

Curing and Thermal Behavior of Poly(allyl azide) and Bismaleimides

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ABSTRACT: The reaction of poly(allyl azide) (PAA; number-average molecular weight = 1800 g/mol) with *N*-phenyl maleimide, 4,4'-bis(maleimidodiphenyl) ether, 4,4'-(bismaleimidodiphenyl) sulfone, and 1,6-bismaleimido hexane is described in this article. As indicated by Fourier transform infrared studies, the azido group reacted with the highly electron-deficient olefinic bond of *N*-phenyl maleimide or bismaleimides in a 3 + 2 cycloaddition reaction under mild reaction conditions. The curing of PAA with bismaleimides (10–30 phr) was monitored with differential scanning calorimetry. In freshly prepared samples of PAA and bismaleimides, a broad exothermic transition was observed in the temperature range of 150–280°C and could be attributed to the loss of N₂ from PAA and the curing of bismaleimides. The heat of the exothermic reaction (ΔH) depended on the

structure and composition and was in the range of 800–1413 J/g. Isothermal heating in an air oven at 40°C (2 days) followed by 60°C (5–6 days) resulted in the conversion of a sticky, viscous liquid into an elastic, nonsticky material. No significant difference in the ΔH values of uncured and cured samples was observed, and this indicated the reaction of fewer azido groups with the bismaleimides (dipolarophiles). In the thermogravimetry traces, a mass loss was indicated in the temperature range of 130–280°C due to the loss of nitrogen from the azido group. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 779–786, 2006

Key words: copolymerization; curing of polymers; FTIR; cross-linking and degradation

INTRODUCTION

Low-molecular-mass azido polymers, such as poly(glycidyl azide) (GAP), poly(azidomethyl methyloxetane), and poly(bisazidomethyl oxetane), have been used as high-energy binders and fuels in rocket technology.^{1–3} The traditional method of curing these resins is to mix hydroxy-terminated low-molecular-weight azido polymers (number-average molecular weight ~2000–3000) with diisocyanates and a chain extender (trimethylol propane).^{4,5} In a typical propellant formulation, high-energy additives (ammonium nitrate or ammonium perchlorate), a pyrolant (metallic powder), and plasticizers are also added.

There are certain problems that are encountered when isocyanates are used as curing agents for hydroxy-terminated binders. The most serious is the evolution of CO₂ due to the reaction of isocyanates with moisture. This leads to the formation of numerous voids in the cured explosive, resulting in a decrease in the loading density, mechanical performance, and safety. Moisture therefore has to be expelled before curing with isocyanates to prevent bubble formation.

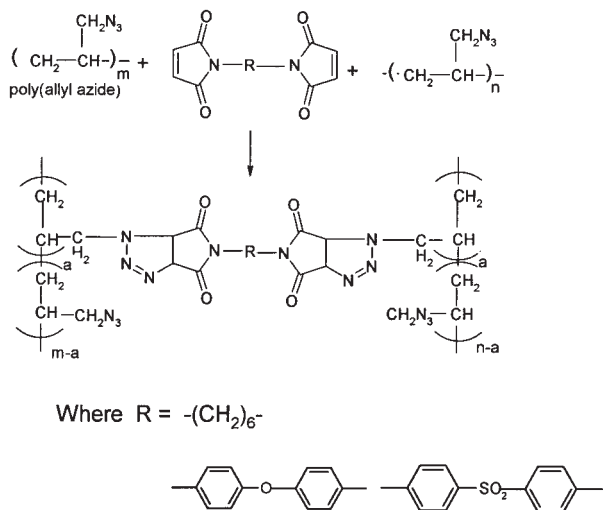
The second problem is a significant decrease in the energy output of plastic bonded explosives or propellants because of the inert properties of diisocyanates and chain extenders. A third problem is the loss of the plasticizing effect during the curing of the hydroxyl group of the prepolymer with isocyanates. Curing causes an increase in the glass-transition temperature of GAP, and it increases with an increase in the NCO/OH ratio.⁶

