Effect of structure on thermal behaviour of nadimide resins: 1

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This paper describes the synthesis and characterization of high char yield forming nadimide resins. Ten nadimide end-capped oligomeric resins were prepared by reacting endo-5-norbornene-2,3-dicarboxylic acid anhydride (nadic anhydride), 1,3-bis(3-aminobenzamide)/9,9-bis(*p*-aminophenyl)fluorene-3,3',4,4'-benzophenone tetracarboxylic acid dianhydride/pyromellitic dianhydride/2,2-bis(3,4-dicarboxylphenyl)-hexafluoropropane dianhydride. Structural characterization of resins was performed by elemental analysis, *FT*i.r. and ^{1}H n.m.r. Thermogravimetric studies revealed a multistep decomposition. Cured resins exhibited very high char yields in the range 63 to 77%.

(Keywords: nadimides; addition polyimides; char yield; amide amine; cardo amine)

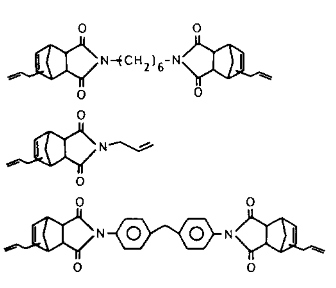
INTRODUCTION

In the past few decades there has been an expanding demand for lightweight, corrosion resistant, high performance composite materials that can replace conventional materials used in the construction of space vehicles, civil and military aircrafts, marine structures etc. These advanced composites basically consist of high performance thermoset and thermoplastic resins and fibres such as carbon, glass, Kevlar, boron, silicon carbide and quartz. In 1989, thermosets accounted for about 99% of the advanced composite parts market. Amongst the thermosets, epoxies account for about 80–90% of resins, followed by bismaleimides, PMR resins and polyimides. A wide variety of epoxy resins with good performance characteristics, and an upper use temperature of 177°C have been developed. For better performance in a hot–wet environment, the use of bismaleimides, nadimides and polyimides has been reported[1].

Endo-5-norbornene-2,3-dicarboximide (nadimide) end-capped polyimides have been investigated as matrix resins for advanced fibre reinforced composites[2–4]. PMR-15, with use temperatures approaching 600°F (315°C), is a widely used polyimide developed at NASAs Lewis Research Centre and commercialized by Ferro Corp. These resins have been structurally modified by changing the structure of diamine to improve thermal behaviour and mechanical properties. For example, 4,4'-oxydianiline or 1,1-bis(4-amino phenyl)-2,2,2-trifluoroethane have been used instead of 4,4'-diaminodiphenylmethane/Jeffamine for improving thermo-oxidative stability[5].

There are, however, certain problems associated with these PMR resins. PMR-15 is an alcoholic solution of the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid, the dimethyl ester of benzophenone tetracarboxylic acid and 4,4'-diaminodiphenylmethane. Because of the volatile nature of the constituents[6,7], both the solution and the prepregs have to be stored at low temperatures (−18°C). The shelf-life of monomers in solution is also limited. Another problem is the toxicity of the resin because the solution contains a large quantity (~17 wt%) of aromatic diamine which is highly carcinogenic.

In preformed nadimide oligomers these problems can be eliminated. Hence the latest developments in the nadimide end-capped resins have been in this direction. IP 960 is a newly reported, fully imidized nadimide terminated oligoimide (synthesized by CEMOTA) which has several advantages over PMR-15[8]. Ferro Corp. has also announced a new nadimide resin that does not contain free methylene dianiline. Allyl nadicimide resins with the following backbone structures have been developed by Ciba Geigy.



In most of the state-of-the-art resins, char yields at 800°C in nitrogen atmosphere range from 30 to 60% (ref. 9). In our continued effort to develop resins with better char yields the present investigations were undertaken. Resins with high char yields and high temperature capability are needed for ablative purposes.

