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THERMAL BEHAVIOUR OF BISITACONIMIDE AND BISNADIMIDE BLENDS

A. Solanki, V. Choudhary and I. K. Varma[*]

Centre for Polymer Science and Engineering, Indian Institute of Technology, Delhi, Hauz Khas,
New Delhi-110016 India

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Abstract

This paper describes the thermal behaviour of blends of bisitaconimide (*I*) and bisnadimide (*N*) resins of similar structures. Bisitaconimides/bisnadimides based on 4,4'-diaminodiphenyl ether (*E*); 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (*B*); 1,3-bis(4-aminophenyl)benzene (*R*) and 1,4-bis-(4-aminophenyl)benzene (*H*) were prepared and were designated as *E-I*/*E-N*; *B-I*/*B-N*; *R-I*/*R-N* and *H-I*/*H-N* respectively. Itaconimides had lower melting points and curing temperatures than that of corresponding nadimides. The blends of bisitaconimides and bisnadimides were prepared in the ratios of 1:3, 1:1, 3:1 by solution mixing (chloroform/acetone). A decrease in the melting point and characteristic curing temperatures was observed in the blends. Thermal stability of cured resin blends was only marginally affected by the blend composition.

Keywords: bisitaconimides, bisnadimides, blends, imide resins, thermal behaviour

Introduction

Addition polyimides, such as nadimide, maleimide or ethynyl terminated imide resins are a leading class of thermosetting polyimides. Such polymers exhibit outstanding thermo-oxidative stability, exceptional dielectric properties and excellent resistance to humidity at elevated temperatures. However, the processing of these polymers causes problems because of high curing temperatures and, in some cases a very narrow processing window.

Blending of addition polyimides with several thermoset resins and thermoplastics was carried out in the past aiming at improving the processability and performance. Co-curing of allyl nadimides with phosphorus containing nadimide resin [1] yielded products with improved char yield and better processability. Blending of bismaleimides (*M*) and nadimides (*N*) [2] resulted in a decrease in curing temperatures and enhancement of char residue. Blends of chain extended bismaleimide with bismaleimides showed a decrease in melting point and curing temperature [3].

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[*] Author to whom all correspondence should be addressed.

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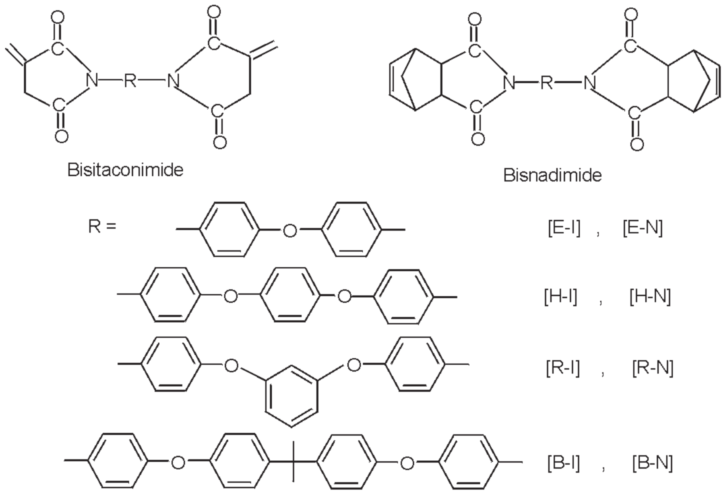
Bisnadimide resins cure at higher temperatures (>280°C). The chemical processes that take place on heating the nadimides are a) isomerisation (above 200°C), b) Retro Diels Alder's reaction (RDA) and double Diels Alder's adduct formation and c) polymerisation. Retro Diels Alder's reaction of the norbornene end groups as suggested by Lauver [4], leads to maleimide groups and cyclopentadiene, which then undergo a thermally induced free radical polymerisation reaction to a cross-linked polymer containing cyclopentene crosslinks. Polymerisation of nadimide, maleimide, cyclopentadiene and double Diels Alder's adduct takes place at high temperature (>270°C). Thus in-situ formation of maleimido end-caps takes place in nadimides. In bismaleimides, on the other hand, the maleimido end-cap is present from the beginning. In case of itaconimides [5, 6] only isomerisation to citraconimides and polymerisation has been reported. The curing starts at a lower temperature in these resins [7].