An alternative approach is the use of the [3 + 2] cycloaddition reaction of the azide groups with appropriate dipolarophiles. Azides are 1,3-dipolar compounds and readily undergo a cycloaddition with olefinic or acetylene esters and amides to yield a five-membered heterocyclic ring (i.e., 1,2,3-triazoline or 1,2,3-triazole).^{7,8} Such additions are always *cis* and usually regiospecific.^{9,10} The triazolines thus obtained are thermally labile and lose nitrogen to yield aziridines. Therefore, the reactions are carried out at low temperatures and can take weeks for completion. Rigid alkenes such as norbornene react with azides on heating to form *exo*-adducts.¹⁰

Curing a glycidyl azide polymer with a variety of dipolarophiles such as multifunctional acrylic or acetylene esters (dimethylene glycol diacrylate, tetraethylene glycol diacrylate, ethylene glycol diacrylate, hexanediol diacrylate, pentaerythritol tri/tetraacrylate, and acrylic amide) has been reported in the literature.^{11,12}

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Scheme 1 Curing of PAA with bismaleimides.

In our earlier article,¹³ we reported the curing and thermal behavior of poly(allyl azide) (PAA) with ethylene glycol dimethacrylate. Although few reports have been published on the curing of azido polymers with acrylic or acetylene esters/amides, no reports are available on the use of addition polyimides [i.e., bismaleimide, bisitaconimide, and endo-5-norbornene-2,3-dicarboximide-(nadimide) end-capped resins] as curing agents. It was therefore decided to carry out a systematic study of the 3 + 2 cycloaddition reaction between bismaleimides of different backbone structures and PAA.¹⁴

This article describes the curing and thermal behavior of PAA with novel dipolarophiles, that is, bismaleimides, as curing agents. The azido group is highly nucleophilic and is expected to add easily to the electron-deficient double bond of the addition polyimide to form a triazolone ring according to the reaction in Scheme 1.

EXPERIMENTAL

PAA¹³ and bismaleimides^{15–17} [i.e., 4,4'-bis(maleimidodiphenyl) ether (BE), 4,4'-(bismaleimidodiphenyl) sulfone (BS), and 1,6-bismaleimido hexane (BH)] were synthesized according to the method reported in the literature. The melting points of BE, BS, and BH were 174–175, 252, and 138°C, respectively. *N*-Phenyl maleimide (97%) was procured from Aldrich Co. (Milwaukee, WI) and was purified by the passage of a chloroform solution through a silica gel column and subsequent recrystallization (mp = 91.8°C).

Monitoring of the reaction

The reaction of *N*-phenyl maleimide with PAA was carried out via refluxing in chloroform, and the reac-

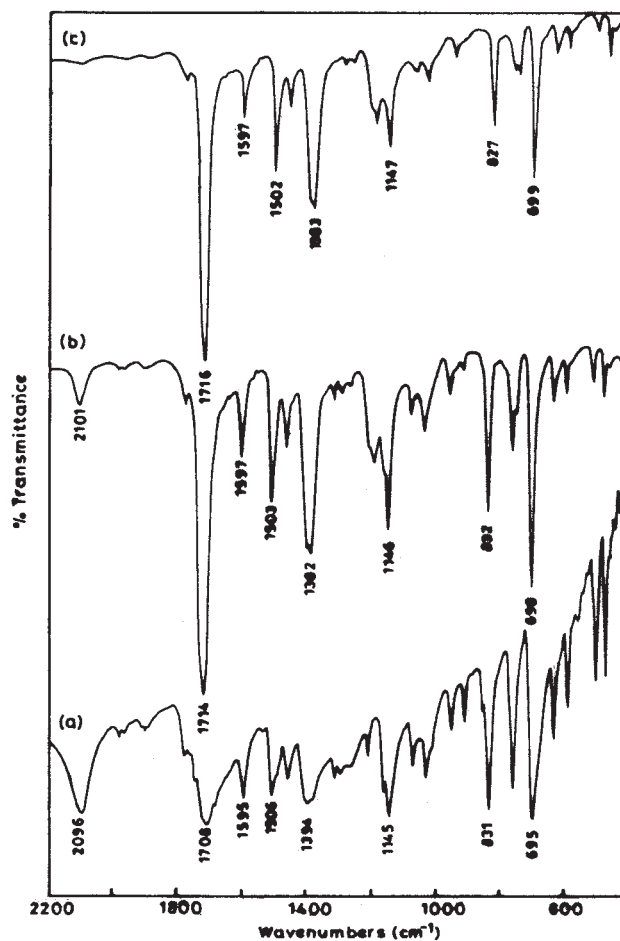


Figure 1 FTIR spectra of PAA and *N*-phenyl maleimide (azido/imide molar ratio = 1 : 1) at different times: (a) 1, (b) 2, and (c) 5 h.

