

Development and study of the thermal and electrical behaviour of TGDDS epoxy nanocomposites for high-performance applications

K. Shree Meenakshi · E. Pradeep Jaya Sudhan

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Abstract The present work focuses on a comparative study of the thermal and electrical behaviour of N,N'-tetraglycidyl diaminodiphenylsulphone (TGDDS) denoted as 'B' to find the suitability for its use in high-performance applications. The synthesis of the tetraglycidyl epoxy was done and they were characterized by FT-IR (Fourier transform infrared spectra) and nuclear magnetic resonance spectra (¹H-NMR and ¹³C-NMR). Nanoclay and POSS-amine nanoreinforcements denoted as N1 and N2 were incorporated into the synthesized epoxy resins. Curing was done using diaminodiphenylmethane (DDM) and bis(3-aminophenyl)phenylphosphine oxide (BAPPO) curing agents denoted as X and Y, respectively. The thermal behaviour of the tetraglycidyl resins and their corresponding nanocomposites was studied by thermogravimetric analysis (TGA). The electrical behaviour, namely dielectric strength, comparative tracking index (CTI), volume resistivity, surface resistivity and arc resistance of the nanocomposites were also studied and the interesting results obtained are discussed.

Keywords Epoxy resin · Thermal stability · Electrical behaviour · Thermogravimetric analysis

Introduction

Nanotechnology has created a key revolution in the twenty-first century exploiting the new properties, phenomena and functionalities exhibited by matters when dealt at the level

of few nanometers. At this level, the physical, chemical and biological properties of materials differ in fundamental and valuable ways from properties of individual atoms and molecules or bulk matter. Research and development in nanotechnology is directed towards understanding and creating new materials, devices and systems that exploit these new properties. Epoxy resins have several excellent properties such as excellent toughness, adhesion and chemical resistance (Clayton 1988; Kornmann et al. 2002; Potter 1970; May and Tanaka 1973; Bouer 1979; Lee and Neville 1967; Mark and Gaylord 1969; Yee and Pearson 1986; Kinloch et al. 1983). However, they do not possess adequate thermal and mechanical properties to meet the requirements of high-performance structural products. Hence, modification of epoxy resins using suitable modifiers such as phosphorus, sulphone, silicone, polyhedral oligomeric silsesquioxanes (POSS) and nanoclay is mandatory. Demands for epoxy resins are extremely high because of their wide application as adhesives, coatings and as advanced composites in aerospace and electronic industries (Hergenrother et al. 2005, Choi et al. 2001). Incorporation of sulphone unit into the epoxy resin makes the resin become transparent, helps the resin withstand exposure to water, chemicals, increases the resistance of the resin to thermal oxidation and leads to easy processing.

Polyhedral oligomeric silsesquioxanes (POSS) reagents are emerging as a new chemical technology for the nano-reinforced organic–inorganic hybrids and the polymers incorporating POSS monomers are becoming the focus for many studies due to the simplicity in processing and the excellent mechanical properties, thermal stability and flame retardation (Li et al. 2001). POSS are a family of nanoscale inorganic cage structures containing a robust silicon/oxygen framework that are intermediate between silica (SiO₂) and silicone (R₂SiO). POSS can be easily

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incorporated into common plastics by means of copolymerization, blending or grafting. Incorporation of POSS into polymers like acrylics, styryls, epoxy and polyethylene has led to enhancements in thermal stability, mechanical properties, glass transition, degradation temperatures, oxygen permeability, reduced flammability and heat evolution as well as modified mechanical properties relative to conventional organic systems (Choi et al. 2001).

