

Synthesis of silicon-containing bisnadiimide

Preparation and characterization of semi-interpenetrating network systems of silicon- and fluorine-containing polyimides

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Abstract Silicon-containing thermosetting bisnadiimide (BNI) was synthesized using Bis (amino propyl) tetramethyl disiloxane and nadic anhydride, and fluorine-containing thermoplastic polyamic acid (FPA) was synthesized from 4,4'-(hexafluoroisopropylidene) bis phenoxy dianiline and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride [6-FDA]. The semi-interpenetrating network (s-IPN) systems in various ratios were prepared via solution casting of FAA and crosslinkable BNI, and then curing them up to 370 °C in order to achieve an optimum combination to be used for advanced high temperature composite applications. The polyimides and s-IPN were characterized using NMR and FTIR spectroscopy. The thermo-oxidative and water uptake properties of these polyimides and s-IPNs were investigated. The thermogravimetric analysis (TG) showed increase in thermal stability with the increase in thermoplastic polyimide proportion.

Keywords Bisnadiimide · Bis (amino propyl) tetramethyl disiloxane · Nadic anhydride · 4,4'-(hexafluoroisopropylidene) bis phenoxy dianiline · Semi-interpenetrating network systems · Polyimides · s-IPN

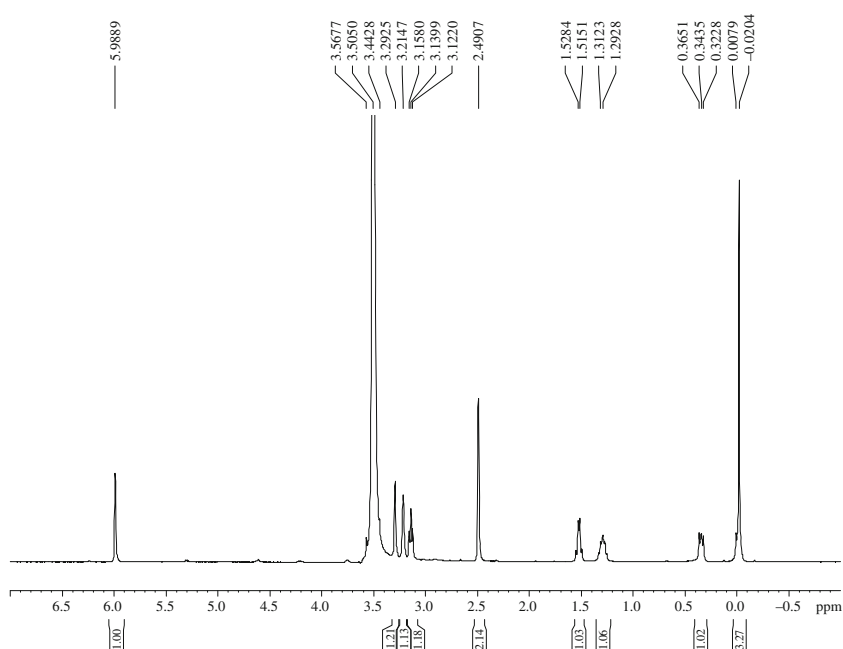
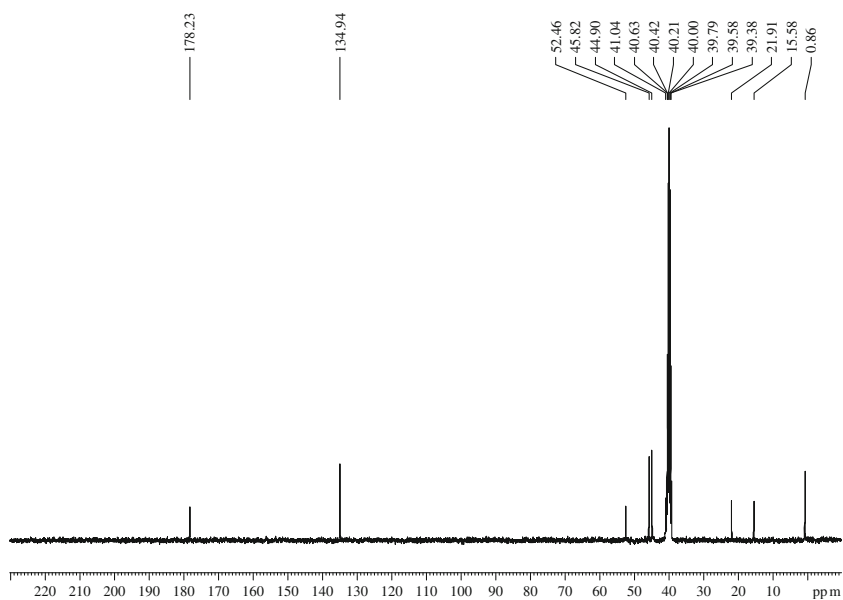
Introduction