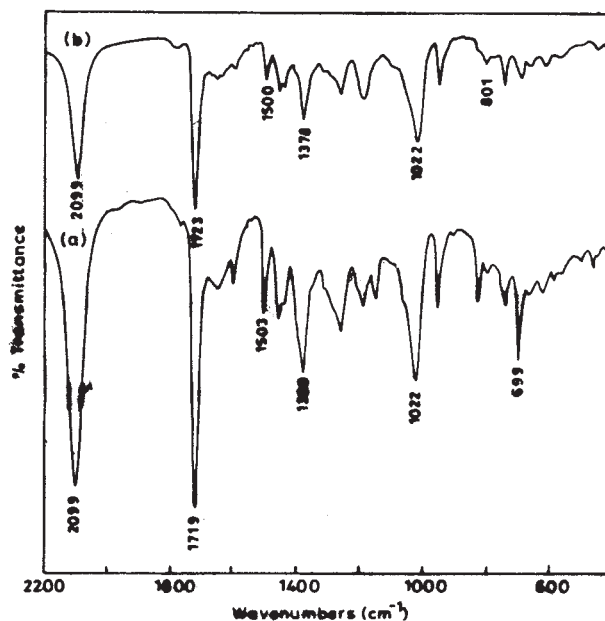


Figure 2 FTIR spectra of PAA and *N*-phenyl maleimide (azido/imide molar ratio = 1 : 1) at different times: (a) 2 and (b) 5 h.

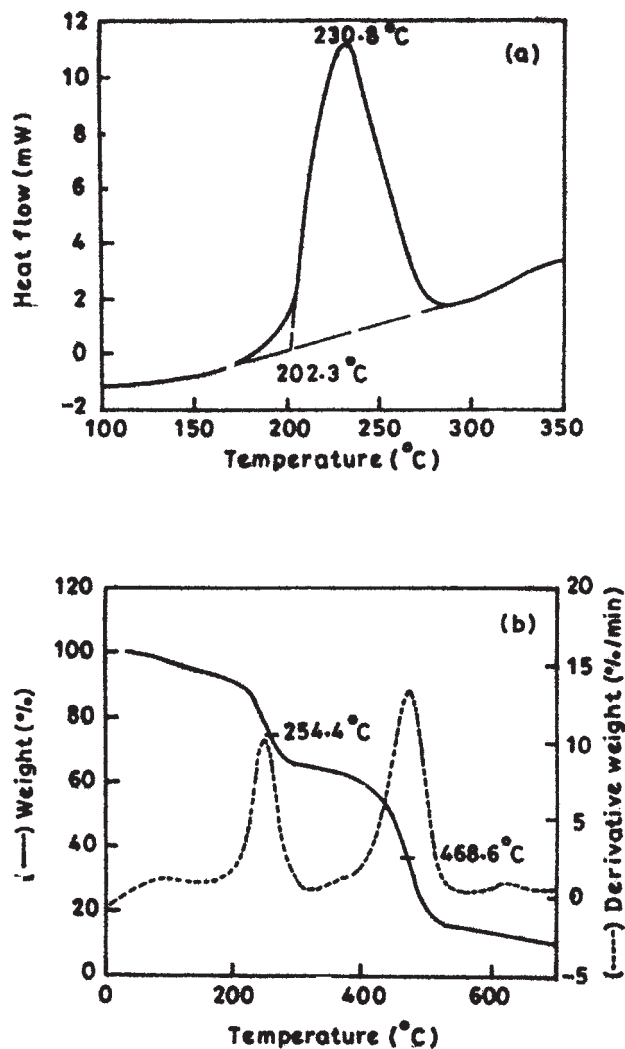
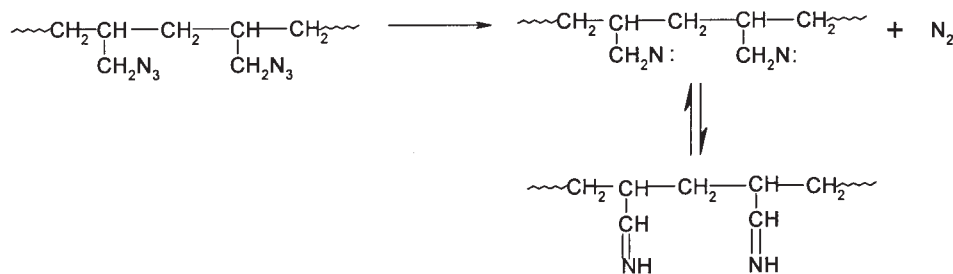


