was stirred overnight at room temperature. The insoluble amic acid was separated by filtration, washed with acetone to remove remaining maleic anhydride, and dried under vacuum at 60°C for 20 h. A 1000-mL three-necked flask was charged with the amic acid (0.50 mol), acetic anhydride (1.50 mol), triethylamine (0.50 mol), and nickel (II) acetate tetrahydrate (0.05 mol). The solution was refluxed for 5 h under a nitrogen atmosphere and poured into cold water. The precipitate was collected and washed with sodium bicarbonate solution till free from acetic acid and finally with water and dried. The product was recrystallized from $CHCl_3$/MeOH or benzene.

2,2-Bis[4-(4-Maleimidophenoxy)phenyl]propane (BPPP)

The product was recrystallized from benzene and the yellow solid was obtained in 62% yield; mp 119–120°C; IR (KBr) ν (cm^{-1}) 3100 (=C—H), 2975 (C—H), 3480, 1720 (C=O), 1240 (—O—), 1400, 1150 (C—N—C); ^1H-NMR ($CDCl_3$) δ (ppm) 7.36–6.83 (m, 16H, aromatic), 6.79 (s, 4H, olefinic), 1.67 (s, 6H, methyl).

Bis[4-(3-Maleimidophenoxy)phenyl]sulfone (3,3′-BPPS)

Recrystallization of the product from benzene gave yellow solid in 77% yield; mp 104–108°C; IR (KBr) ν (cm^{-1}) 3090 (=C—H), 1710 (C=O), 1380 (C—N), 1240 (—O—), 1140 (SO_2); ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.92–6.97 (m, 16H, aromatic), 6.79 (s, 4H, olefinic).

3,4′-Bismaleimidodiphenylether (3,4′-BDE)

The product was recrystallized from 5 : 2 $CHCl_3$/MeOH and the yellow solid was obtained in 54% yield; mp 207–208°C; IR (KBr) ν (cm^{-1}) 3070 (=C—H), 3450, 1700 (C=O), 1390, 1140 (C—N—C); ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.48–7.10 (m, 8H, aromatic), 6.86 (s, 4H, olefinic).

1,2-Bis(4-Maleimidophenoxy)ethane (BPE-1)

The product was recrystallized from 5 : 2 $CHCl_3$/MeOH, and the yellow solid was obtained in 51% yield; mp 227–231°C; IR (KBr) ν (cm^{-1}) 3100 (=C—H), 3450, 1720 (C=O), 1400, 1160 (C—N—C), 1250 (—O—); ^{1}H-NMR (DMSO-d_6) δ (ppm) 7.30–7.01 (m, 8H, aromatic), 7.05 (s, 4H, olefinic), 4.38 (s, 4H, methylene).

1,2-Bis[2-(4-Maleimidophenoxy)ethoxy]ethane (BPE-3)

The product was recrystallized from 1 : 1 $CHCl_3$/MeOH, and the yellow solid was obtained in 45% yield; mp 169–176°C; IR (KBr) ν (cm^{-1}) 3100 (=C—H), 3470, 1710 (C=O), 1400, 1160 (C—N—C), 1250 (—O—); ^{1}H-NMR (DMSO-d_6) δ (ppm) 7.26–6.95 (m, 8H, aromatic), 7.04 (s, 4H, olefinic), 4.20–3.64 (m, 12H, methylene).

1,6-Bismaleimidohexane (C_6-B)

Recrystallization of the product from 5 : 3 $CHCl_3$/MeOH gave brown yellow needles in 25% yield; mp 138–139°C (lit.[1] 132°C); IR (KBr) ν (cm^{-1}) 3100 (=C—H), 2950 (C—H), 3450, 1700 (C=O), 1405, 1125 (C—N—C); ^{1}H-NMR ($CDCl_3$) δ (ppm) 6.73 (s, 4H, olefinic), 3.53 (t, 4H, N—$\underline{CH_2}$), 1.40 (m, 8H, methylene).

4,4′-Bismaleimidodiphenylmethane (BDM)

The bismaleimide, BDM, was a commercial material and recrystallized from 1 : 1 $CHCl_3$/MeOH and used; mp 159–160°C (lit.[8] 157–158°C).

Measurement of Thermal and Mechanical Properties

Differential scanning calorimetry (DSC) was employed with a Du Pont Model 910 at a heating rate of 10°C/min in air.

Gel time was measured in the following manner. Bismaleimide monomers were heated at 200°C on a brass plate, and tack-free time was measured and defined as gel time.