The semi-interpenetrating networks (s-IPN's) are an important category of mixture of two polymers in which one polymer is cross linkable while other is linear. The aim

of preparation of s-IPN's is to incorporate the properties of both the polymers, thereby not only imparting flexibility to the system but also imparting high thermal stability. In this way, an optimum combination can be achieved for desired properties of specific application. s-IPN's has been prepared using different polymer combinations, such as polyimide–polyimide [1–4], polyimide–nafion [5], polyimide–POSS [6], polycaprolactone–poystyrene [7], polydimethyl siloxane–PMAA [8], polyurethane–benzyl starch [9], polyurethane–polystyrene [10], polyurethane–polyvinyl chloride [11], polyether–polyacrylate [12], etc. and investigated for their various properties.

Polyimides are in fact some of the most widely investigated class of polymers which are in use, particularly in high temperature aerospace, microelectronics, printed circuits, high performance adhesives, etc. [13–18]. Here in this article, we report the synthesis of new s-IPN's obtained via sequential method by mixing crosslinkable bisimide and thermoplastic linear polyimide in various ratios in order to develop an optimum matrix resin for high temperature composite applications. It has been reported that long carbon chain and (O–Si) bond offers better flexibility and good thermo-oxidative stability to the polymer network [19–25], so we have synthesized crosslinkable polyimide from silicon-containing long chain diamine, bis (amino propyl) tetramethyl disiloxane, and nadic anhydride. It has been shown that introduction of fluorine atom in polymer backbone not only decreases the polarisability of the polymer but also increases the thermo-oxidative stability [26–28], so in order to obtain high temperature s-IPN's, we have chosen linear polyimide obtained by 6-FDA and 4,4'-(hexafluoroisopropylidene) bis phenoxy dianiline. The thermosetting BNI and thermoplastic FPA were mixed in 90:10 to 50:50 ratios in dry DMAc casted on a glass petri dish dried at temperatures up to 250 °C in

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Fig. 1 ^1H NMR spectrum of BNI**Fig. 2** ^{13}C NMR spectrum of BNI

%C 62.19, %H 7.46. Found: %C 61.88, %H 7.86. The ^1H and ^{13}C NMR spectrum of BNI is given in Figs. 1 and 2.

Preparation of FPA

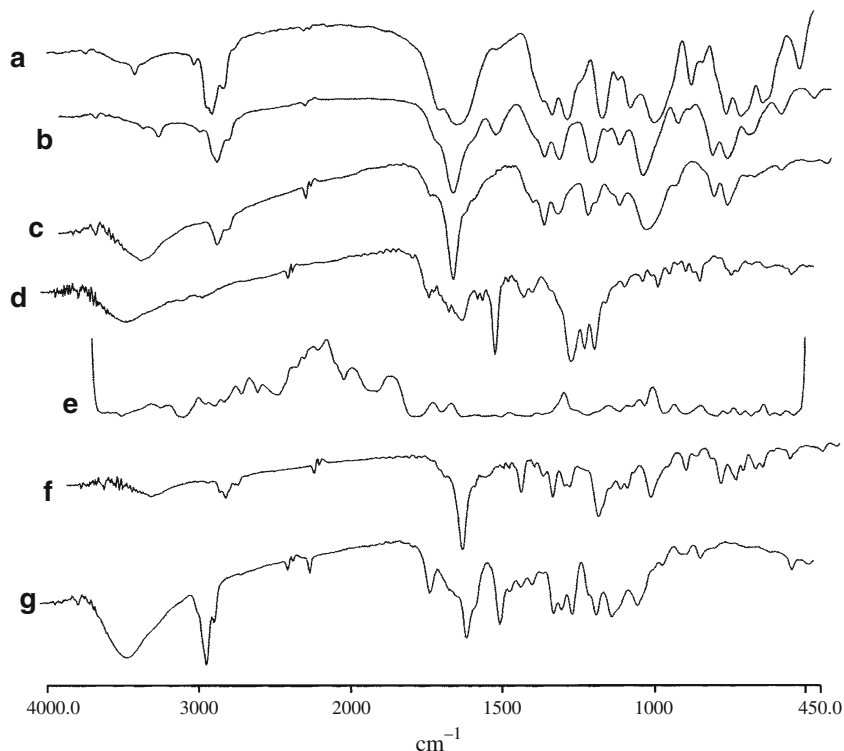
To a stirred solution of 4,4'-(hexafluoroisopropylidene) bis phenoxy dianiline (50 g, 0.0965 mol) in dry DMAc (300 mL) under N_2 atmosphere at room temperature, 6-FDA (46.86 g, 0.0965 mol) was added gradually and the reaction mixture was allowed to stir for 8 h. The reaction mixture was

