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THE THERMAL BEHAVIOUR OF BLENDS OF TRISNADIMIDE WITH BISMALEIMIDE RESINS

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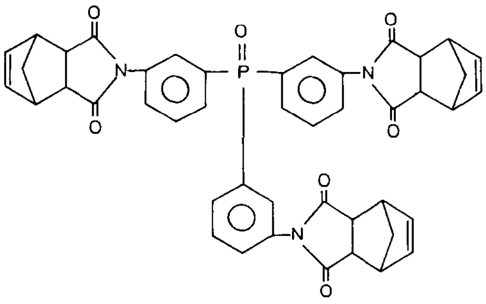
ABSTRACT

The thermal behaviour of blends of tris(3-nadimidophenyl)-phosphine oxide (TNI) and bis(4-maleimidophenyl)methane (BMI) was evaluated by using differential scanning calorimetry and thermogravimetry. A decrease in the melting point of BMI resin was observed on addition of TNI. The heat of fusion depended on the blend composition and increased by increasing the BMI content. The exothermic peak temperature (due to curing reaction) in the blends was lower, thereby indicating that curing of these blends can be done at lower temperatures. The overall thermal stability of the blends was only marginally affected by the blend composition.

INTRODUCTION

In a previous paper [1] we reported the synthesis and characterization of a series of phosphorus-containing *endo*-5-norbornene-2,3-dicarboximide (nadimide) end-capped monomers and oligomers. Amongst these resins, tris(3-nadimidophenyl) phosphine oxide (I trisnadimide, TNI) gave a maximum char yield of 60% at 800 °C in nitrogen atmosphere.



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The curing of this resin could be done at temperatures of > 300 °C. It is desirable to develop addition polyimides which have excellent thermal and flame resistance, but at the same time can be cured at a relatively low temperature.

It is generally believed that the nadimide end-capped monomers and oligomers undergo a reverse Diels–Alder reaction at elevated temperature leading to the formation of maleimide and cyclopentadiene, which then undergo polymerization to yield a highly cross-linked network polymer [2,3]. It may be possible to reduce the curing temperature of nadimides by the addition of preformed maleimide oligomers. A decrease in the exotherm peak position by the addition of bismaleimide to nadimide has been reported previously [2,4]. Such blending studies of nadimide and bismaleimides have not been exploited fully. It was therefore considered of interest to investigate the effect of blending bis(4-maleimidophenyl)methane (bismaleimide, BMI) with tris(3-nadimidophenyl) phosphine oxide.

EXPERIMENTAL

Materials

Tris(3-aminophenyl) phosphine oxide was prepared from triphenyl phosphine oxide (Koch-Light) by nitration and subsequent reduction, according to the procedure reported elsewhere [5]. Glacial acetic acid (BDH) and acetic anhydride (BDH) were distilled at normal pressure before use. Nadic anhydride (E-Merck) was recrystallized from acetic anhydride and then from chloroform. Maleic anhydride (BDH) and 4,4′-diaminodiphenyl methane (BDH) were used as received.

Procedure

TNI was prepared in glacial acetic acid as described previously [1]. The details of bismaleimide BMI synthesis [6] have been reported elsewhere.

Six blends were prepared by using TNI and BMI in appropriate quantities and grinding them together in a pestle and mortar for thorough mixing. The composition of these blends is given in Table 1.

A DuPont 1090 thermal analyser with a 910 DSC module was used for studying the curing behaviour of these blends. A sample of about 11 ± 2 mg was heated from room temperature to 450 °C in static air at a heating rate of 10 °C min^{-1}.

A DuPont 1080 thermal analyser with a 951 TG module was used to assess the relative thermal stabilities of the nadimide resins. Thermogravimetric traces were recorded in nitrogen atmosphere (flow rate, 100 cm^3 min^{-1}) at a heating rate of 10° C min^{-1}. A sample size of 11 ± 1 mg was used.