Thermal gravimetric analysis (TGA) was employed with a Shimadzu Model TG-20 at a heating rate of 10°C/min in air or in a nitrogen atmosphere.

Thermomechanical analysis (TMA) was conducted with a Rigaku Denki Model TMA8140 at a heating rate of 10°C/min in air.

Dynamic mechanical analysis (DMA) was conducted on rectangular strip measuring 40 × 10 × 2 mm by using a Du Pont Model 982 between −150 and 400°C at a heating rate of 10°C/min.

Flexural testing (JIS K6911) was conducted on a Shimadzu Model S-500 Autograph.

RESULTS AND DISCUSSION

Synthesis and Thermal Properties of Bismaleimides

The diamines, 1,2-bis(4-aminophenoxy)ethane (1d) and 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane (1e), were prepared according to the method of Feld et al.[7] [eq. (1)]. The bismaleimides were prepared from the corresponding diamines and maleic anhydride by a modification of the method of White et al.[5] [eq. (2)].

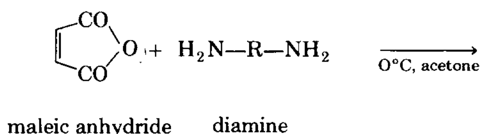
Table I shows thermal properties of the new bismaleimides containing ether bonds and known bismaleimides. One of known bismaleimides, 4,4′-bismaleimidodiphenylmethane (BDM) had a short gel time and immediately polymerized after having been melted, because there was small difference between the melting point and the onset temperature for the curing reaction (T_1). The aliphatic bismaleimide, 1,6-bismaleimidohexane (C_6-B), had a very short gel time and high reactivity compared with the aromatic bismaleimides used in this study.

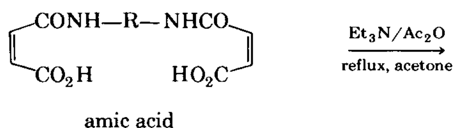
The bismaleimides containing ether bonds (BPPP, 3,3′-BPPS, BPE-3) had long gel times (long potlife of melt), because there were large difference between the mp and the T_1. A large lowering in the mp must be due to the flexible molecular structure containing ether bonds.

TABLE I
Thermal Properties of Bismaleimides

Bismaleimide	mp[a] (°C)	T_1[b] (°C)	T_{exo}[c] (°C)	T_2[d] (°C)	GT[e] (s)
BPPP	121	203	302	344	510
3,3′-BPPS	104	198	211, 272	330	1060
3,4′-BDE	212	217	236, 318	365	—
BPE-1	230	240	245	280	—
BPE-3	176	236	274	334	1710
BDM	158	174	233	316	130
C_6-B	143	177	234	322	20

[a] Melting point by DSC.
[b] Onset temperature for curing reaction by DSC.
[c] Exothermal peak temperature by DSC.
[d] Temperature for completion of reaction by DSC.
[e] Gel time at 200°C





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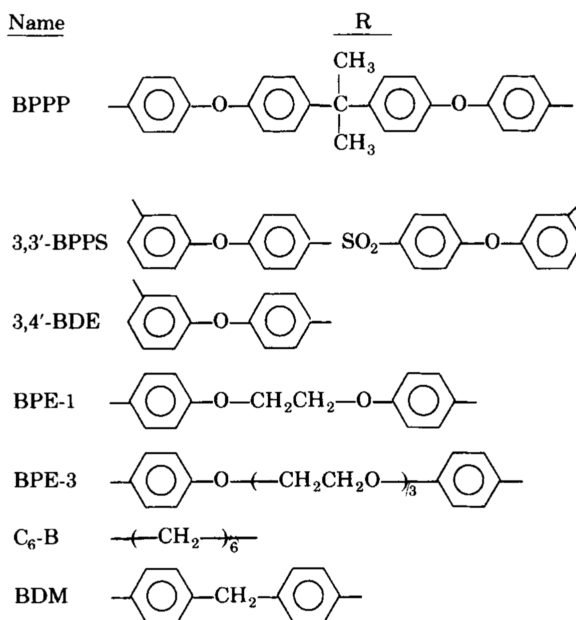

This finding indicates that the introduction of ether bonds into the bismaleimide molecule can improve the handling and processing characteristics of the bismaleimide.

TABLE II
Thermal Properties of Cured Bismaleimide Resins

Cured resin	T_d[a] In air (°C)	T_d[a] In N_2 (°C)	T_g[b] (°C)
BPPP	412	464	312
3,3′-BPPS	414	436	288
3,4′-BDE	431	483	313
BPE-1	385	436	317
BPE-3	334	394	285
BDM	416	500	342
C_6-B	392	468	—

[a] Initial weight loss temperature of bismaleimide resin, cured for 10 h at 280°C, by TGA.
[b] Glass transition temperature of bismaleimide resin, cured for 10 h at 280°C, by TMA.