Nadimides as well as maleimide resins contain 1, 2-disubstituted double bonds, which have a very low tendency to homopolymerize due to kinetic considerations. The propagation step is extremely slow due to steric interactions between the β-substituent of the propagating species and the two substituents of the incoming monomer molecules [8]. Itaconimide end-capped resins contain 1,1-disubstituted double bond, which is more reactive. Copolymerisation of 1,2-disubstituted double bond with monosubstituted olefin is well documented in literature and is the basis of unsaturated polyester technologies [9].

In this paper thermal behaviour of blends of bisitaconimides (*I*) and bisnadimides (*N*) is reported. Four nadimide and itaconimide resins of the following structure were prepared by reacting appropriate diamines with nadic anhydride or itaconic anhydride.



Experimental

Materials

Chloroform (Qualigens fine chemicals), phosphorus pentoxide (Merck), and 4,4'-diaminodiphenyl ether (Fluka) were used as received. Acetic anhydride (BDH) and glacial acetic acid (Merck) were distilled before use. The diamines *B*, *R* and *H* were prepared in the laboratory according to the procedure reported elsewhere [10]. Acetone (Qualigens fine chemicals) was kept over potassium carbonate for 24 h and distilled before use. Itaconic anhydride was prepared from itaconic acid (Aldrich) using phosphorus pentoxide as a dehydrating agent and chloroform as solvent [5] and nadic anhydride was purified by crystallisation from acetic anhydride. Sodium acetate (Sarabhai Chemicals) was fused in a porcelain dish over a burner and stored in a dessicator.

Synthesis of imides

The imides were prepared by the condensation reaction of anhydrides and the amines in a molar ratio 2:1, using acetone or glacial acetic acid as solvent. Typical procedures for synthesis of bisitaconimide and bisnadimide are given below.

Appropriate diamine (1 mole) was dissolved in dry acetone and 2 moles of itaconic anhydride were added slowly and the mixture refluxed for several hours. Cyclodehydration of intermediate amic acid was done using sodium acetate and acetic anhydride.

In case of nadimides, one mole of diamine was dissolved in glacial acetic acid and 2 moles of nadic anhydride were added slowly and the mixture was refluxed for 8–9 h. The imide resins were precipitated in ice-cold water, washed with water, sodium bicarbonate solution, water and dried in oven at 50–75°C. The imides were then purified by column chromatography using silica column and chloroform as solvent.

Characterisation

Imide resins were characterised by recording IR spectra in film form using Biorad Digilab FTS-40 FT-IR spectrometer.

^{1}H-NMR spectra were recorded using a Bruker AC 300 MHz. Spectrometer, $CDCl_3$ or DMSO-d_6 as a solvent and tetramethyl silane (*TMS*) as an internal standard.

A DuPont 2100 thermal analyser having a 910 DSC module and 951 TG module was used for thermal characterisation. DSC scans were recorded in static air atmosphere using 7±2.5 mg of sample and a heating rate of 10°C min^{-1}. The curing exotherm was characterized by determining: T_i – temperature where the curing starts, T_{exo} – temperature of peak position of exotherm, T_f – temperature of end of curing exotherm.

Thermogravimetric studies were carried out in nitrogen atmosphere (flow rate 60 cm^3 min^{-1}) at a heating rate of 20°C min^{-1} (sample mass 10±2 mg).

Preparation of blends

The blends were prepared by solvent (acetone/chloroform) mixing of the itaconimides and nadimides for about ten minutes and then removing the solvent in air. The blends were prepared by mixing 1:3, 1:1, 3:1 (mass/mass) ratios of itaconimides and nadimides and are designated as I_1N_3, IN, I_3N_1 with a prefix of the letter designation of the amine.