TABLE 1

Fusion characteristics of TNI/BMI blends

Bismaleimide (%w/w)	Fusion characteristics (°C)			ΔH_f (J g^{-1})
	T_1	T_2	T_3	
9.0	116.5	146.6	161.0	8.5
16.5	125.0	145.0	158.0	–
59.0	117.5	147.2	167.5	33.9
67.0	117.5	150.3	170.0	39.6
77.0	112.5	153.0	175.0	47.0
91.0	115.0	154.4	170.0	50.4

The TG curve was characterized by determining: (i) the initial decomposition temperature (T_i) (the temperature where the TG plot deviates from the baseline); (ii) the final decomposition temperature (T_f); and (iii) the temperature of the maximum rate of weight loss (T_{max}). T_i and T_f were obtained by extrapolation. The percentage char yield (Y_c), which is the residual weight at 800 °C in nitrogen atmosphere, was also recorded from the TG curves.

RESULTS AND DISCUSSION

In the DSC curves of the TNI resin, no endothermic transition due to melting was observed. On the other hand, for BMI resin a sharp endotherm with a peak temperature of 156 °C was observed. The addition of BMI to TNI resulted in the appearance of a broad endotherm in the temperature range 115–170 °C. At the low weight percentage of BMI (i.e. $< 20\%$), the endothermic peak was not well defined [Fig. 1(a and b)]. However, on increasing the BMI content the peak became well defined and at high concentration of BMI (i.e. $> 90\%$) the transition became sharp [Fig. 1(c and d)]. The melting transition was characterized by determining the temperatures of onset (T_1), peak position (T_2) and of completion of the endotherm (T_3). The heat of fusion (ΔH_f) was also determined from the area under the endothermic transition. These results for various blends are tabulated in Table 1. Blending had no effect on T_1. However, the endothermic peak position (T_2 and T_3) were affected by blend composition. An increase in BMI content resulted in an increase in these characteristic temperatures. The ΔH_f values also depended on the blend composition and an almost linear relationship between ΔH_f and the BMI content of the blend was observed (Fig. 2).

Effect of blending on the curing exotherm

In the DSC traces of TNI, the curing exotherm was observed in the temperature range 285–355 °C with the exothermic peak position (T_{exo}) at

