

Synthesis, Characterization, and Thermal Properties of Tris (3-Aminophenyl) Phosphine Oxide-Based Nadimide Resins

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ABSTRACT: This article describes the synthesis, characterization, and thermal properties of nadimides obtained by reacting endo-5-norbornene-2,3-dicarboxylic acid anhydride (nadid anhydride) (NA), 4,4'-oxodiphthalic anhydride (ODA), 1,4,5,8-naphthalene tetra carboxylic dianhydride (NTDA) in glacial acetic acid/DMF. Structural characterization of the resins was done by elemental analysis, IR, ¹H-NMR, and ¹³C-NMR. The DSC scan showed the endothermic transition in the temperature range of 120–270°C. Multistep decomposition was observed in the TG scan of uncured resins in nitrogen atmosphere. Isothermal

curing of the resins was done at 250 and 300°C for 1 h in an air atmosphere. These cured resins were stable to (350 ± 30)°C and decomposed in a single step above this temperature. This may be due to the retro Diels Alder (RDA) reaction. The char yield of the resins increased significantly on curing. The char yield was highest for P-2N resin and this could be due to the presence of rigid skeleton i.e. naphthalene. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1628–1634, 2008

Key words: curing; nadimide; thermal stability; char yield

INTRODUCTION

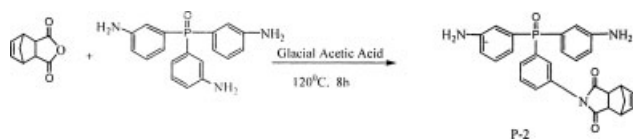
Endo-5-norbornene-2,3-dicarboximide (nadimide) end-capped polyimides are a leading class of thermosetting polyimides and have been investigated as matrix resins for advanced fiber-reinforced composites.^{1–3} In combination with high strength and high modulus fibers such as glass and carbon, these resins have been used in several demanding high temperature applications. They are also find applications as adhesives, dielectrics in production of integrated circuits, and as resins for assembly and packaging in microelectronics.^{4,5} Fire hazards and the environmental concern of using halogen-based system have necessitated the search for new halogen free fire retardant additive. Novel approaches for developing new flame retardant polymer focus on various alternatives for: high temperature stable materials that decompose generating flame suppressants, nonflammable polymers, mixture of plastics with flame retardants.^{6–8} Recent research efforts in this area have been primarily directed toward the development of new and improved resins capable of better elevated temperature performance than the

state-of-the-art systems.^{9–12} Structural modifications of these resins have been done in the past to improve high temperature performance. Besides halogen and metal oxides, nitrogen and phosphorous are a feasible alternative for use as a flame retardant elements and incorporation of this elements into the polymer backbone generally leads to an improvement in flame resistance and high-temperature performance of the polymers.^{13,14} However, the instability of the poly(amide acid) solution, poor resin flow, residual solvent, and water evolution created porosity in the composites. These limitation of the resins necessitated the development of a new synthetic route where a monomeric mixture of dimethyl ester of benzophenone tetracarboxylic acid, methyl bicyclo [2.2.1] hept-5-ene-2,3-dicarboxylate and diamine were used impregnation of reinforcement. This concept has been termed as polymerization of monomeric reactants (PMR resins), residual solvent is required to provide the necessary tack and drape to the prepreg in such resins formulations.^{15,16} Thermal cyclization of these resins is believed to proceed by endo–exo isomerization (between 200 and 250°C) reverse Diels Alder reaction (above 260°C) and further copolymerization between cyclopentadiene and maleimide units. The cross linked polymer formed by curing above 285°C is mainly saturated having units derived from endo and exo structure.^{17,18} The structure of these resins can be easily altered by the changing the structure

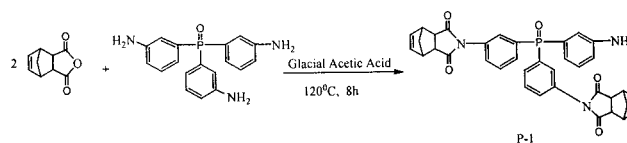
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Scheme 1 Synthesis of mononadimide.