Results and discussion

Structural characterization of imide resins

Bisnadimides were white and bisitaconimides yellow. Itaconimides were obtained in 60–70% yield whereas higher yields (~80%) were obtained in nadimides.

In the IR spectra of imide resins (Fig. 1) the peaks at 1710±10 and 1770±10 cm^{-1} due to the imide groups were observed. A peak at 1665±10 cm^{-1} due to vinylic double

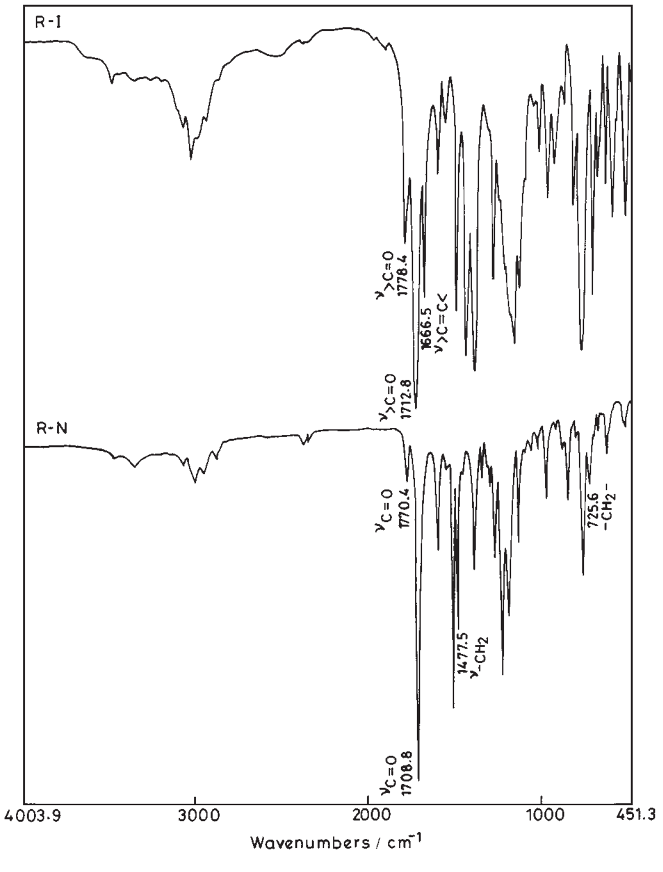


Fig. 1 FT-IR spectra of *R-I* and *R-N*

bond was observed in itaconimides while in nadimides absorption bands due to $-CH_2$-group were obtained at 1477 and 725 cm^{-1}.