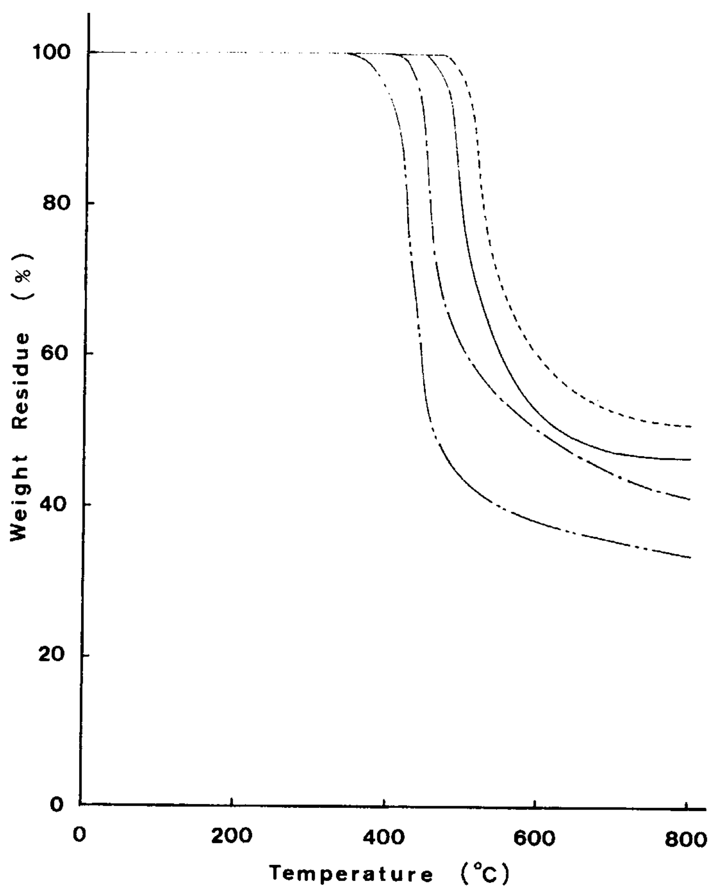

Fig. 1. Thermogravimetric analysis of bismaleimide resins, cured for 10 h at 280°C, in N_2: (---) BDM; (——) BPPP; (—-—) BPE-1; (—--—) BPE-3.

Thermal Properties of Cured Bismaleimide Resins

The initial weight loss temperature T_d of the cured bismaleimide resins is shown in Table II and the TG curves are indicated in Figure 1. The resins containing aromatic ether bonds (BPPP, 3,3′-BPPS, 3,4′-BDE) as well as BDM resin showed high T_d values. As expected, the values of T_d for these aromatic resins were greater than the T_d of the aliphatic resin (C_6-B).

On the other hand, the T_d values of the resins containing oxyethylene linkages (BPE-1, BPE-3) were less than the T_d of the resins containing aromatic ether bonds. The T_d of BPE-3 resin, in particular, lowered, owing to its extended oxyethylene chains. These results suggest that the ethylene—oxygene linkage (CH_2CH_2—O) is liable to be broken in comparison with the phenyl—oxygene (Ph—O), or phenyl—methylene (Ph—CH_2) linkages.

The glass transition temperature T_g for the cured bismaleimide resins were measured by thermomechanical analysis (TMA). The influence of curing conditions (time and temperature) on the T_g is indicated in Figures 2 and 3. The values of T_g increased with increasing curing time, and kept almost constant above 10 h. The T_g values for the resins cured for 10 h at 280°C are shown in Table II. The cured resin of BDM showed higher T_g compared with the other resins. The low T_g for cured BPPP resin must result from relatively long distance between cure sites in the BPPP molecule. The T_g of cured 3,3′-BPPS lowered further, because the resin had an unsymmetrical structure in the molecule. The cured resins containing oxyethylene linkages (BPE-1, BPE-3) showed low T_g values owing to their flexible molecular structures.