Scheme 2 Synthesis of bisnadimide.

of aromatic diamine/aromatic tetracarboxylic acid dianhydride, and the molar ratios of the various constituents. The availability of a wide range of starting components has provided structural design flexibility. These resins thus have a potential for controllable high performance characteristics. There is a need to examine the performance of preformed nadimide resins in low boiling organic solvents can help in overcoming the problems of solvent retention in the prepregs. The shelf life of preformed nadimide resins is better than the poly(amide-acid)s which are susceptible to hydrolytic cleavage. The toxicity of PMR resins would also be reduced.^{19,20} The present article deals with the effect of the structure of performed nadimide resins on tris(3-aminophenyl phosphine) oxide (TAP) on thermal characteristics and these show good char forming characteristics, moisture resistance, and processability than the resins formed by reaction of TAP with benzophenone tetracarboxylic dianhydride/pyromellitic dianhydride.

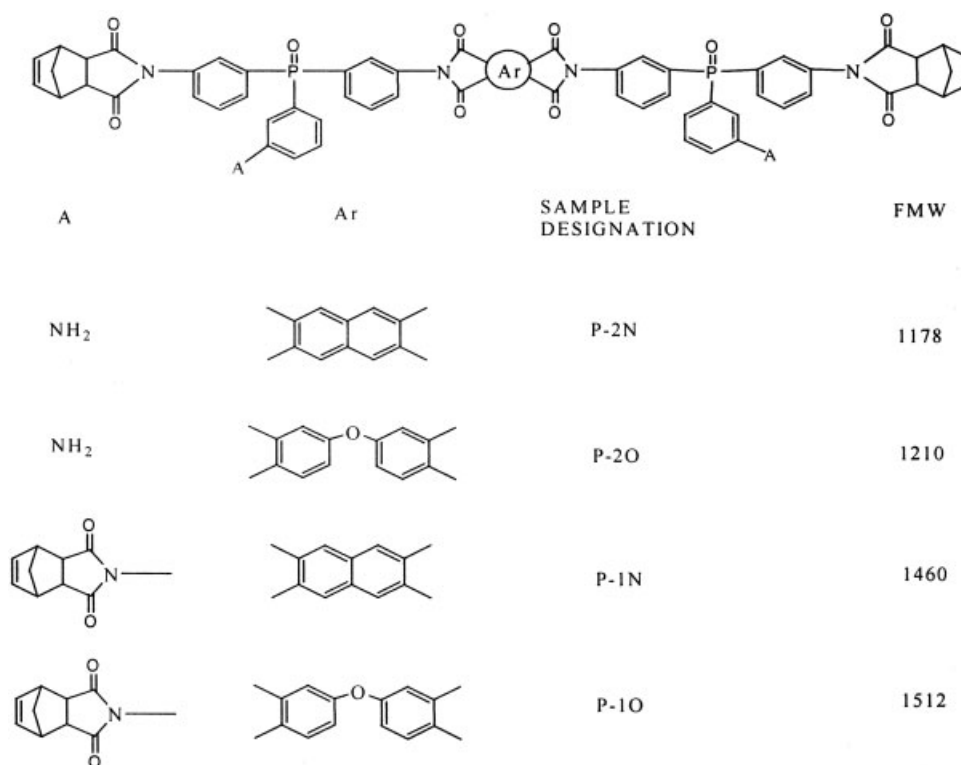
EXPERIMENTAL

Materials

Nadic anhydride (NA), 1,4,5,8-naphthalene tetra carboxylic anhydride (NTDA) and 4,4'-oxo diphthalic anhydride (ODA) all were purchased from Aldrich and were used as received. Glacial acetic acid (SRL) and acetic anhydride (CDH) were distilled at atmospheric pressure before use. Acetone (Spectrochem) was dried over sodium sulfate overnight, refluxed for 1 h and distilled at atmospheric pressure. *N,N*-dimethyl formamide (DMF) (Qualigen) was dried by keeping it over phosphorous pentoxide (P_2O_5) for 72 h followed by distillation under reduced pressure. Sodium acetate (Qualigen) was used as such. TAP was prepared according to the method reported elsewhere.¹⁰

Synthesis of nadimides

Several nadimide oligomers¹¹ were prepared by reacting NA with TAP according to the reaction Schemes 1 and 2.



Scheme 3 Structure of chain-extended nadimides.