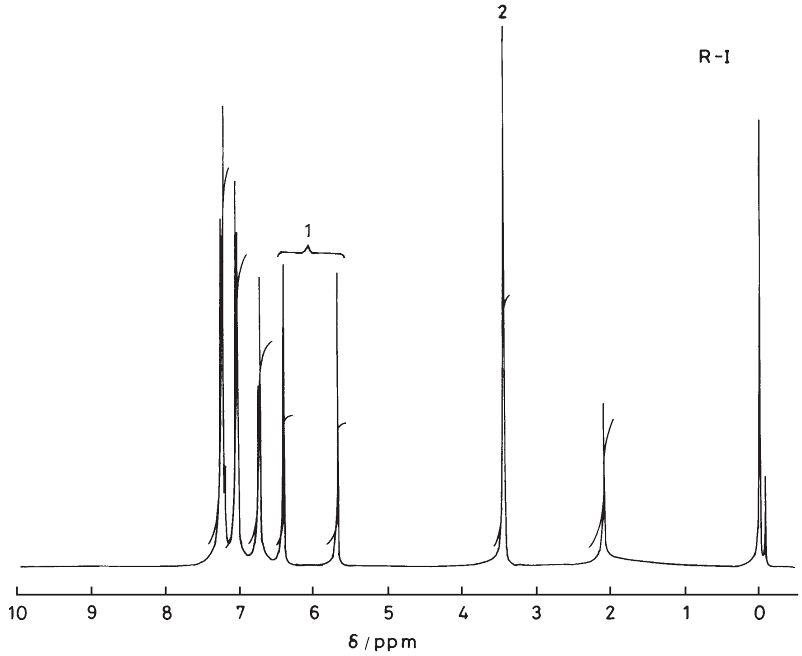


Fig. 2 ^{1}H-NMR spectrum of *R-I*

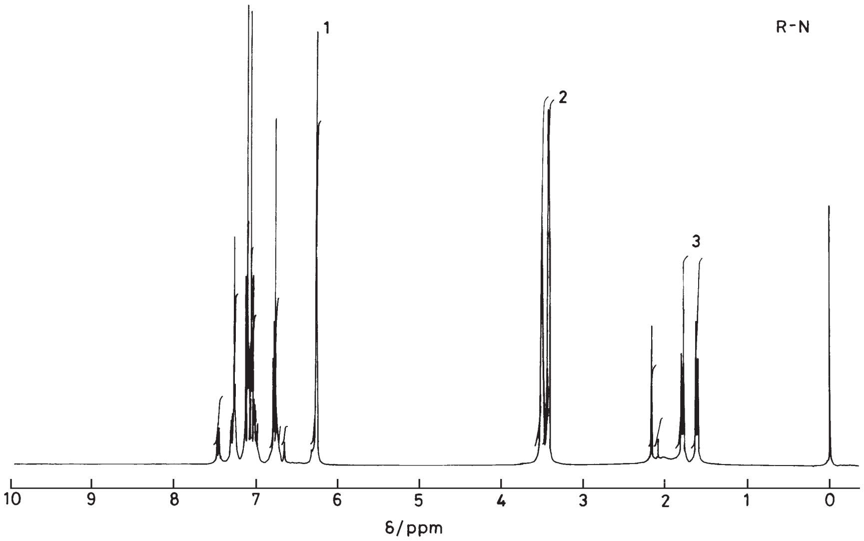


Fig. 3 ^{1}H-NMR spectrum of *R-N*

In the ^{1}H-NMR spectra of itaconimides (Fig. 2), methylene protons were observed at δ=3.4 ppm, vinylidene proton at δ=5.6 and 6.5 ppm (singlets), and aromatic protons between δ=7–8 ppm. A proton signal at 2.06±0.05 ppm due to isomerization of itaconimide to citraconimide was observed in all itaconimides. In case of nadimides (Fig. 3), olefenic protons were present at δ=6.25 ppm, methylene protons of the bridge at δ=1.6–1.8, aromatic protons between 7–8 ppm and remaining aliphatic protons at δ=3.4–3.5 ppm.

Thermal characterisation of imide resins and their blends

DSC studies

The exothermic transitions in bisnadimides under consideration were observed in the DSC scans above 290°C, which is higher than that of corrresponding itaconimides. However, itaconimides cured at lower temperatures (180–216°C).

Table 1 DSC results of itaconimide and nadimide blends

Resins	Characteristic temperatures/°C							
	T_{mI}	T_{mN}	T_{i1}	T_{exo1}	T_{f1}	T_{i2}	T_{exo2}	T_{f2}
R-I	164	–	182	223	283	–	–	–
$R\text{-}I_3N_1$	166	–	185	219	276	318	331	376
R-IN	181	–	187	216	267	292	311	353
$R\text{-}I_1N_3$	176	197	186	220	256	–	–	–
R-N	–	207	–	–	–	325	337	382
B-I	83	–	216	257	311	–	–	–
$B\text{-}I_3N_1$	134	–	188	229	301	303	326	355
B-IN	153	–	172	208	289	289	320	346
$B\text{-}I_1N_3$	138	167	175	182	259	–	–	–
B-N	–	174	–	–	–	289	338	379
E-I	186	–	200	206	311	–	–	–
$E\text{-}I_3N_1$	188	–	191	196	221	–	–	–
E-IN	182	244	186	196	234	287	315	331
$E\text{-}I_1N_3$	177	256	–	–	–	288	332	–
E-N	–	258	–	–	–	321	332	375
H-I	193	–	199	210	245	–	–	–
$H\text{-}I_3N_1$	198	275	–	–	–	–	–	–
H-IN	193	281	–	–	–	292	305	329
$H\text{-}I_1N_3$	190	290	–	–	–	298	311	339
H-N	–	292	–	–	–	300	311	348

DSC scans of blends (Table 1) revealed significant changes in the melting points and characteristic curing temperatures of imide resins depending upon the structure of the constituent imides. The difference between:

a) the melting point of the constituents,
b) curing temperature and
c) blend composition affected the curing behaviour.