In this paper, we report the synthesis of preformed nadimide oligomers using two aromatic diamines. Aromatic tetracarboxylic acid dianhydrides were also used to increase the formula weight of resins by chain extension. The aromatic diamines used were 1,3-bis(3-aminobenzamide) (ABB) and 9,9-bis(*p*-aminophenyl) fluorene (APF). Studies on bismaleimide resins based on

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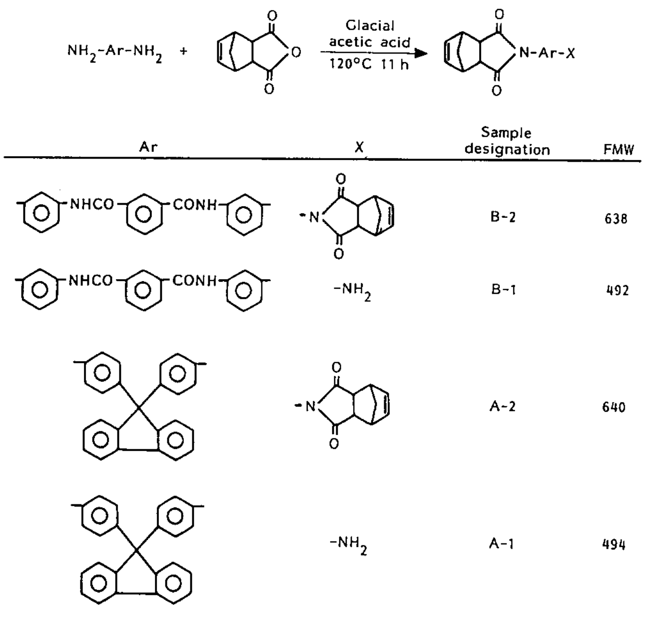
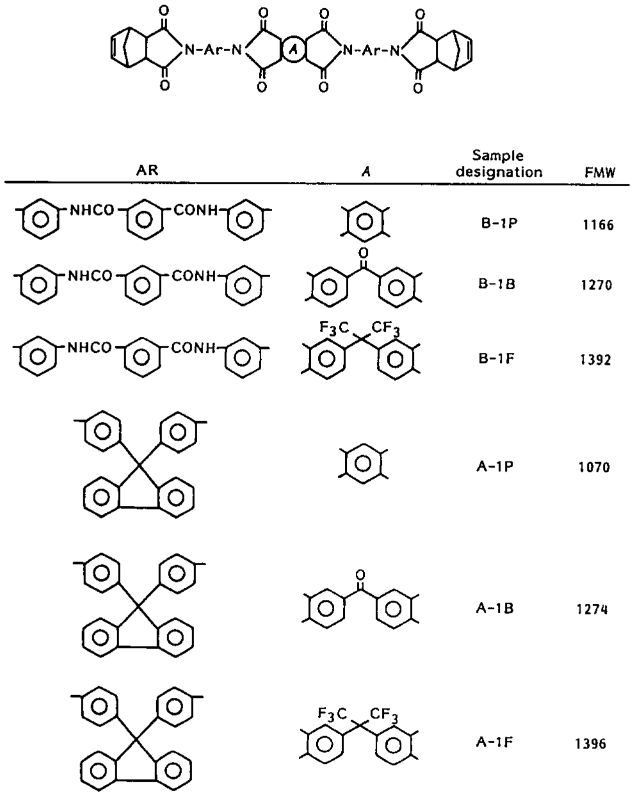
ABB or APF and 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) have been reported earlier[10,11].