TABLE I
Physical Characteristics of Nadimide Resins

Sample designation	Yield (%)	Color	Solubility				
			Acetone	CHCl ₃	DMF	DMAc	DMSO
P-1	95	Brown	++	++	++	++	++
P-2	96	Gray	++	++	++	++	++
P-1N	58	Light yellow	--	--	++	++	++
P-1O	49	Brown	--	--	++	++	++
P-2N	54	Dark brown	--	--	++	++	++
P-2O	53	Light brown	--	--	++	++	++

(--) Insoluble; (++) highly soluble.

NA (1 or 2 mol) was dissolved in glacial acetic acid (30 mL) at 60°C and 1 mol of TAP was added in portions. The solution was heated for 8 h at 120°C. The resulting product was precipitated in ice-cold water when brown/grey colored solid was formed. The crude was washed initially with water then with aqueous solution of sodium bicarbonate. Filtered the solid and dried under vacuum at 50–60°C overnight. The product was recrystallized with chloroform.

Chain extension with dianhydrides

NTDA/4,4'-oxo diphthalic anhydride (ODA) was used for chain extension.¹¹ The structure of the oligomers along with the sample designation and formula molecular weight is given in Scheme 3.

Mononadimide(P-2)/bisnadimides(P-1) (0.01 mol) was dissolved in dry DMF (20 mL) at 60°C and 0.005 mol of NTDA/ODA was added in portions. The solution was heated for 4 h followed by chemical cyclization of the amide acid to imide, using sodium acetate and acetic anhydride as the cyclodehydrating agent. The resulting product was precipitated in ice-cold water when a colored solid was formed. After washing with water and aqueous solu-

tion of sodium bicarbonate, the solid was filtered and dried under vacuum at 50–60°C overnight. The product was crystallized first with chloroform and then with dry methanol.

Characterization

A Nicolet BX-I FTIR spectrophotometer was used for recording the spectra of various nadimides in KBr pellets. ¹H-NMR and ¹³C-NMR spectra were recorded on a BRUKER AVANCE II 400 NMR spectrometer using DMSO-*d*₆ or CDCl₃ as solvents and tetramethylsilane as an internal standard. Elemental analysis was carried out using EURO EA 3000 elemental analyzer.

TA 2100 thermal analyzer having a 910 DSC module was used for studying the curing behavior. A sample of 10 ± 2 mg was heated from room temperature to 350°C in static air atmosphere at heating rate 10°C/min.

A Rheometric thermal analyzer having a 1500 TG module was used for assessing the relative thermal stability of the nadimide resins. Thermogravimetric traces were recorded in a nitrogen atmosphere (flow rate 60 mL/min) at a heating rate of 10°C/min and sample size of 10 ± 2 mg was used in each experiment. The relative thermal stability of various resin

TABLE II
Results of Elemental Analysis of Nadimide Resins

Sample Designation	Formula	C (%)	H (%)	N (%)
P-1	C ₃₆ H ₃₀ N ₃ O ₅ P	70.18 (70.35)	4.68 (4.88)	6.82 (6.81)
P-2	C ₂₇ H ₂₄ N ₃ O ₃ P	69.14 (69.23)	5.12 (5.128)	8.924 (8.974)
P-1N	C ₈₆ H ₆₀ N ₆ O ₁₄ P	70.68 (70.68)	4.09 (4.10)	5.72 (5.753)
P-1O	C ₈₈ H ₆₂ N ₆ O ₁₅ P ₂	68.98 (69.84)	4.10 (4.12)	5.458 (5.555)
P-2N	C ₆₈ H ₄₈ N ₆ O ₁₀ P ₂	69.24 (69.26)	4.071 (4.074)	7.112 (7.132)
P-2O	C ₇₀ H ₅₀ N ₆ O ₁₁ P ₂	69.35 (69.42)	4.11 (4.132)	6.88 (6.94)

The numerical values within parenthesis represent calculated values.

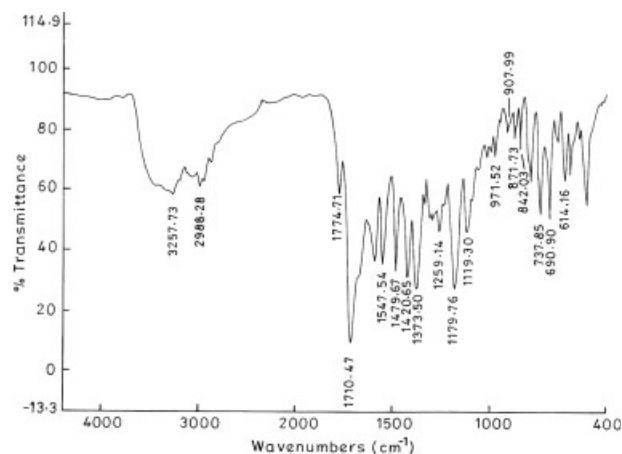


Figure 1 FTIR spectrum of nadimide resin P-2O.