Two exothermic transitions were observed in several blends and a decrease in curing temperature was observed. The exotherm at lower temperature may be due to crosslinking of itaconimide and nadimide and the high temperature exotherm may be due to evolution of cyclopentadiene as well as co-curing of resins.

Similar behaviour was observed in *R-I*/*R-N* (Fig. 4) and *B-I*/*B-N* blends, while that of *H-I*/*H-N* and *E-I*/*E-N* was the same. In case of imides prepared from amines *R* and *B* the blends having ratios 3:1 and 1:1 of itaconimide and nadimide respectively single melting peaks were observed while in case of 1:3 there were two melting peaks. The melting endotherm in case of 1:1 blend was sharp while that for 3:1 was broad. This indicates that the blend having 1:1 composition may be completely misci-

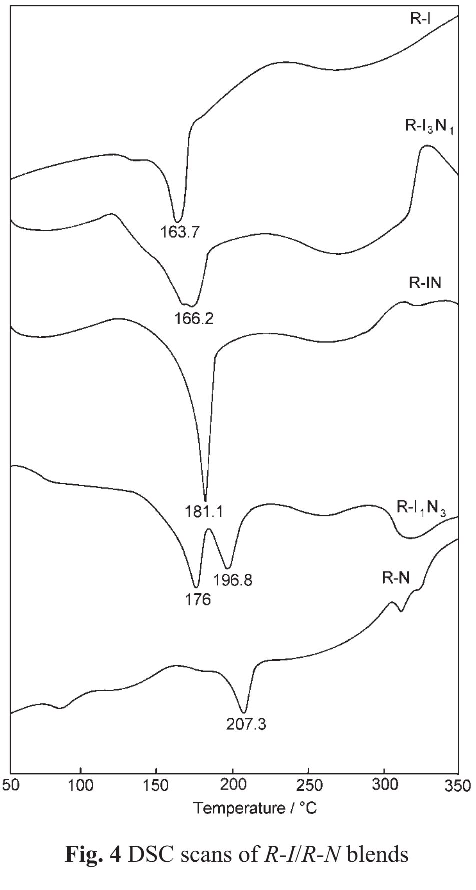


Fig. 4 DSC scans of *R-I*/*R-N* blends

ble. In case of *H-I*/*H-N* and *E-I*/*E-N* blends two distinct melting peaks were observed in all the compositions except *E*-I_3N_1 where a single melting peak was observed.

The curing exotherm in case of 1:1 itaconimide and nadimide blend was observed at lower temperatures than that of other blend compositions and pure imides in all the blends. In case of *H-I* and *E-I* imides the curing exotherm was obtained immediately after melting and as a result, the exotherms in the blends were not well defined.

Thermogravimetric analysis

Thermal stability of resin blends (Table 2) cured isothermally at 200°C for 2 h was comparable in all the blends. TG traces (Fig. 5) were characterized by determining extrapolated initial decomposition temperature (T_e), extrapolated final decomposition temperature (T_{ef}) and mass loss in this temperature range. The temperature of maximum rate of mass loss (T_{max}) was determined from differential thermogravimetric traces (DTG). Two-step decomposition was observed in all the blend compositions and pure imides except in *B-I* and *E-N* where a single-step and three-step decomposition respectively were observed. The mass loss in the first step ranged from 5–16% for the pure nadimides and blends while that for pure itaconimides it was only 2–3%. It is reported that in nadimides at this temperature there may be evolution of cyclopentadiene due to reverse Diels Alder's reaction. The maximum mass loss in the temperatue range 250–400°C was observed in nadimides and for blends it decreased as the amount of itaconimide increased. However, a major mass loss occurred above 400°C in all the blends and pure imides. The % char yield in the blends at 800°C was in the range of 33–42% which is comparable with that of pure imides.