Ten nadimide oligomers were prepared using 5-norbornene 2,3-dicarboxylic anhydride(NA), ABB/APF, and pyromellitic dianhydride(PMDA)/BTDA/2,2-bis (3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F). For the synthesis of these resins, NA was reacted with ABB and APF in 1:1 and 2:1 molar ratios to give mono- and bisnadimides, respectively (*Scheme 1*). The mononadimides were chain extended with PMDA/BTDA/6F in 2:1 molar ratio. The reaction scheme for the synthesis of nadimides along with resin designation and formulated molecular weight (FMW) is given in *Scheme 2.*



Scheme 1 Reaction scheme for synthesis of nadimides



Scheme 2 Structure of chain extended nadimides

EXPERIMENTAL

Materials

Glacial acetic acid (BDH), acetic anhydride (BDH) and *N,N*-dimethylformamide (DMF) (BDH) were distilled at atmospheric pressure before use. Anhydrous sodium acetate (Sarabhai Chemicals) was obtained by fusion. Nadic anhydride (NA) (E. Merck), the tetracarboxylic acid dianhydrides PMDA (Fluka), BTDA (Koch Light) and 6F (Hoechst) were purified by recrystallization from acetic anhydride.

Synthesis of nadimides

Appropriate quantities of NA and ABB/APF in glacial acetic acid (20 ml) were refluxed for several hours until the reaction was complete. The mono- and bisnadimides were recovered by precipitation. The precipitated resins were washed several times with water and aqueous sodium bicarbonate and dried. The nadimide resins thus obtained were dissolved in DMF, filtered and precipitated in water and dried.

Chain extension with dianhydrides

Each of the mononadimides (0.01 mol) was mixed with DMF (20 ml) at 60°C, and 0.005 mol of BTDA/PMDA/6F was added in portions. The solution was heated for 4 h followed by chemical cyclization of the amic acid to imide, using sodium acetate and acetic anhydride as the cyclodehydrating agent. This reaction was carried out for 4 h. The resulting chain extended nadimide resins were recovered by precipitation in water and after washing with water and aqueous sodium bicarbonate were dried under vacuum.

Characterization

A Nicolet MX-I *FT*i.r. spectrophotometer was used for recording spectra of various nadimides in KBr pellets. ^1H n.m.r. spectra were recorded on a Jeol-JNM-FX 100 FT n.m.r. spectrophotometer with $DMSO\text{-}d_6$ as solvent and tetramethylsilane as an internal standard.

A DuPont 9900 thermal analyser with a 910 d.s.c. module was used for studying the curing behaviour. A sample of about 10 ± 2 mg was heated from room temperature to 450°C in static air at 10°C min^{-1}.

A DuPont 1090 thermal analyser with a 951 TG module was used for assessing the relative thermal stability of the nadimide resins. Thermogravimetric traces were recorded in nitrogen atmosphere (flow rate 100 ml min^{-1}) at a heating rate of 10°C min^{-1}. A sample size of 10 ± 2 mg was used. Isothermal curing was also done at 250 and 325°C for 1 h each. D.s.c. and t.g.a. traces of the uncured and cured samples were recorded. The relative thermal stability of various resin samples was evaluated by determining (i) initial decomposition temperature (T_1); (ii) temperature of maximum rate of weight loss (T_{max}); and (iii) char yield at 800°C. If decomposition proceeded in more than one step then the weight loss at each step was also noted.

Table 1 Physical characteristics of nadimides

Sample designation	Colour	Yield (%)	Melting point (°C)	Solubility DMF	DMSO	$CHCl_3$
B-2	White	90	293	+	+ +	– –
B-1	White	95	208	+ +	+ +	– –
B-1P	Pale white	62	–	+ +	+ +	– –
B-1B	Pale white	56	–	+ +	+ +	– –
B-1F	Light brown	79	–	+ +	+ +	– –
A-2	White	86	301	+	+ +	– –
A-1	White	88	–	+	+ +	– –
A-1P	Brown	54	273	+ +	+ +	– –
A-1B	Pale yellow	62	–	+ +	+ +	– –
A-1F	Brown	61	–	+ +	+ +	– –

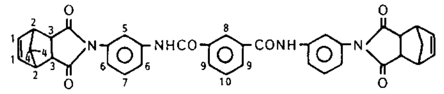
(– –) Insoluble; (+) partially soluble; (+ +) highly soluble

RESULTS AND DISCUSSION

The nadimide oligomers were obtained in powder form with colour ranging from white to brown and yield ranging from 54 to 95%. Some of the physical characteristics of the oligomers are shown in *Table 1*. Elemental analyses (C, H, N) of some of the nadimide samples were performed using acetanilide as a standard. Results of elemental analyses are shown in *Table 2*.