Figure 3 (a) DSC trace in an air atmosphere and (b) TG trace in an N_2 atmosphere for PAA.

tion was monitored with Fourier transform infrared (FTIR) spectroscopy. A drop of the reaction mixture was placed on a KBr disc, and IR was recorded after the evaporation of the solvent. The azido/imide molar ratio was kept at 1 : 1 or 10 : 1.

FTIR of polymer samples was recorded with a PerkinElmer 2000 FTIR spectrometer (Wellesley, MA).



Scheme 2 Reaction sequence depicting the decomposition of PAA.

Curing of PAA

The curing behavior of PAA and samples of PAA with various amounts (10–30 phr) of bismaleimides was evaluated with a TA 2100 thermal analyzer with a 910 differential scanning calorimetry (DSC) module. A heating rate of $5^\circ\text{C}/\text{min}$ in a static air atmosphere and a sample mass of 4 ± 1 mg were used. For the thermal characterization of PAA and bismaleimides, the samples were prepared by thorough mixing of PAA and requisite quantities of bismaleimides in Teflon boats.

The exothermic transition observed in the temperature range of $150\text{--}280^\circ\text{C}$ was characterized by the determination of the temperatures of (1) the onset of the exotherm (T_i), (2) the extrapolated onset (T_o), and (3) the end of the exotherm (T_e) and the exothermic peak temperature (T_p). The heat of the reaction (ΔH) was determined from the area under the exothermic transition.

Studies on the isothermal curing of PAA with bismaleimides were also carried out in an air oven at 40 (2 days) and 60°C for several days. DSC was used for the evaluation of the changes in the exothermic transition in these samples after heating at 40°C for 2 days and then after heating at 60°C for 0–6 days.

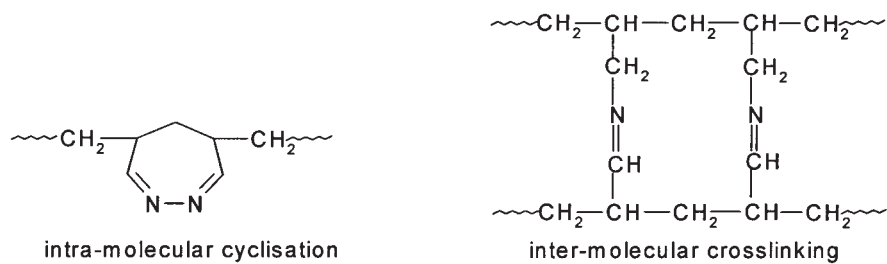
Thermogravimetric analysis

A TA 2100 thermal analyzer with a 951 thermogravimetry (TG) module was used for the thermal characterization of PAA and isothermally cured PAA and bismaleimides in a nitrogen atmosphere (flow rate = 60 mL/min). A sample mass of 5 ± 1 mg was used, and the rate of heating was $10^\circ\text{C}/\text{min}$. The relative thermal stability of these samples was estimated by a comparison of (1) the initial decomposition temperature (IDT), (2) the final decomposition temperature (T_f), and (3) the temperature of the maximum rate of mass loss (T_{max}) and char yield at 600°C .

RESULTS AND DISCUSSION

Monitoring of the reaction between PAA and maleimides

Structural changes taking place during the reaction of PAA and *N*-phenyl maleimide or bismaleimides were



Scheme 3 Intramolecular and intermolecular reactions of imino groups.