Although the organic–clay complexes have been recognized for a long time, the interest in studying these layered silicate materials as nanoscale-reinforcing agent for polymeric materials has only been developed recently. The introduction of as low as 1–5 wt. % of montmorillonite (MMT) into polymer matrix is well known to result in significant improvement in mechanical strength due to nanometric dimensions and high aspect ratio (Gacitua 2005). The nanoscopic phase distribution as well as synergism between polymer and the layered silicate results in additional properties, such as flame retardation, enhanced barrier properties and ablation resistance. Layered silicates are proven to possess excellent barrier resistance against movement of water or gas molecules and other chemicals due to their high aspect ratio. The present work focuses on a study of the thermal and electrical behaviour of TGDDS nanocomposites to find their suitability for use in high-performance applications.

Experimental

Materials

All chemicals were of reagent grade and were used without further purification. 4, 4'-diamino diphenyl methane (DDM) was obtained from Huntsman, USA. Epichlorohydrin and sodium hydroxide were obtained from SD Fine chemicals, India. Triphenylphosphine oxide, 4,4'-diaminodiphenylsulphone (DDS) were obtained from Alfa-Aaser, Germany. Aminopropyltrimethoxysilane (γ -APS), stannous chloride and sulphuric acid were obtained from Merck (Germany). Tetrahydrofuran (THF) and benzene were obtained from Sisco research laboratories, India. Nanoclay was obtained from Nanocor, USA. Hydrochloric acid was obtained from Hi-pure, India.

Synthesis of N,N'-tetraglycidyl diaminodiphenylsulphone (TGDDS)

Epichlorohydrin (6.25 mol) was taken in a 1-l three-necked round bottom flask provided with a mechanical stirrer, nitrogen atmosphere and a water condenser. This was heated to 50°C in an oil bath. Then 1.5 mol of DDS was added and stirred continuously for 4 h at about 50–55°C

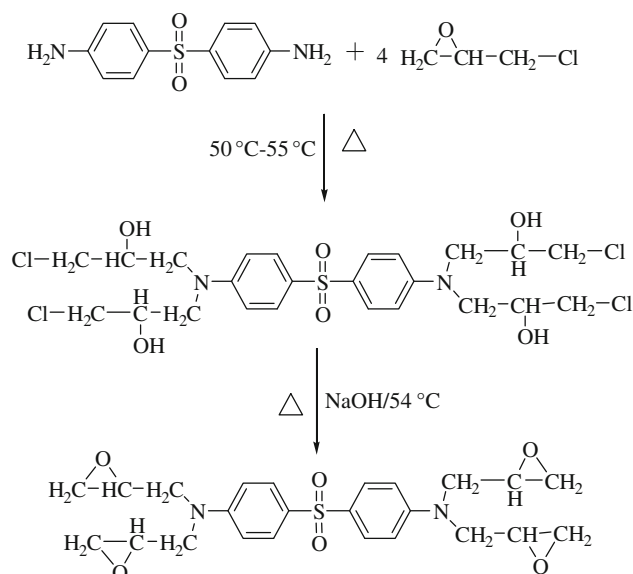
temperature under nitrogen atmosphere. Chlorohydrin, the intermediate product, was formed and the excess epichlorohydrin used was distilled off under vacuum. Then 2.84 mol of 40% NaOH solution was added drop-wise for 1 h at 54°C. The reaction was continued at this temperature for further period of 1 h. The resulting solution was extracted with chloroform. The organic layer was collected and concentrated at a reduced pressure to get the light brown coloured liquid epoxy product (Shih and Ma 1998; Jagdeesh and Shashikiran 2004). The synthesis of TGDDS is shown in Scheme 1.

Synthesis of phosphorus containing diamine

Synthesis of bis(3-aminophenyl)phenylphosphine oxide (BAPPO)

Triphenylphosphine oxide (0.1 M) was taken in a 500-ml round bottom flask equipped with stirrer, nitrogen atmosphere and 200 ml of 96% sulphuric acid was added to it. The reactant was dissolved and the reaction system was cooled to -5°C with an ice/salt bath. A solution (0.4 M) of fuming nitric acid in 100 ml of sulphuric acid was added drop wise over a period of 2 h. The reaction system was kept at room temperature for another 8 h. The reaction mixture was hydrolyzed over ice. After the melting of ice, the mixture was extracted with chloroform and washed with aqueous sodium bicarbonate solution until neutral pH. The solvent was removed. The solid product bis(3-nitrophenol)phenylphosphine oxide (BNPPO) was recrystallized from absolute ethanol.