In the *FT*i.r. spectra of nadimide resins, characteristic bands due to imide groups appeared at 1780 ± 10 and 1720 ± 10 cm^{-1}. The presence of NH_2 groups in the mononadimides B-1 and A-1 was indicated by NH stretching at 3230 cm^{-1}. In samples containing BTDA, a broad absorption band was observed at 1700 cm^{-1} with a shoulder at 1660 cm^{-1} which is due to carbonyl stretching of the benzophenone groups. The $\nu_{C=O}$ band for amide groups in ABB based resins was observed at 1680 cm^{-1}.

The ^1H n.m.r. spectra of all the resin samples were recorded in DMSO-d_6 for structural characterization. The chemically equivalent protons resonating at different positions in bisnadimide B-2 can be grouped as follows:



Among the aromatic protons (numbered 5–10) which were observed in the region $\delta = 7.2$–8.2 ppm (*Figure 1*), proton 8(1H, S) appeared downfield ($\delta = 8.2$ ppm) followed by the proton at position 9(2H, d $\delta = 8.0$ ppm). The remaining proton resonance signals in this region, i.e. 5(2H), 6(4H), 10(1H) and 7(2H), were very close to each other and hence difficult to distinguish. The integration of the protons in this region i.e. $\delta = 7.69$–7.2 corresponded to 9H. The olefinic protons at 1 were observed at $\delta = 6.2$ ppm (4H) and amide protons (11) at $\delta = 10.1$–10.3 ppm (2H, S). The methylene protons (4) were observed at $\delta = 1.62$ ppm (4H, S) whereas protons 3 and 2 (8H) appeared in the region $\delta = 3.36$–3.5 ppm. Integration in this region was slightly complicated because of the residual protons of solvent DMSO-d_6 and moisture in the solvent. Therefore, the ratio of total aromatic protons to olefinic protons was used for structural characterization of nadimide resins. In the resin B-1, an NH_2 group appeared at $\delta = 2.08$ ppm.

Table 2 Results of elemental analysis of nadimide results

Designated structure	Formula	Elemental analysis[a] (%) C	H	N
B-2	$C_{38}H_{30}O_6N_4$	70.1 (71.47)	4.8 (4.70)	9.2 (8.77)
B-1P	$C_{68}H_{46}O_{12}N_8$	69.3 (69.98)	4.8 (3.94)	7.1 (9.6)
B-1B	$C_{75}H_{50}O_{13}N_8$	64.1 (70.86)	4.7 (3.93)	7.7 (8.81)
B-1F	$C_{77}H_{50}O_{12}N_8$	61.2 (66.37)	4.5 (3.59)	6.9 (8.0)
A-2	$C_{43}H_{32}O_4N_2$	75.5 (80.6)	4.9 (4.38)	5.6 (4.37)
A-1P	$C_{78}H_{50}O_8N_4$	77.7 (80.0)	5.2 (4.27)	5.4 (4.78)
A-1B	$C_{85}H_{54}O_9N_4$	73.9 (80.06)	5.0 (4.08)	4.9 (4.39)