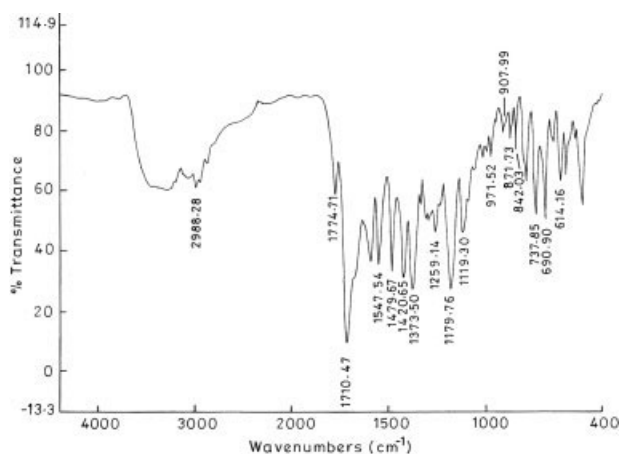


Figure 2 FTIR spectrum of nadimide resin P-10.

samples was evaluated by determining (a) the initial decomposition temperature (T_i), (b) the temperature of maximum rate of weight loss (T_{max}), and (c) the char yield (Y_c) 800°C.

RESULTS AND DISCUSSION

The nadimides oligomers were obtained in powder form having a yellow to brown color. The physical characteristics of the nadimide oligoimides are given in Table I. The yields were in the range of 49–96%. The sample P-1 and P-2 were highly soluble in low boiling solvents. The results of elemental analysis (C, H, and N) of a nadimide resins (Table II) showed a good correlation between observed and calculated values.

In the FTIR spectra of nadimide resins, characteristic bands due to imide groups appeared at 1770 ± 20 and $1720 \pm 10 \text{ cm}^{-1}$ ($\nu_{C=O}$) and 1375 ± 10 and $749 \pm 10 \text{ cm}^{-1}$. The presence of NH_2 groups in mononadimide P-2 was indicated by N—H stretching at

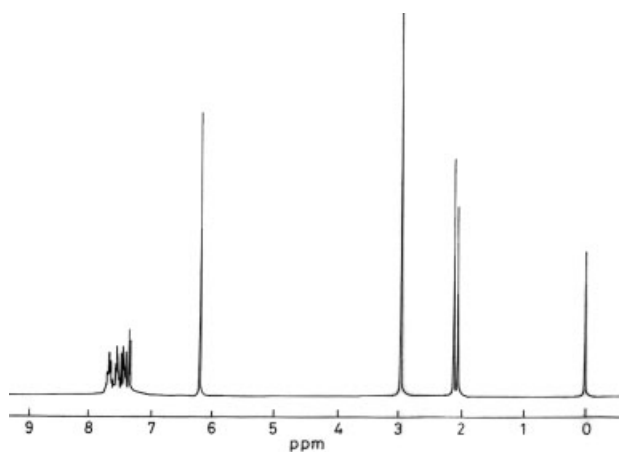


Figure 3 $^1\text{H-NMR}$ spectra of nadimide resin P-2O.

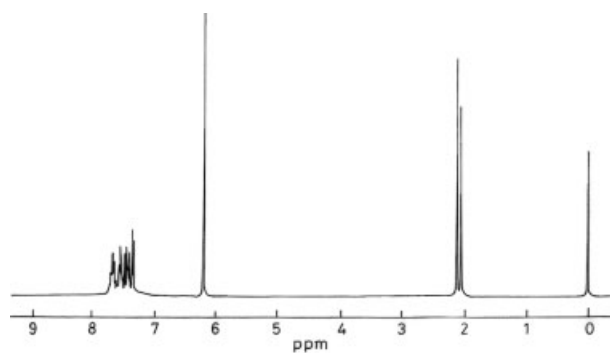


Figure 4 $^1\text{H-NMR}$ spectra of nadimide resin P-1O.