poured in ice-cool water to precipitate FPA, which was dried under vacuum to furnish dried FPA (95.5 g). mp 69 °C (by DSC); FT-IR (KBr cm^{-1}) 1174, 1251, 1503, 1650, 1718.

Preparation of s-IPN's

s-IPN's were prepared using BNI and FPA in ratios of 90:10 to 50:50, respectively. The preparation of a typical 70:30 ratio sIPN's involved stirring of 0.7 g of BNI and 0.3 g of FPA in 10 mL of dry DMAc for 1 h, and then the mixture

Fig. 3 FTIR spectrum of: *a* BNA, *b* BNI, *c* cured BNI, *d* FPA, *e* FPI, *f* uncured 70:30 BNI/FPA s-IPN, *g* cured s-IPN



was poured on a glass petri dish which was then heated in a vacuum oven at 100, 150, 200, 250, 300, 350, 360 °C for 4 h and then post curing at 370 °C for 6 h, respectively.

Results and discussion

FTIR analysis for curing

The FTIR analysis of BNA showed two carbonyl peaks at 1698 and 1751 corresponding to -NHC=O and -OC=O while C=C peak was merged with the broad carbonyl peaks, which upon imidization in BNI showed peak at 1646 due to C=C stretching which was merged with C=O peak at 1700. The BNI upon curing showed C=O peak at 1699, while peak due to C=C stretching disappeared. The characteristic peak at 1074 due to Si-O stretching was observed in all these cases. The peak at 1650 and 1718 in FPA upon imidization shifted to 1767 in fluorinated polyimide [FPI]. The merged peaks at 1698 in a typical uncured 70:30 BNI/FPA s-IPN systems diminished in cured system and peak at 1700, 1721, and 1775 appeared. The FTIR spectrum of all the above compositions has been shown in Fig. 3.

DSC analysis

The melting, imidization, and curing behaviors of BNA, BNI, FPA, FPI and their various s-IPN compositions were investigated via DSC. The DSC scan of BNA showed