[a] Figures in parentheses indicate calculated values

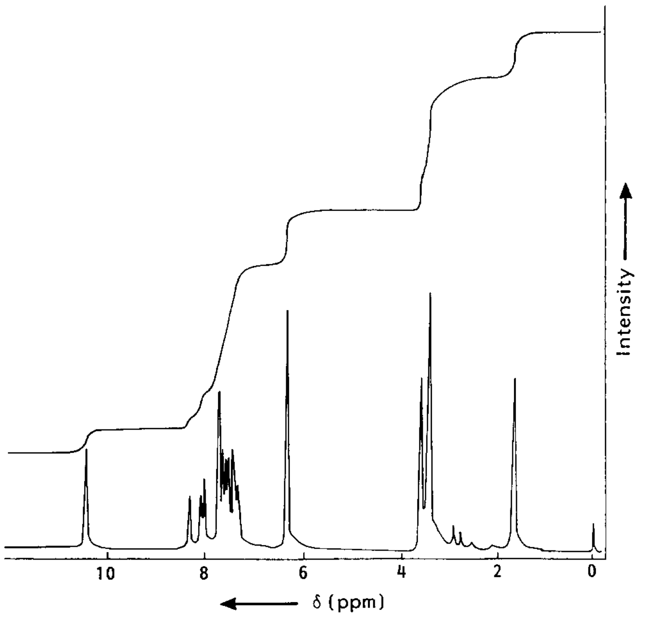


Figure 1 ^1H n.m.r. spectrum of nadimide resin B-2

For the chain extended nadimides, the presence of tetracarboxylic acid dianhydrides was indicated by an increase in aromatic protons. The aromatic protons were observed at $\delta = 7.2$–8.4 ppm in B-1B while in resins B-1F and B-1P the aromatic protons were in the region $\delta = 7.2$–8.26 ppm.

In the ^{1}H n.m.r. spectrum of bisnadimide A-2 (*Figure 2*), the aliphatic protons were observed at similar positions as in ABB based resins. The aromatic protons were observed around $\delta = 7.0$–7.9 ppm. In the chain extended nadimide A-1B the aromatic protons appeared at $\delta = 7.0$–8.1 ppm.

The structure of the various synthesized nadimide resins was confirmed using ^{1}H n.m.r. spectra.

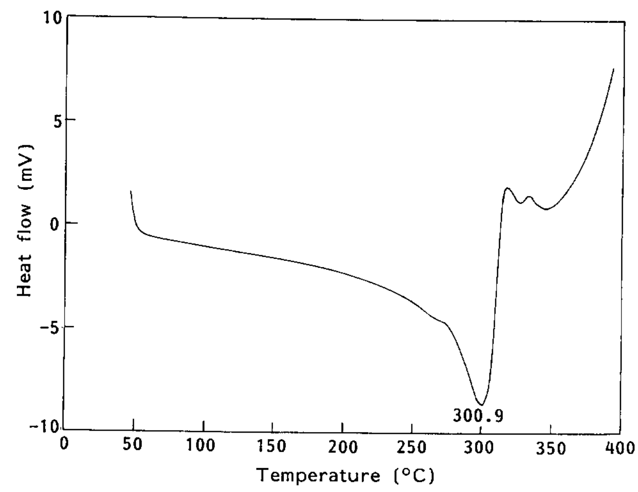


Figure 3 D.s.c. trace of uncured nadimide resin B-2

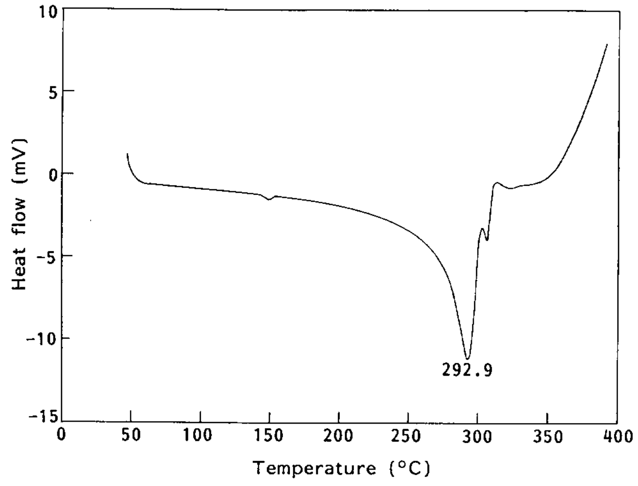


Figure 4 D.s.c. trace of uncured nadimide resin A-2

Curing behaviour of nadimides

In the d.s.c. traces, well-defined melting endotherms were observed for B-2, B-1, A-2 and B-1P (*Table 1*). In most cases melting was immediately followed by curing, so curing exotherms were not well defined. However, in B-2, B-1, B-1P and A-1 curing exotherms were observed. D.s.c. traces of B-2 and A-2 are shown in *Figures 3* and *4*.