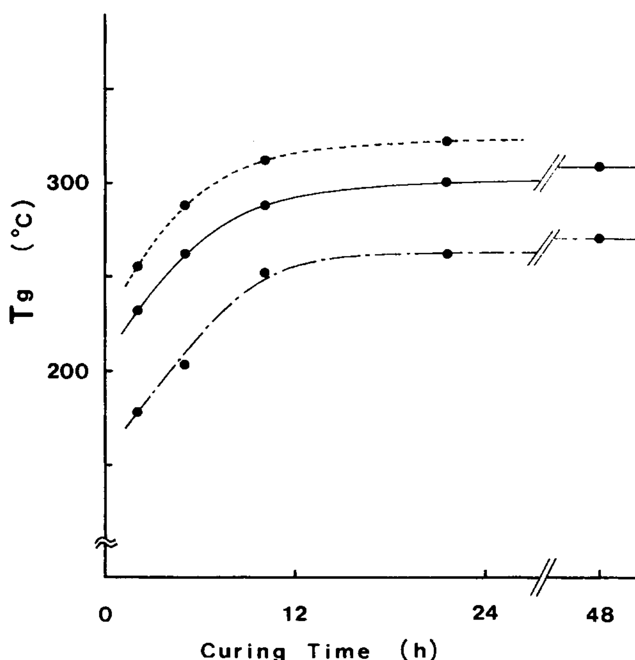

Fig. 2. Dependence of glass transition temperature T_g on curing time and temperature; curing condition: (——●-) BPPP, 230°C; (—●-) BPPP, 250°C; (---●--) BPPP, 280°C.

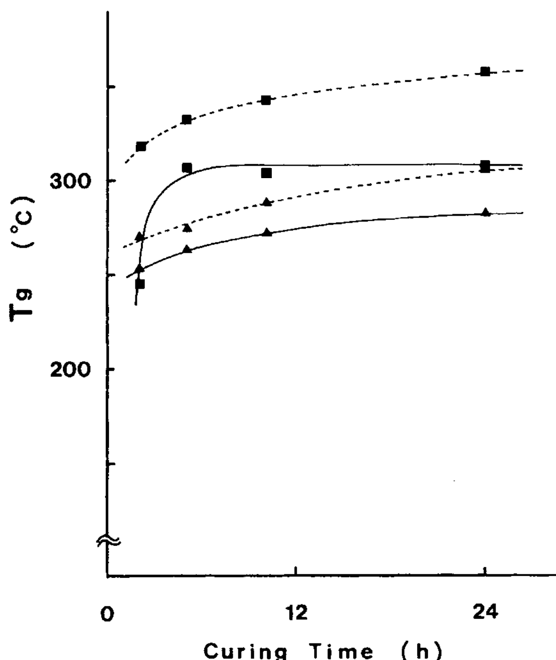

Fig. 3. Dependence of glass transition temperature T_g on curing time and temperature; curing condition: (—■—) BDM, 250°C; (---■---) BDM, 280°C; (—▲—) 3,3′-BPPS, 250°C; (---▲---) 3,3′-BPPS, 280°C.

The T_g of the cured resins of BPPP, 3,3′-BPPS, and BDM increased when the curing temperature increased from 250 (or 230) to 280°C, as shown in Figures 2 and 3. The values of T_g of BPPP resin, cured for 24 h at 230, 250, and 280°C were 262, 300, and 322°C, respectively. The difference in T_g between the resins cured at 230 and 250°C was larger than that between the resins cured at 250 and 280°C. This fact suggests that BPPP treated for 10 h at 280°C yielded the resin with an almost completely cured structure.

The dependence of the T_g values on the curing temperature could be explained by the following curing process according to the theory of Gillham.[9] When the bismaleimides are treated at a fixed temperature for a long time, the resulting resins have rigid structures in which the mobility of the polymer segments is very reduced at the temperature. These resins still have unreacted functional groups and exhibit temporary glass transition temperatures. As the resins are treated at a curing temperature near the apparent T_g, the mobility of reactive sites increases, and the curing reactions start again to yield resins with more cured structure and higher temporary T_g. Such a curing process must proceed until the resins with fully crosslinked structure are obtained.

Dynamic Mechanical Analysis (DMA) of Cured Bismaleimide Resins

The dynamic mechanical properties of the bismaleimide resins were indicated in Figure 4. The $\tan\delta$ peak at -65°C for BDM resin is attributed to β-relaxation of the cured bismaleimide. The α-relaxation (T_g) of BDM resin, however, was not observed within the temperature range of DMA. The