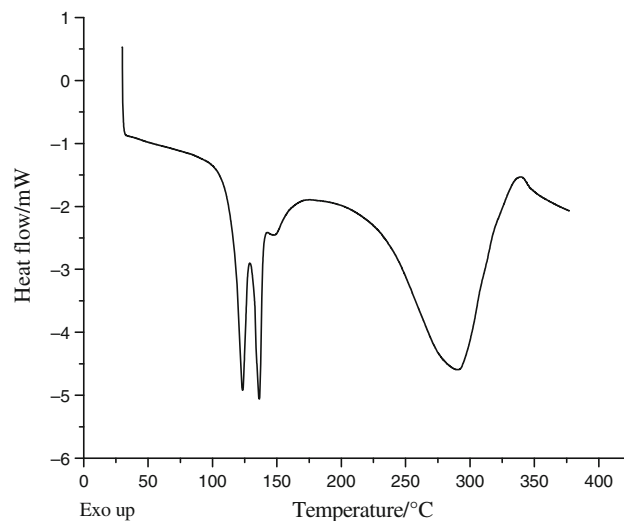
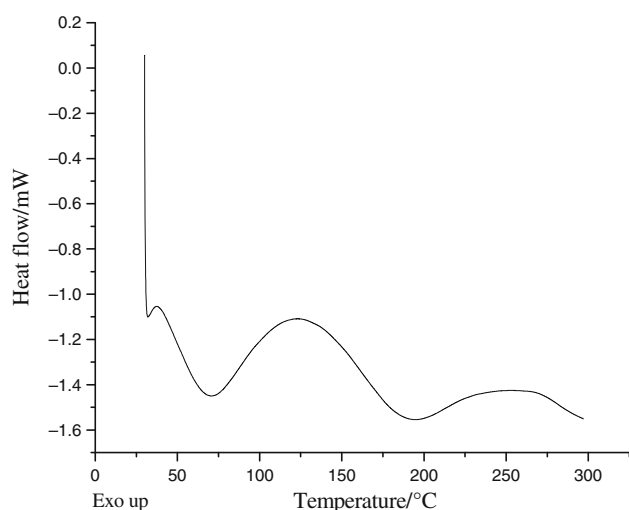
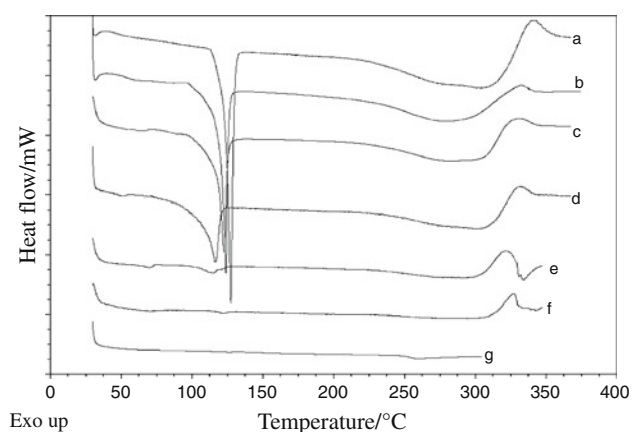


Fig. 4 DSC analysis of BNA

melting at 123 °C, while its imidization occurred between 132 and 141 °C with maximum rate at 136 °C (Fig. 4). The DSC spectrum of BNI showed melting at 129 °C, while its curing started at 305 °C with maximum rate of curing at 342 °C and finished at 360 °C. The modulated DSC scan of cured BNI showed glass transition temperature (T_g) at 142 °C. The DSC analysis of FPA showed melting at 69 °C and its imidization occurred from 139 to 243 °C with maximum rate at 182 °C (Fig. 5). The DSC scan of


Fig. 5 DSC analysis of FPA

Fig. 6 DSC analysis of samples a–g treated up to 250 °C

FPI showed glass transition temperature (T_g) at 253 °C. The s-IPN combinations **b–g** treated up to 250 °C so as to just imidize the systems, showed consistent decrease in melting point (T_m) with the increase in thermoplast content. The curing profile of these s-IPN systems showed consistent decrease in final curing temperature (T_{end}) with the increase in thermoplast content (Fig. 6; Table 1).

The DSC analysis of fully cured samples of **a–g** showed regular increase in T_g with the increase in thermoplast proportion. (Fig. 7; Table 1).

TG analysis

The TG analysis of BNA showed 8% loss in mass from 131 to 140 °C due to imidization (Fig. 8). A 30% weight loss was observed in both BNA and BNI from 300 to 350 °C during curing due to complex cross linking and loss of cyclopentadiene molecule (Fig. 9). The onset of degradation of cured BNI started at 445 °C, and endset took place at 520 °C with maximum rate of degradation at 486 °C. The char yield at 800 °C was found to be 30%. The limiting oxygen index (LOI) calculated from Krevelen's equation [29] was found to be 29.5%.

$$\text{LOI} = 17.5 + 0.4(\sigma)$$

where σ is the % char yield at 800 °C.