Isothermal curing of the nadimides was performed at 250°C for 1 h and also at 325°C for 1 h in air atmosphere. The resins thermally treated at 250°C readily dissolved in DMF, therefore indicating low molecular weight products. Resins insoluble in DMF were obtained when thermal treatment was done at 325°C. However, curing at this temperature resulted in weight loss (1–12%). This may be attributed to the loss of cyclopentadiene generated during retero-Diels Alder reaction of the nadimide group[12]. In d.s.c. traces of cured samples no exotherm was observed.

T.g.a. traces of uncured nadimide resins in nitrogen atmosphere indicated a multistep decomposition. Traces of A-1P and B-1B are shown in *Figures 5a* and *b*. Detailed results are given in *Table 3*. The onset temperature of decomposition for the bisnadimides B-2 and A-2 was ~40 ± 10°C higher than the corresponding mononadimides B-1 and A-1, respectively. The T_{max} values for chain extended nadimides were similar to the mononadimides, indicating that the structure of the bridging unit does not affect the temperature of maximum rate of weight loss. Char yields of the chain extended nadimides were higher than the corresponding mononadimides. APF based nadimides showed higher char yields than ABB based resins. The range of char yields for the uncured nadimide resins was 35–52%. Resins cured at 325°C exhibited a one-step decomposition. T.g.a. traces of B-1B and A-1P are shown in *Figures 5c* and *d*. Detailed results are given in *Table 4*. The char yield at 800°C (Y_c) increased significantly in cured resins. Amongst the ABB based resins the char yield of B-1P was highest followed by B-1B and B-1F. Similarly, A-1P showed the highest char yield amongst the APF based resins followed by A-1B and A-1F.

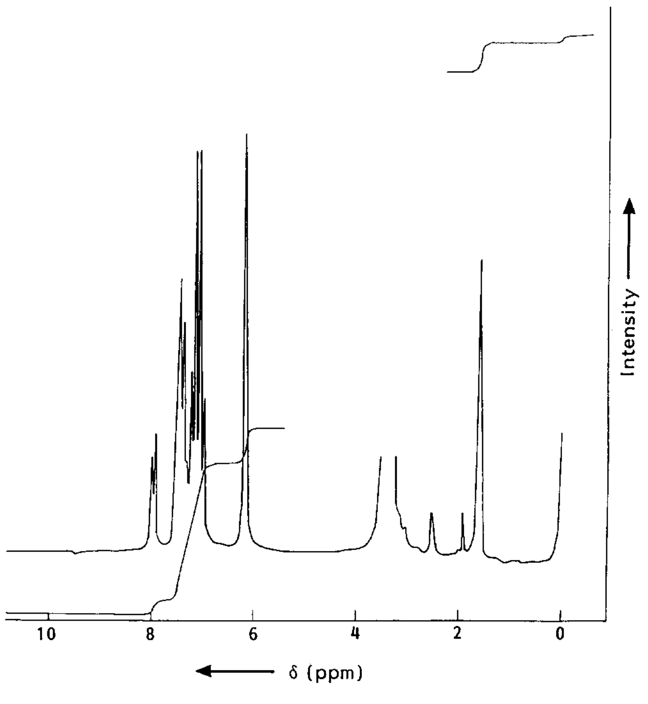


Figure 2 ^{1}H n.m.r. spectrum of nadimide resin A-2

In conclusion these studies clearly indicate that nadimide resins based on cardoamine APF as well as amide amine ABB give very high char yields. Such resins therefore have potential application in ablative purposes. Further studies in this direction are in progress.