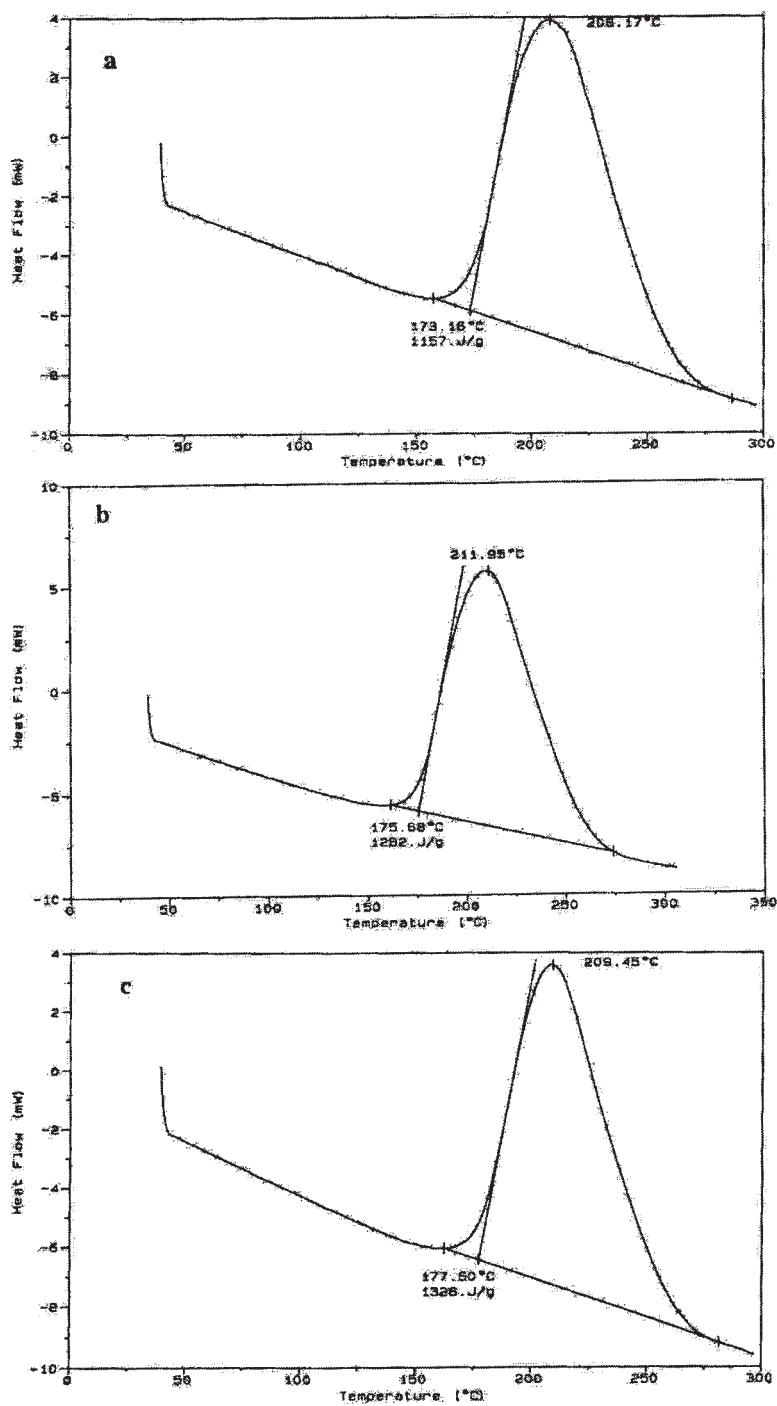


Figure 4 DSC scans of PAA cured with BS: (a) PSB-0, (b) PSB-1, and (c) PSB-5.

TABLE I
DSC of PAA Isothermally Cured with BH (10–30 phr) at 40°C for 2 Days and Kept at 60°C for Various Intervals of Time (Heating Rate = 10°C/min)

Sample	BH (phr)	Time (days)	T_i (°C)	T_o (°C)	T_p (°C)	T_e (°C)	ΔH (J/g)
PHA-0	10	0	151.4	168.7	202.8	278.4	1318
PHA-5		5	146.6	175.9	192.4	278.4	1020
PHB-0	15	0	146.0	166.2	201.7	277.0	1053
PHB-1		1	151.6	168.0	197.2	273.2	1072
PHB-5		5	152.0	166.5	199.2	273.0	1379
PHC-0	30	0	153.4	170.0	201.4	270.3	1028
PHC-1		1	152.0	171.4	200.1	270.9	984.7
PHC-5		5	152.0	171.4	199.1	275.0	869.1

monitored by IR spectroscopy. The carbonyl stretching band of the imide group (observed in bismaleimides at $1705 \pm 10 \text{ cm}^{-1}$) shifted to higher frequencies via heating with PAA. The carbonyl group of maleimides is conjugated with the double bond. Once the 3 + 2 cyclic dipolar addition reactions take place between PAA and maleimides, the double bond is removed, and hence an increase in the carbonyl frequency is expected to take place (Scheme 1).