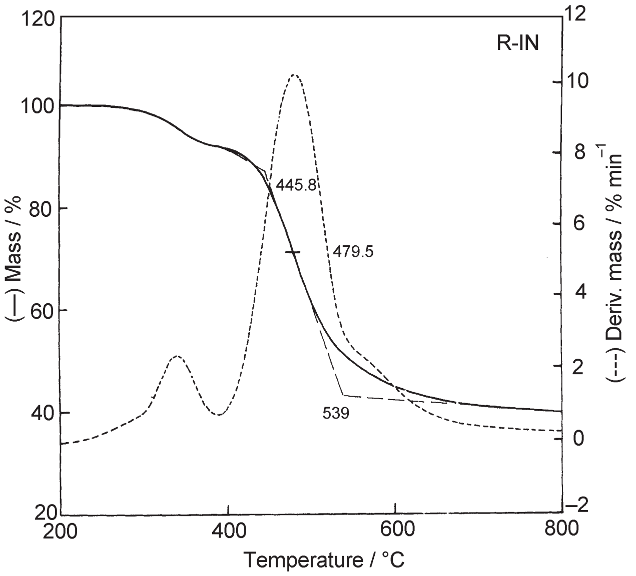


Fig. 5 TG trace of *R-IN* blend

Table 2 TG results of itaconimide and nadimide blends

Resins	Characteristic temperatures/°C				
	T_e	T_ef	T_max	Mass loss/%	Char yield/% (800°C)
$R\text{-}I$	286	413	323	2	
	445	541	490	59	39
$R\text{-}I_3N_1$	268	382	341	5.2	
	447	537	478	57.4	37.4
$R\text{-}IN$	295	386	341	7.7	
	446	539	479	54	38.3
$R\text{-}I_1N_3$	295	358	333	12.5	
	440	530	465	51.7	36
$R\text{-}N$	300	368	332	16.2	
	427	518	452	47.6	36.2
$B\text{-}I$	464	460	499	65	35
$B\text{-}I_3N_1$	286	400	341	5.4	
	473	556	513	60.6	34
$B\text{-}IN$	291	395	350	6.3	
	473	560	510	57	36.7
$B\text{-}I_1N_3$	295	409	363	8.4	
	480	551	515	54	36
$B\text{-}N$	300	386	354	12.2	
	463	556	504	51.8	36
$E\text{-}I$	290	395	323	3	
	457	542	482	58	39
$E\text{-}I_3N_1$	254	391	314	4.2	
	457	536	481	56.4	39.4
$E\text{-}IN$	261	330	302	12.3	
	454	540	478	52.7	35
$E\text{-}I_1N_3$	264	335	313	14.5	
	467	540	486	49.8	35.7
$E\text{-}N$	232	291	264	2.2	
	312	365	344	16.1	
	474	530	486	48.1	33.6
$H\text{-}I$	245	382	282	2	
	427	524	454	56	42
$H\text{-}I_3N_1$	284	368	324	4	
	452	550	495	56	40
$H\text{-}IN$	279	350	302	4.6	
	433	551	467	56	39.4
$H\text{-}I_1N_3$	281	341	307	7.3	
	434	550	463	50	42.7
$H\text{-}N$	282	323	309	14	
	449	539	471	49	37

Conclusions

- Significant changes in curing exotherms and melting points are observed in all the blends of itaconimides and nadimides depending upon the structure of the constituent imide resins.
- Blend composition also affected the curing exotherm. In case of 1:1 composition in all the blends the curing exotherm is at a lower temperature than other blend compositions and pure imides.
- The thermal stability of cured imides evaluated at 200°C was only marginally affected by blending. The % char yield in the blends at 800°C was 33–42% which is comparable to pure imides.

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