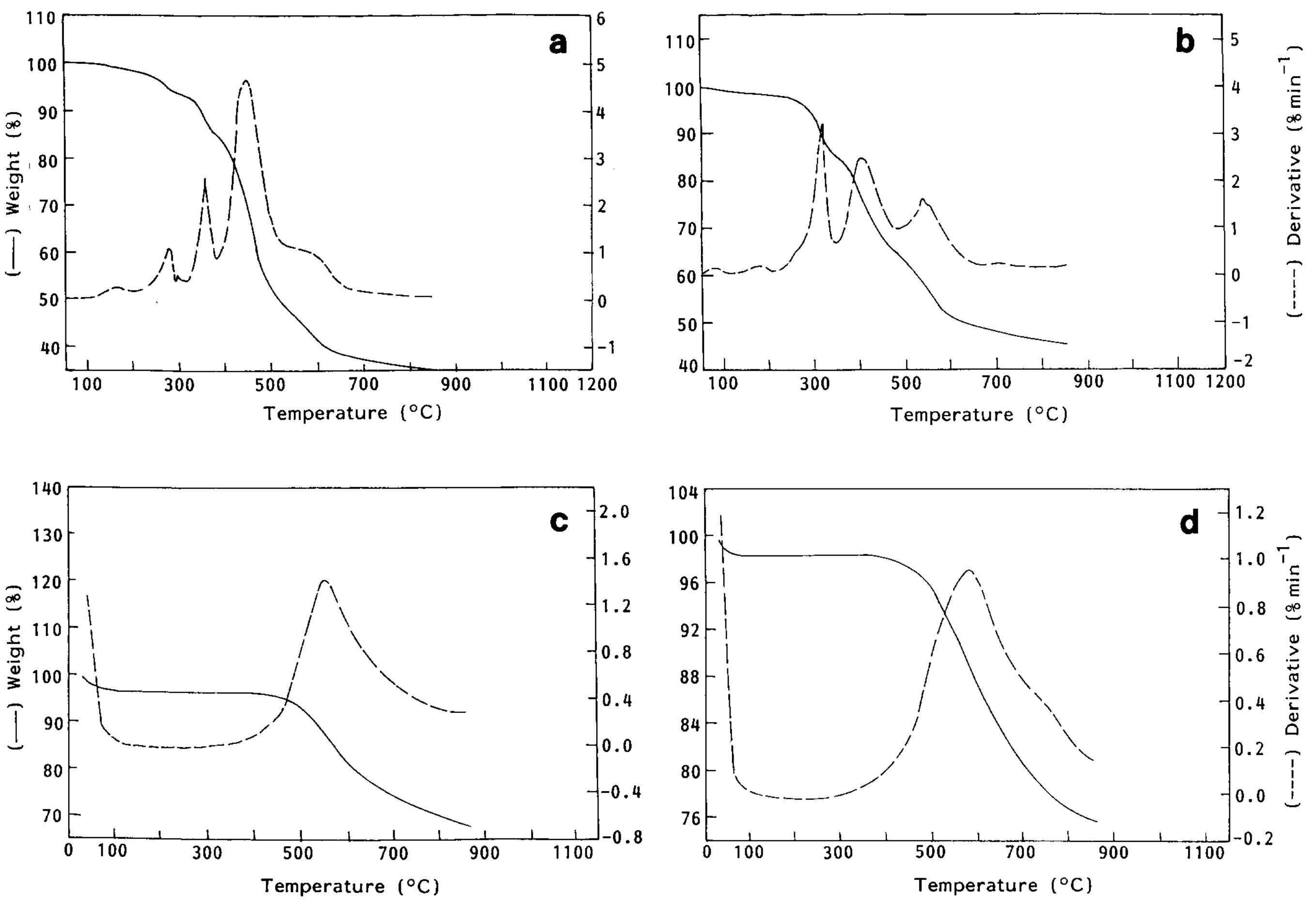


Figure 5 T.g.a. traces of nadimide resins: (a) uncured A-1P; (b) uncured B-1B; (c) cured B-1B; (d) cured A-1P