$3260 \pm 30 \text{ cm}^{-1}$. An absorption band due to $\text{P-C}_6\text{H}_5$ and $-\text{P}=\text{O}$ were observed at 1422 and 1180 cm^{-1} . A strong absorption band due to Ar-O-Ar linkage was obtained at $1112 \pm 10 \text{ cm}^{-1}$. The IR spectrum of P-2O and P-1O are shown in Figures 1 and 2.

The $^1\text{H-NMR}$ spectra of P-1 and P-2 were recorded in CDCl_3 , whereas $\text{DMSO-}d_6$ was used as a solvent for P-1N, P-1O, and P-2N and P-2O resins. The aromatic protons appeared at δ 7.2–8.0 ppm and olefinic protons at δ 6.17 ppm. The NH_2 group appeared at δ 3.4 ppm. A doublet due to methylene proton was also observed at 1.6–1.7. $^1\text{H-NMR}$ of P-2O and P-1O are shown in Figures 3 and 4.

In the $^{13}\text{C-NMR}$ spectra of nadimide resins, a characteristic signal due to imide carbon was observed at 169 ppm. A singlet was observed due to olefinic carbon at 136 ppm. A characteristic signal of methylene ($-\text{CH}_2$) and methine ($-\text{CH}$) carbon appeared at 49 and 42 ppm. Aromatic carbons were observed in the region of 128–132 ppm. $^{13}\text{C-NMR}$ of P-1N is shown in Figure 5. Thus, the structure of nadimide resins synthesized in the present work was confirmed.

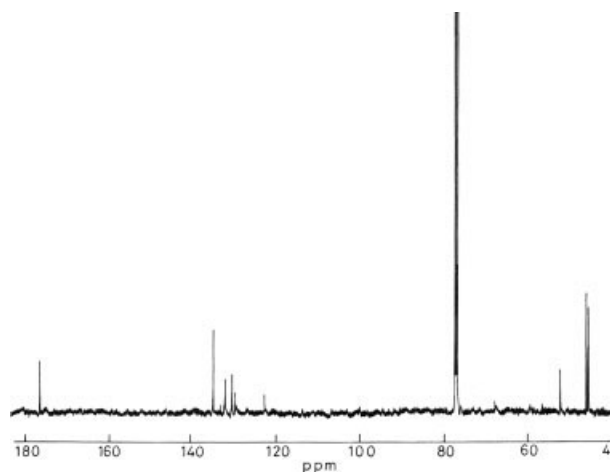


Figure 5 $^{13}\text{C-NMR}$ spectra of nadimide resin P-1N.

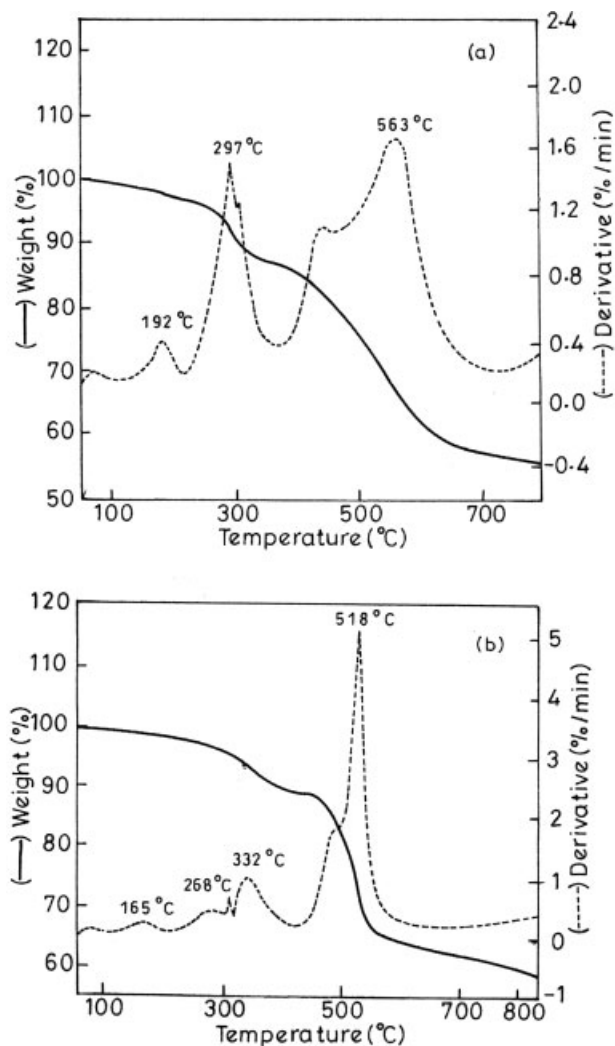


Figure 6 TG traces of uncured nadimide resin (a) P-1O and (b) P-1N in nitrogen atmosphere at heating rate 20°C/min.