The TG analysis of FPA showed 9% weight loss from 130 to 230 °C due to imidization and loss of water molecules (Fig. 10). The polymer backbone decomposition started at 526 °C with maximum rate of decomposition at 560 °C and endset at 642 °C. The char yield of FPI at 800 °C was found to be 55%, and LOI on base of Krevelen's equation was 39.5%. The TG analysis of various cured samples of s-IPN systems revealed consistent increase in maximum rate of decomposition, final decomposition temperature char yield and LOI values with

Table 1 DSC analysis of samples a–g

Sample no.	Mass ratio BNI/FPA	$T_m/^\circ\text{C}$	$T_{ons}/^\circ\text{C}$	$T_{max}/^\circ\text{C}$	$T_{end}/^\circ\text{C}$	$T_g/^\circ\text{C}$	Curing window/ $^\circ\text{C}$
a	100:00	129	305	342	361	142	56
b	90:10	125	286	334	352	155	66
c	80:20	123	297	330	350	158	53
d	70:30	116	308	338	348	177	40
e	60:40	114	305	322	338	187	33
f	50:50	114	313	326	338	216	17
g	00:100	069	–	–	–	252	–

T_m melting point, T_{ons} onset curing temperature, T_{max} maximum curing rate temperature, T_{end} endset curing temperature, T_g glass transition temperature