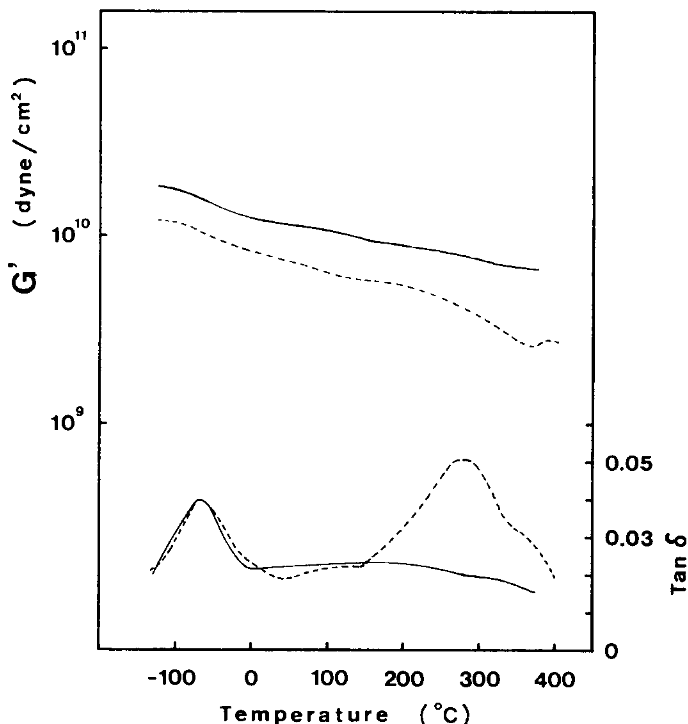

Fig. 4. DMA results for the bismaleimide resins, cured for 10 h at 280°C: (——) BDM; (---) BPPP.

α-relaxation temperature for BDM resin may be above 360°C. The tan δ peaks at -65 and 270°C for BPPP resin are attributed to β- and α-relaxations, respectively. The peak temperatures in tan δ are different from the glass transition temperatures obtained from TMA. This result is to be expected from differences in both the types of measurement and thermal histories of specimens.

The dynamic modulus G' of the bismaleimide resins did not change clearly over the temperature range -140–360°C, indicating that the introduction of ether linkages into the bismaleimides does not injure their mechanical properties at high temperature.

Mechanical Properties of Cured Bismaleimide Resins

The flexural strength and the flexural modulus of the cured bismaleimide resins are shown in Figure 5. The values of flexural strength and modulus of BDM resin were 3.3 and 491 kgf/mm^2, respectively. This resin is extremely rigid and brittle because of its high crosslink density. The flexural strength for BPPP, 3,3′-BPPS, and BPE-1 resins was 1.6–1.9 times greater than that for BDM resin, whereas the flexural moduli for the former resins were lower than that for the latter resin. In addition, the flexural strength for BPE-3 containing relatively long oxyethylene chain was about three times greater than that for BDM, whereas the flexural modulus considerably decreased.

These results suggest that the introduction of ether linkages into the bismaleimide molecules increased the strength and flexibility of the cured

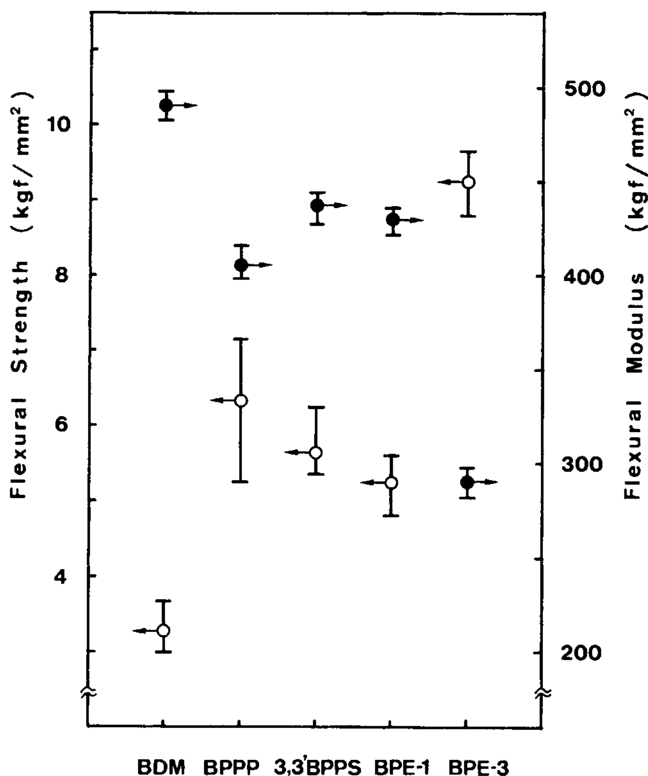

Fig. 5. Flexural strength and flexural modulus of bismaleimide resins, cured for 10 h at 280°C.

resins. In particular, BPPP resin containing an aromatic ether linkage showed the improved flexibility without significant reductions in heat-resistant properties.

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