Curing and thermal behavior of uncured nadimide resins

The thermal stability of uncured nadimide resins was determined by recording TG/DTG derivative trace in nitrogen atmosphere. Figure 6(a,b) shows TG/DTG traces of uncured nadimide resins i.e. P-1O and P-1N. The relative thermal stability of the uncured resins was compared by noting initial decomposition temperature (T_i), final decomposition temperature (T_f), temperature of maximum rate of weight loss (T_{max}), and percent char yield (Y_c) at 800°C. The results are summarized in Table III. The TG traces of uncured nadimide resins in nitrogen revealed a multistep decomposition. In the DSC scan of P-1O resins an endothermic transition with peak position at 115°C was present and exothermic peak of resins was observed above 250°C. In P-1N a broad endotherm above 150°C with a peak at 237°C was observed. Figure 7(a,b) shows the DSC scans of

TABLE III
Results of Thermogravimetric Analysis of TAP-Based Uncured Nadimide Resins

Sample designation	FMW	T_i (°C)	T_{MAX} (°C)	T_f (°C)	Y_c (%)
P-1	614	125	165	210(2.0)	49.2
		250	320	380(9.0)	
		380	525	610(31.0)	
P-2	468	135	160	200(2.5)	52.0
		250	350	390(8.5)	
		390	495	590(27.5)	
P-1N	1460	120	166	195(1.2)	41.0
		240	268	295(2.3)	
		305	332	385(14.3)	
		410	518	580(27.0)	
P-1O	1512	69	123	150(1.6)	39.0
		250	294	369(2.4)	
		372	519	549(15.2)	
		450	563	670(32.0)	
P-2N	1178	140	192	210(4.0)	47.0
		210	297	330(11.2)	
		450	563	670(32.0)	
		385	555	670(28.0)	
P-2O	1210	110	155	210(3.0)	44.0
		225	325	385(9.5)	
		385	555	670(28.0)	

FMW, Formula Molecular Weight.

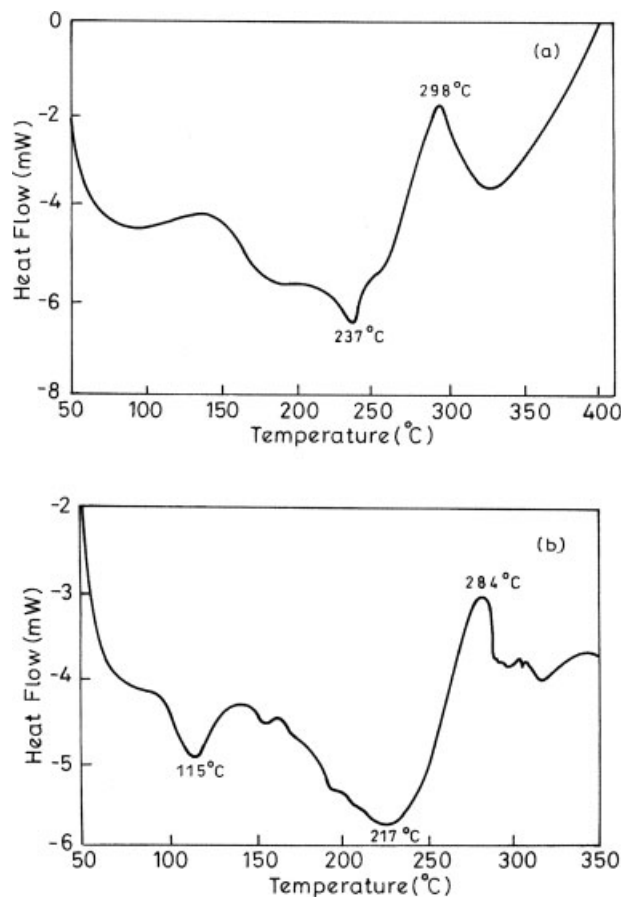


Figure 7 DSC scans of nadimide resin (a) P-1O and (b) P-1N at heating rate 10°C/min under nitrogen atmosphere.