Fig. 7 DSC analysis of cured samples a–g

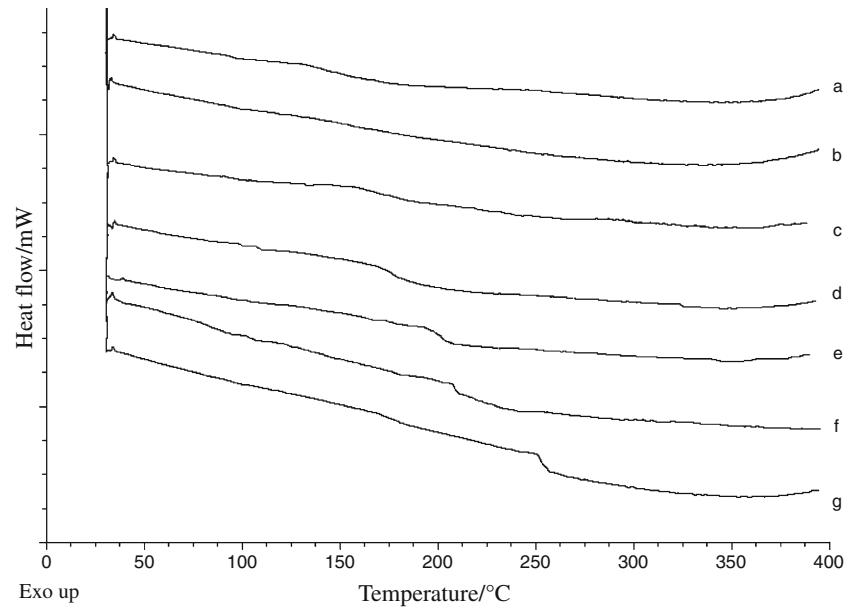


Fig. 8 TG analysis of BNA

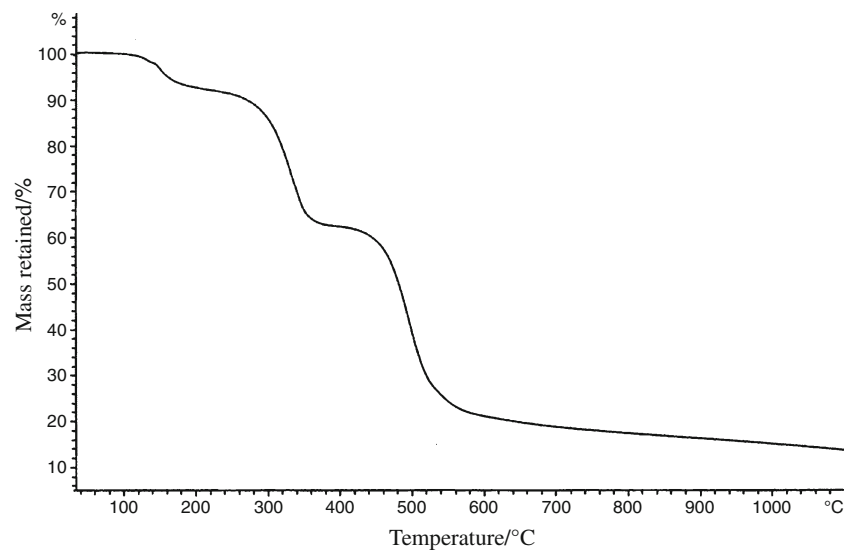


Fig. 9 TG analysis of BNI

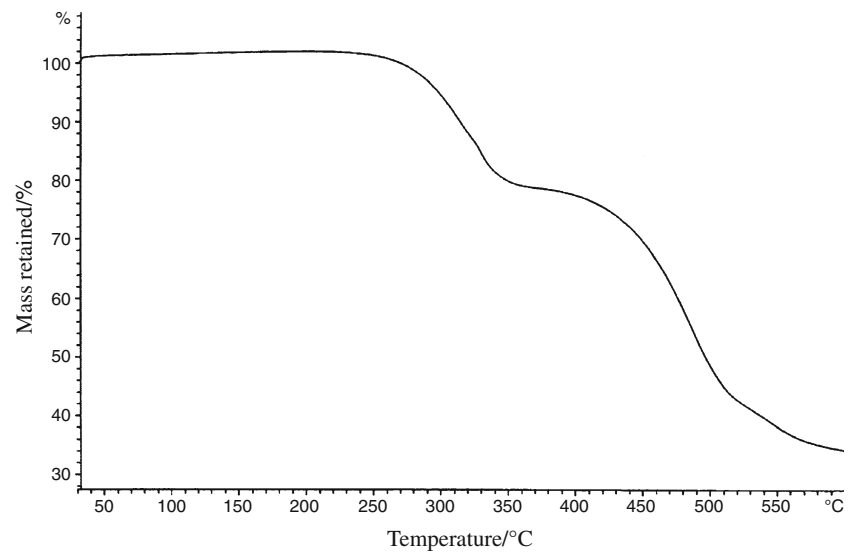
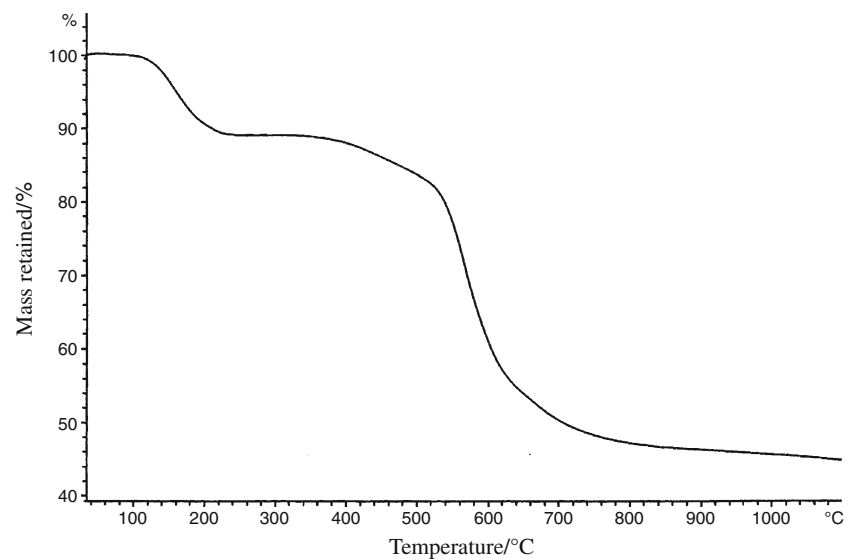


Table 2 TG analysis of cured samples

Sample no.	Mass ratio BNI/FPA	$T_{\text{ons}}/^{\circ}\text{C}$	$T_{\text{max}}/^{\circ}\text{C}$	$T_{\text{end}}/^{\circ}\text{C}$	Char yield at 800 $^{\circ}\text{C}/\%$	LOI/%
a	100:00	445	486	520	30	29.5
b	90:10	430	494	543	37	32.3
c	80:20	444	495	543	38	32.7
d	70:30	466	504	547	38	32.7
e	60:40	442	498	577	39	33.1
f	50:50	458	525	602	46	35.9
g	00:100	526	560	642	55	39.5

T_{ons} onset degradation temperature, T_{max} maximum degradation temperature, T_{end} final degradation temperature

Fig. 10 TG analysis of FPA**Table 3** Isothermal ageing for 300 h at 300 $^{\circ}\text{C}$

Sample No.	Mass ratio BNI/FPA	Mass loss after 300 h/%
a	100:00	9.52
b	90:10	9.10
c	80:20	8.50
d	70:30	7.70
e	60:40	6.80
f	50:50	5.90
g	00:100	2.50