When the molar ratio of *N*-phenyl maleimide to azido groups was kept at 1:1, the absorption band due to the azido group disappeared completely after 5 h (Fig. 1). However, when less *N*-phenyl maleimide was used (azide/imide molar ratio = 10 : 1; Fig. 2), the intensity of the azido absorption band at $2098 \pm 3 \text{ cm}^{-1}$ was reduced, and a shift in the position of the imido carbonyl to higher frequencies was observed.

In the reaction of PAA with bismaleimides (10–30 phr), only a marginal decrease in the intensity of the azido group was observed, whereas the carbonyl absorption band due to the imide group shifted to a higher frequency. A new absorption peak due to ring breathing vibrations of 1,2,3-triazoline was observed at $1122 \pm 5 \text{ cm}^{-1}$. These studies thus confirmed the cyclic dipolar addition reaction of PAA with bismaleimides.

Thermal behavior of PAA and bismaleimides

The DSC scan [Fig. 3(a)] of PAA showed an exothermic transition in the temperature range of 155–274°C, with T_p at 231°C. The liberated energy was 1099 J/g. The TG trace of PAA [Fig. 3(b)] showed an initial mass loss of 7%, which could be attributed to the moisture and low-molecular-mass oligomers. The main decomposition proceeded in two stages of mass loss. The first step of the decomposition occurred in the temperature range of 160–322°C. The exothermic transition observed in DSC was at a lower temperature range (155–274°C). This difference in the temperatures of DSC and TG studies could be attributed to the difference in the heating rates used. A mass loss of 28.3% was

observed. Therefore, the exothermic transition observed in DSC of PAA accompanied by a mass loss in thermogravimetric analysis (28.3%) could be attributed to the breakdown of the azido group (Scheme 2).

The major mass loss observed above 400°C (~59%) was due to the breakdown of the polymer backbone leading to the formation of hydrogen, carbon monoxide, carbon dioxide, methane, ammonia, hydrogen cyanide gas, and other higher hydrocarbons.¹⁸ Char residues of 15% at 600°C and 7% at 800°C were obtained, and this may have been due to the formation of a crosslinked structure by the reaction of an imine intermediate (intermolecular and intramolecular)^{19,20} (Scheme 3).

The bismaleimides do not homopolymerize under ambient conditions. Thermal polymerization has to be carried out above 150°C to get the crosslinked product.

Bismaleimide resins cure on heating above their melting point to yield a crosslinked network polymer that is infusible and insoluble in organic solvents. For example, BE cured above its melting point (174–175°C), as indicated by the appearance of an exothermic transition ($T_o = 194^\circ\text{C}$ and $T_p = 262^\circ\text{C}$), and T_o and T_p were 260 and 273°C, respectively, for the BS resin. The ΔH values were in the range of 150–200 J/g.

Curing of PAA with bismaleimides

The curing of PAA was performed with three different bismaleimides containing (1) flexible aliphatic units (hexamethylene; BH), (2) aromatic rings having flexible ether linkages (BE), or (3) a strong electron-withdrawing group sulfone (BS) as the bridging unit between the maleimide end caps. The bismaleimide content was varied to evaluate the effect of the concentration on curing (10–30 phr). This corresponded at 10 phr to azide/maleimide ratios of 1 : 0.06, 1 : 0.47, and 1 : 0.02 for BH, BE, and BS, respectively. Thus, the azide groups were much higher in concentration than the maleimide under investigation.