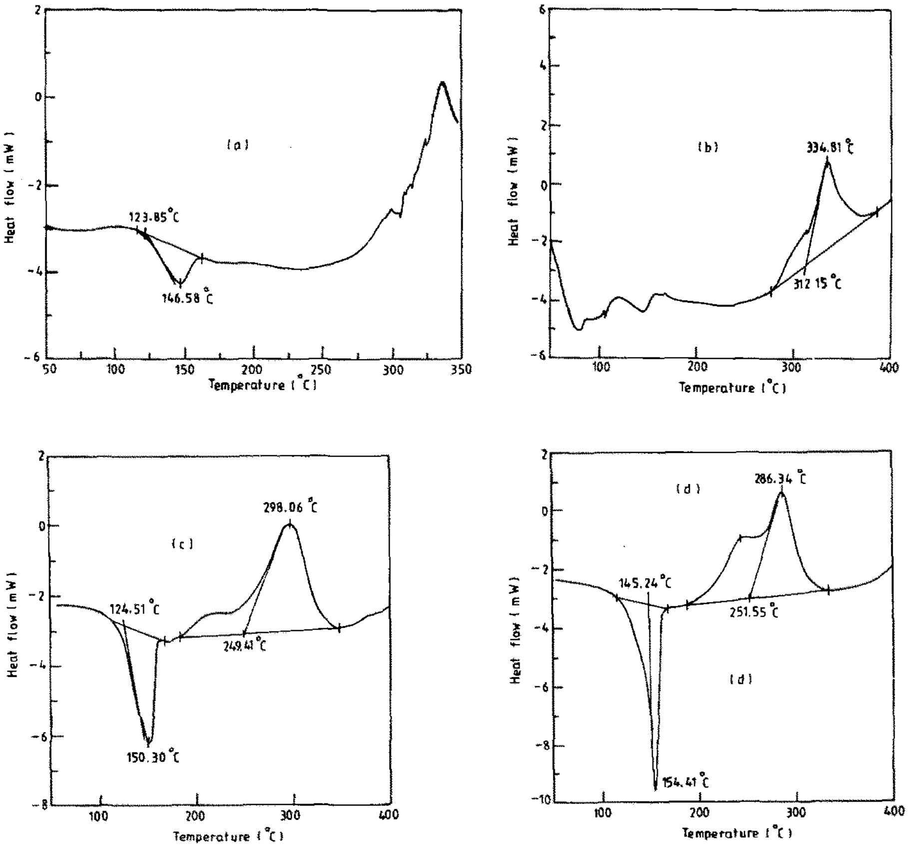

Fig. 1. DSC curves of TNI:BMI blends containing (a) 9.0%, (b) 16.5%, (c) 67.0%, and (d) 91.0% BMI (w/w).

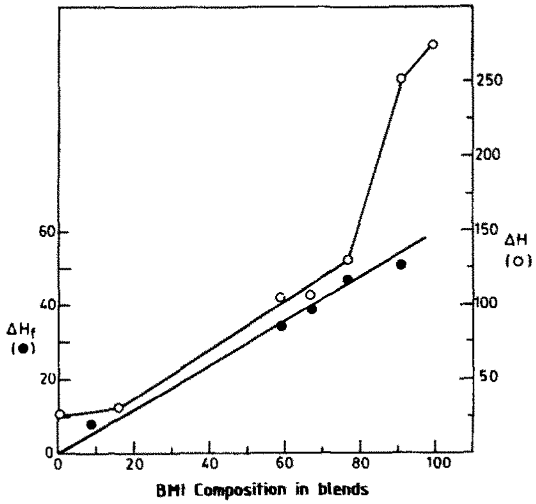

Fig. 2. The effect of the BMI content of the blends on (●) the heat of fusion and (○) the heat of curing reaction.

TABLE 2

The curing characteristics of TNI/BMI blends

Bismaleimide (%w/w)	Curing characteristics (° C)			ΔH (J g^{-1})
	T_i	T_{exo}	T_f	
0.0	285.0	334.0	355.0	25.5
9.0	250.0	335.0	–	–
16.5	260.0	335.0	385.0	58.4
59.0	185.0	286.0	347.5	105.9
67.0	187.0	290.0	350.0	107.5
77.0	179.5	250.0	350.0	130.5
91.0	192.5	286.3	332.5	251.5

334° C. The heat of curing was found to be 25.5 J g^{-1}. On the other hand, in BMI the curing started at 194° C and T_{exo} was at 260° C. The heat of curing was 221 J g^{-1}.

The addition of a low concentration of BMI (< 20%) to TNI did not alter the curing characteristics of TNI [Fig. 1(a and b)] and T_{exo} remained unaffected (Table 2). When the BMI content was increased (> 50%), the temperature of onset of curing (T_i and T_{exo}) decreased significantly (Table 2). When the BMI content was > 65%, the exothermic transition showed bimodal characteristics. The low-temperature peak (i.e. 240 ± 10° C) in-

TABLE 3

TG studies of TNI/BMI blends

Bismaleimide (%w/w)	T_i (° C)	T_{max} (° C)	T_f (° C)	Y_c (%)
0.0	142	158	179	
	310	327	375	
	480	501	515	60
9.0	210	286	340	
	465	502	509	59
16.5	100	130	175	
	200	251	375	
	465	480	508	60
59.0	120	133	145	
	204	–	312	
	474	487	507	57
67.0	120	288	314	
	478	491	513	54
77.0	137	290	308	
	483	496	517	54
91.0	137	279	310	
	485	498	519	54

creased with increasing BMI content, whereas the high-temperature peak appeared at 295 ± 5 °C. On the basis of these results it can be concluded that at high BMI content in the blend, temperature of onset of curing and T_{exo} are reduced for both BMI and TNI resins. The heat of curing, however, increased significantly on increasing the BMI content in the blend (Fig. 2).