Table 3 T.g.a. of uncured nadimide resins

Sample	T_1 (°C)	T_{max} (°C)	T_2 (°C)	Y_c (%)
B-2	286	308	326 (19.45)	42.0
	326	441	541 (40.56)	
B-1	236	279	325 (12.75)	39.0
	325	399	530 (35.84)	
	530	552	640 (13.00)	
B-1P	287	309	350 (12.19)	40.0
	350	421	520 (43.01)	
B-1B	294	319	365 (12.90)	46.0
	365	402	475 (19.99)	
	475	540	625 (19.95)	
B-1F	279	320	355 (15.50)	43.0
	355	419	470 (19.48)	
	470	557	660 (21.19)	
A-2	262	315	410 (11.69)	41.5
	498	514	552 (47.34)	
A-1	234	268	300 (13.98)	35.5
	355	456	537 (51.04)	
A-1P	236	278	305 (6.33)	36.0
	305	357	380 (8.14)	
	380	449	518 (50.29)	
A-1B	148	170	215 (2.72)	46.0
	293	341	380 (11.56)	
	380	473	586 (41.04)	
A-1F	100	148	220 (4.75)	52.0
	250	309	340 (10.19)	
	370	394	610 (27.21)	

Figures in parentheses indicate percentage weight loss at each step

Table 4 T.g.a. of cured nadimide resins

Sample	T_1 (°C)	T_{max} (°C)	Y_c (%)
B-2	476	561	69.5
B-1	492	575	74.0
B-1P	483	563	72.5
B-1B	483	554	70.0
B-1F	465	553	64.45
A-2	451	525	64.0
A-1	365	472	63.0
A-1P	470	575	77.0
A-1B	443	594	72.5
A-1F	435	463	69.5

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REFERENCES

1 Thayer, A. M. *Chem. Eng. News* 1990, 37
2 Serafini, T. T., Delvigs, P. and Lightsey, G. R. *J. Appl. Polym. Sci.* 1971, **16**, 90

3 Delvigs, P., Serafini, T. T. and Lightsey, G. R. *Proc. 17th SAMPE Natl Symp.* April 1972

4 Serafini, T. T., Delvigs, P. and Alston, W. B. *Proc. 27th SAMPE Natl Symp.* May 1982

5 Alston, W. B. 'High Temperature Polymer Matrix Composites' (Ed. T. T. Serafini), Noyes Data Corp., 1987, p. 186

6 Kranbuehl, D. E., Delos, S. E., Yi, E. C. and Mayer, J. T. *Proc. 2nd International Conference on Polyimides* Ellenville, October 1985, p. 469

7 Young, P. R. and Sykes, G. F. Graphite/Polyimide Composites, NASA Conf. Publ. 1979, NASA CP 2079, p. 361

8 Malinge, J., Rabilloud, G., Sillion, B., Garcin, C., Bardin, I. and Berthier, J. M. *Mater. Sci. Monogr.* **41**, 'Looking Ahead for Materials and Processes' (Eds J. D. Bossu, G. Briens and P. Lissac), Elsevier, 1987, p. 454

9 Varma, I. K. and Mittal, H. P. *J. Macromol. Sci. Chem.* 1989, **A26**, 937

10 Varma, I. K., Sharma, S. *Polymer* 1985, **26**, 1561

11 Varma, I. K., Fohlen, G. M. and Parker, J. A. *J. Polym. Sci., Polym. Chem Edn* 1982, **20**, 283

12 Varma, I. K. in 'Advances in Composite Materials' (Ed. P. Ramakrishnan), Oxford and IBH Pub. Co., 1990, p. 85