TABLE II
DSC of PAA Isothermally Cured with BE or BS (10–30 phr) at 40°C for 2 Days and Kept at 60°C for Various Intervals of Time (Heating Rate = 10°C/min)

Sample	Time (days)	BE (phr)	T_i (°C)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
PEA-0	10	0	158.0	174.2	204.7	281.3	1413
PEA-1		1	150.0	173.9	205.1	275.0	1257
PEA-6		6	150.0	172.7	203.7	273.6	1275
PEB-0	15	0	158.8	169.8	201.1	279.1	903
PEB-1		1	154.1	173.2	203.3	273.3	1190
PEC-0	30	0	154.0	174.4	196.4	273.7	1166
PEC-1		1	148.6	175.4	195.8	275.7	1016
PEC-6		6	144.6	174.6	196.5	277.7	800.8
PSB-0	15	0	158.8	173.2	208.2	275.7	1157
PSB-1		1	162.6	175.7	212.0	273.2	1282
PSB-5		5	162.8	177.6	209.5	275.0	1326

This controlled the crosslink density of the cured product.

The blends of PAA and bismaleimide were initially sticky masses, regardless of the composition of the blends. Isothermal heating at 40°C for 2 days resulted in a marginal change in the physical characteristics. When isothermal heating was performed at 60°C for several days, the sticky mass converted into a non-sticky, elastic product.

The PAA blends with bismaleimides BH, BE, and BS have been designated as PH, PE, and PS, respectively. The concentration of the bismaleimides is indicated by A (10 phr), B (15 phr), or C (30 phr) after the letter designation of the blend. The duration of isothermal curing (0 days, 1 day, 5 days, etc.) is indicated by the number after the letter designation of the formulation. Thus, blends of PAA and BE (10, 15, and 30 phr) cured for 5 days are designated PEA-5, PEB-5, and PEC-5, respectively.

The DSC scans of PAA isothermally cured with bismaleimide BS are shown in Figure 4. Similar scans were recorded for all samples, and the data are summarized in Tables I and II. A comparison of the curing characteristics of PAA and its blends showed only marginal changes in the T_i and T_o values. The exothermic peak position of PAA was 231°C, but the addition of structurally different bismaleimides reduced it by 20–30°C. ΔH was 1099 J/g for PAA, but in most blend samples, the ΔH value was either equal to or higher than this value. Slightly lower values were observed only in PEC-6, PEB-0, PHC-1, and PHC-5 samples. The observed exotherm in the PAA bismaleimides samples arose because of two reactions: (1) the loss of N_2 from PAA to yield nitrenes and (2) the curing of bismaleimides. The ΔH values of the bismaleimides were lower than the heat that evolved during nitrene formation. These results thus indicate that only a few azide groups had reacted with bismaleimides at 60°C and a large proportion was available for the decomposition of these energetic binders. Bismaleimides did

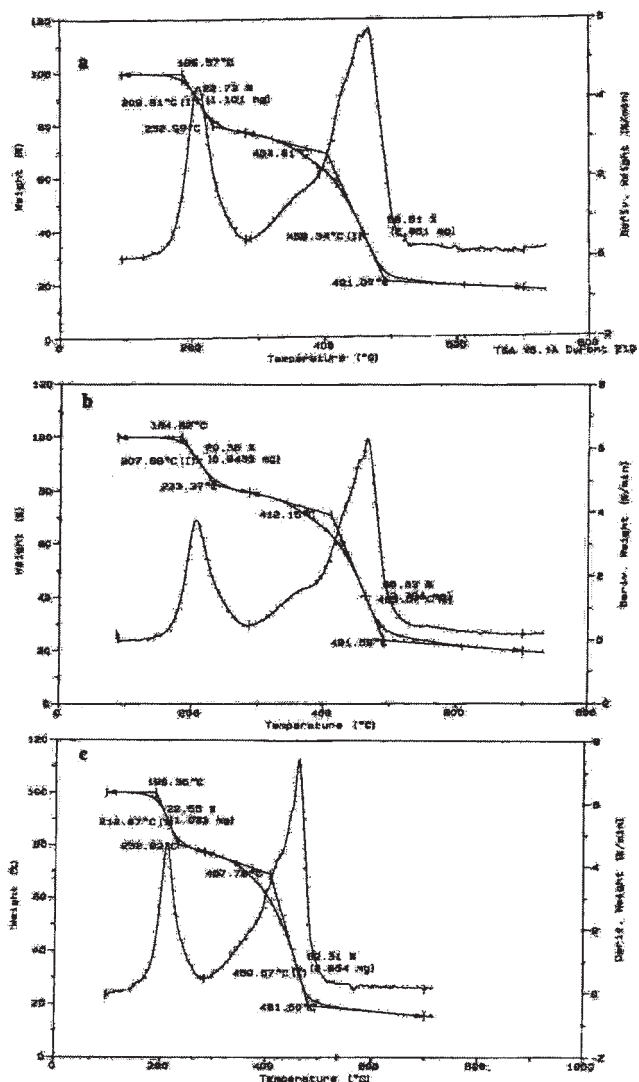


Figure 5 TG traces of PAA cured with BE and BS: (a) PEA-6, (b) PEB-5, and (c) PSB-1.