TABLE IV
Result of Thermogravimetric Analysis of TAP-Based Cured Nadimide Resins

Sample designation	T_i (°C)	T_{MAX} (°C)	Y_c (%)
P-1	492	562	64.0
P-2	485	515	72.0
P-1N	465	540	72.0
P-1O	420	545	69.0
P-2N	430	520	67.5
P-2O	454	542	72.5

P-1O and P-1N at heating rate 10°C/min. In the corresponding TG trace, weight loss of ~ 0.5% was observed in the temperature range of 50–120°C. The DSC scan of P-2N and P-2O showed an endothermic transition 130°C because of the absorbed moisture. Up to 3% weight loss was seen for this transition in the TG trace. T_1 , T_{max} , and T_2 showed higher values for naphthalene-based nadimides (i.e P-2N and P-1N). The char yield was tend to be dependent on the structure of nadimides and it was highest for P-2N and lowest for P-1O. This could be due to the rigid structure of naphthalene as it form 6-membered imide ring which is thermodynamically more stable. Thus in resins P-1N,P-1O, P-2N, and P-2O char yield was in the order: P-2N > P-2O > P-1N > P-1O.

Curing of nadimide resins

Isothermal curing of the nadimide and maleimide resins was done at 250°C for 1 h in air atmosphere. Weight loss observed during such a treatment ranged from 1.0–4%. These results are summarized in Table IV. These resins readily dissolved in DMAc, indicating thereby only a partial curing. The TG traces of these resins were also similar to those corresponding uncured resins. Therefore, the resins were further heated for 1 h. Resins insoluble in DMAc were obtained by such a treatment. Heating at this temperature resulted in a 5–10% weight loss (Table IV). The cured resins have been designated by appending a prefix C to the letter designation of the resin (Table V). The curing of P-1N and P-1O at 300°C for 1 h led to completely cured product. The cured nadimides was stable up to (425 ± 20)°C showed a single step decomposition.

The weight loss during isothermal curing of nadimides may be attributed to the loss of cyclopentadiene formed as a result of the Retro Diel Alder (RDA) reaction according to the Scheme 4.

Copolymerization of cyclopentadiene with bismaleimide is believed to be the mechanism of crosslinking reaction.

TABLE V
Weight Loss During Isothermal Curing of Nadimides

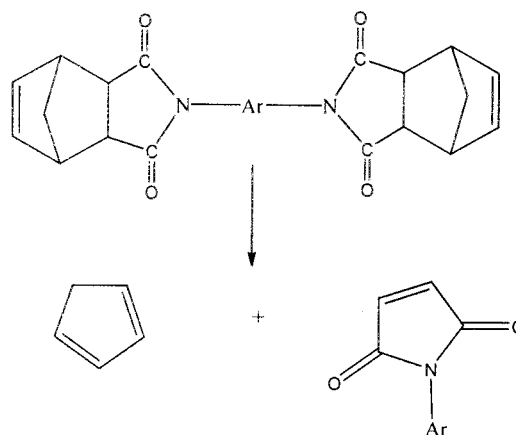
Sample No.	Resin designation	Weight loss	
		250°C (%)	300°C (%)
1	P-1	1.0	11.0
2	P-2	1.5	6.0
3	P-1N	1.5	10.7
4	P-1O	1.0	6.4
5	P-2N	2.2	4.3
6	P-2O	1.5	3.8

Thermal behavior of cured resins

In DSC traces of cured samples, no exotherm was noticeable. The cured nadimides showed only one step decomposition in the TG trace as observed against multistep decomposition in uncured resins. These resins were stable to (350 ± 30)°C and started loosing weight above this temperature. Char yield at 800°C increased significantly on curing. The results are summarized in Table IV.

CONCLUSIONS

A marked improvement in char yield at 800°C was observed on cocuring. The presence of phosphorous content in nadimides increased the char yields of the cocured resins. Char yields of the cured resins nadimides (63–75%) were higher than the uncured nadimides indicating the potential use at higher temperature. From these results, it is concluded that nadimides undergo RDA reaction and the resulting maleimide adds to allyl group via 'ene' reaction. Higher char yields were obtained with nadimides based on NTDA as compared with ODA-based nadimides. The highest char yield was obtained in case of P-2N.



Scheme 4 Retro Diel Alder (RDA) reaction.

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