Effect of blending on thermal stability

The results of the thermogravimetric analyses of the different blends are given in Table 3. The decomposition of the blends occurred mainly in three stages. In a first stage, a weight loss of about 3–5% was noted up to 200 °C (Fig. 3). This could be accounted for either by the evolution of adsorbed moisture or the cyclization of residual amido-acid. In the second stage, a weight loss of 7–8% was observed at 280 ± 20 °C and could be due to the loss of cyclopentadiene via a reverse Diels–Alder reaction [Fig. 3(a and b)]. A weight loss of only 2–3% was observed in blends containing higher

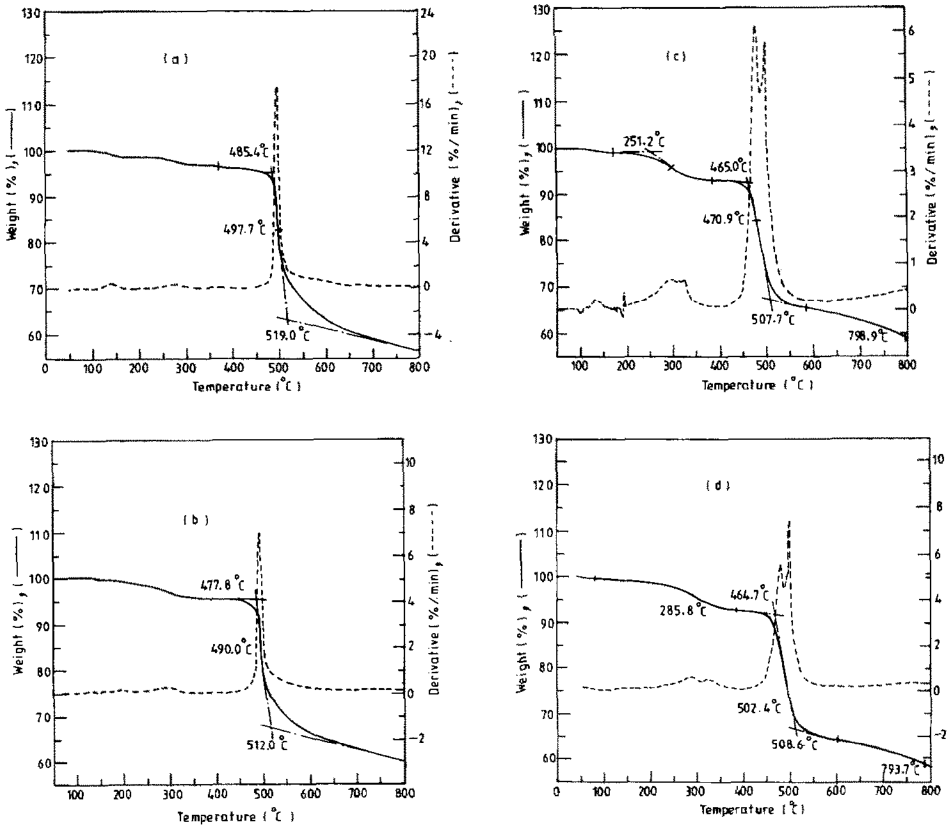

Fig. 3. TG curves of TNI: BMI blends containing (a) 91.0%, (b) 77.0 %, (c) 16.5%, and (d) 9.0% of BMI (w/w).

percentages of BMI [Fig. 3(c and d)]. A lower weight loss at this stage may be due to crosslinking of the evolved cyclopentadiene with the bismaleimide resin.

The largest weight loss was observed in the region 470–520 °C with T_{max} around 485 ± 10 °C. No significant effect was observed on T_{max} or T_f by changing the composition of the blends (Table 3). However, a 6% decrease in the char yield was noted with the increase of BMI content.

These studies indicate that by increasing the BMI content in the blends of trisnadimide, curing can be done at a lower temperature. Such blending did not influence the overall thermal stability of the trisnadimide.

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