TABLE III
Thermal Behavior of PAA Isothermally Cured with BH Resin (Heating Rate = 10°C)

Sample	Bismaleimide (phr)	Time (days)	IDT (°C)	T_{max} (°C)	T_f (°C)	Weight loss (%)	Char yield (%) at 600°C
PHA-1	10	1	155.4	209.4	280.0	22.0	23.4
			297.7	482.1		63.2	
PHA-5		5	153.5	201.5	271.4	27.6	22.5
			296.4	459.8	610.7	57.5	
PHB-1	15	1	124.4	213.8	291.1	22.0	14.8
			300.0	477.0	600.0	63.2	
PHB-5		5	144.4	210.3	291.1	21.9	20.0
			304.4	468.3	555.6	58.5	
PHC-1	30	1	142.8	221.5	275.0	18.2	21.6
			289.3	466.5	628.6	58.4	
PHC-5		5	132.1	194.0	264.3	18.1	20.7
			282.1	461.8	600.0	60.3	

not act as inert materials (as in the case of isocyanates) but contributed toward the heat of curing in the same temperature range in which the azide group undergoes decomposition. Thus, the overall heat that evolved in the temperature range of 150–277°C was either equal to that of neat PAA or greater. The TG traces of the cured resin are shown in Figure 5. The results of the TG studies are summarized in Tables III and IV. A two-step decomposition was observed. A mass loss of 18–23% was observed in the temperature range of 150–280°C. In comparison with pure PAA, a reduction in the mass loss of about 5–10% was observed. The curing of bismaleimides is an addition reaction without the evolution of any volatiles, whereas PAA eliminates N_2 in this temperature range. An increase in the concentration (phr) of bismaleimides reduced the mass loss in this temperature region. The second step of decomposition was observed in the temperature range of 290–310°C with a mass loss of

57–64%. In comparison with PAA, the char residue at 600°C was higher in these resins. This was due to the network formation of cured bismaleimides, which favored condensation and char formation at high temperatures.

CONCLUSIONS

The curing of PAA was carried out under mild conditions with bismaleimides (10–30 phr) as the dipolarophiles. The cured resins were flexible and retained their elastic behavior for several weeks. The ΔH value for the exothermic decomposition of the azido groups was significantly high. This may have been due to the exothermic curing of bismaleimides and the decomposition of azido groups in almost the same temperature range. In contrast to isocyanates, which are generally used for the curing of hydroxy-terminated azido polymers, bismaleimides do not act as inert curing

TABLE IV
Thermal Behavior of PAA Isothermally Cured with 10–30 phr BE/BS Resins (Heating Rate = 10°C/min)

Sample	Bismaleimide (phr)	Time (days)	IDT (°C)	T_{max} (°C)	T_f (°C)	Mass loss (%)	Char yield (%) at 600°C
PEA-1	10	1	135.6	211.8	286.7	24.2	13.5
			295.6	472.4	580.0	62.5	
PEA-6		6	125.0	210.0	282.1	22.7	19.4
			292.8	459.3	610.7	59.5	
PEB-1	15	1	128.9	220.8	297.8	24.5	15.2
			297.8	467.6	573.3	60.3	
PEB-5		5	135.7	207.7	282.1	20.4	22.0
			285.7	463.6	607.1	60.0	
PEB-1	30	1	111.2	203.4	302.1	18.7	25.8
			311.0	464.2	635.5	59.2	
PEB-6		6	142.8	202.7	282.1	18.7	21.6
			292.8	460.7	592.9	62.6	
PSB-1	15	1	124.4	213.8	291.1	22.0	14.8
			300.0	477.0	600.0	63.2	
PSB-5		5	146.5	212.9	275.5	22.0	19.4
			297.7	460.6	532.2	62.3	

agents. An increase in the char residue of the cured resin at 600°C was also observed.

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