Table 4 Water uptake after 48 h

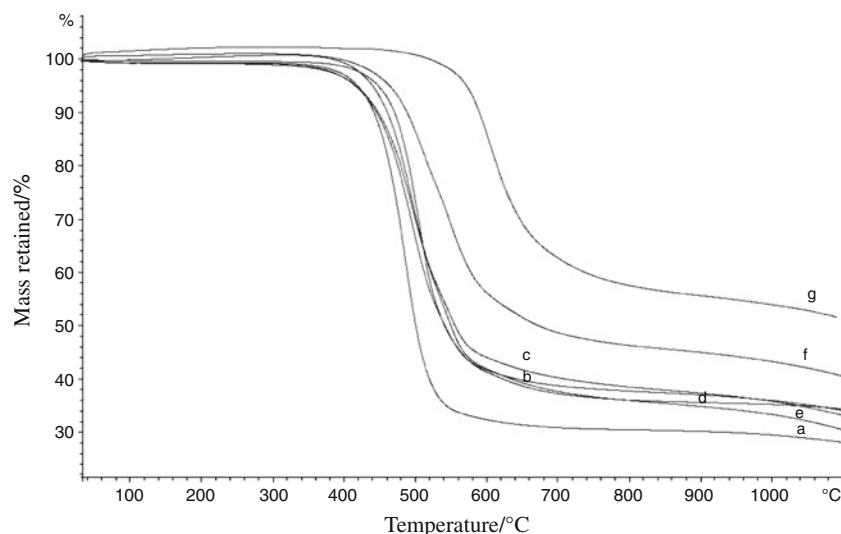
Sample No.	Mass ratio BNI/FPA	Water uptake after 48 h/%
a	100:00	1.75
b	90:10	1.62
c	80:20	1.45
d	70:30	1.25
e	60:40	0.99
f	50:50	0.80
g	00:100	0.50

increase in thermoplast content thereby indicating direct correlation between the char forming properties and flame retardancy (Table 2; Fig. 11).

Isothermal ageing

The isothermal ageing of cured BNI, FPI, and their cured s-IPN's was carried out by keeping their films coated on a

Fig. 11 TG analysis of cured samples a–g



glass petri dish at 300 °C weighing them at 50, 100, 150, 200, 250 and 300 h on a microbalance before and after thermal aging. The % mass loss for 300 h was calculated from the following equation.

$$\text{Mass loss (\%)} = (W_0 - W_{300})100/W_0$$

where W_0 is initial mass of sample at 0 h and W_{300} is the mass at 300 h.

The isothermal ageing showed decrease in % mass loss with increase in the thermoplastic material because of the incorporation of high aromatic content of FPI (Table 3).

Water uptake

The % water absorption by BNI, FPI, and their cured s-IPN's were measured by immersing their films coated on a glass petri dish into deionised water for 96 h at room temperature (~ 30 °C). The films coated on glass petri dish were then taken out wiped with tissue paper and quickly weighted on a microbalance. The water uptake of these glass coated films was calculated from the following equation:

$$\text{Water uptake (\%)} = (W_{48} - W_0)100/W_0$$

where W_0 is initial mass of sample at 0 h and W_{48} is the mass at 48 h.

The water uptake of BNI was 1.75% which was relatively low due to the presence of silicon atom in polymer skeleton because the silicon segments have large steric congestion and molar volume [25]. The water uptake by FPI was only 0.50% which was expected due to high aromatic and low dielectric fluorine content. The % water uptake by their s-IPN systems showed decrease in water absorption with increase in the thermoplast content (Table 4; Fig. 11).

Conclusions

The present study describes the synthesis of new thermo-setting silicon-containing BNI and its characterization using NMR, IR Elemental analysis, TG and DSC, and preparation of its s-IPN's with FPI. The objective of this study was to incorporate varying amount of thermoplast content in thermoset and to study their thermal behavior to be utilized for advanced composite applications. It has been observed that with increase in thermoplast content, there was a gradual decrease in curing window of the s-IPN systems, while there was an increase in glass transition temperature (T_g) of the s-IPN systems. The TG analysis showed that increase in FPI content also increased the char yield as well as limiting oxygen index values. A decrease in weight loss was observed in isothermal ageing for 300 h at 300 °C with increase in proportion of FPI. The water uptake tendency of the s-IPN systems decreased with the increase in thermoplast proportion.

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