A calculated amount BNPPO was taken in a 1,000-ml round bottom flask with 180 g of anhydrous powder tin (II)



Scheme 1 Synthesis of TGDDS

chloride. A solution of 200 ml fuming hydrochloric acid in 400 ml ethanol was introduced into the flask. The reaction mixture was stirred at room temperature for 5 h. The solution was concentrated and then neutralized by 25% of aqueous sodium hydroxide solution. The obtained solution was extracted with chloroform. The organic layer was collected and concentrated under a reduced pressure. The obtained solid was recrystallized from dichloromethane to give a pure product of bis(3-aminophenyl)phenylphosphine oxide (BAPPO). The synthesis of BAPPO (Y) is depicted in Scheme 2.

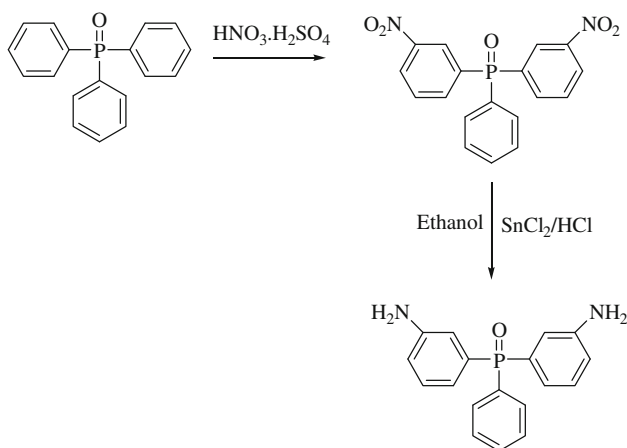
Synthesis of amine functionalized POSS (POSS-NH₂)

The synthesis of POSS-amine was carried out as follows: stoichiometric amount of POSS-triol (1.0 mol) dissolved in dry toluene was mixed with aminopropyl triethoxysilane (1.0 mol) in a 50-ml round bottomed flask and refluxed for 8 h at 90°C. The filtrate was then subjected to solvent evaporation to obtain the desired product, which was confirmed by FT-IR and NMR spectra, respectively. The synthesis is shown in the Scheme 3.

Fabrication of resin laminates

In order to study the properties of the epoxy resins, neat resin laminates were prepared by curing the six different synthesized tetraglycidyl epoxy resins by X and Y curing agents as shown in Table 1.

For the fabrication of nanocomposites, the N1 (Nanocor 1.30E) was dried at 24 h at 50°C under vacuum. The epoxy resin was mixed mechanically in a reaction vessel with the nanoclay at 50°C for 3 h. Then it was further mixed in an ultrasonic bath for 30 min to disperse the clay in the resin. Later, the mixture was cooled to room temperature in 30 min. The curing agent was then added. After mixing



Scheme 2 Synthesis of bis(3-aminophenyl)phenylphosphine oxide (BAPPO)

mechanically for 10 min, the mixture was degassed by a vacuum pump to remove the air bubbles and poured into moulds. The nanocomposites were cured for 3 h at 120°C and post-cured for 2 h at 200°C. After that the resin plaque was cooled to room temperature naturally. The nanoreinforcement N2 was mixed with the epoxy resin and then cured. Blends of epoxy, N2 and curing agent were molten at 100°C for 25 min and then poured into a mould coated with release agent on the inner walls of the mould that was preheated to 120°C. The curing cycle was 180°C for 3 h and 220°C for 2 h. After that the resin plaque was cooled to room temperature naturally, and it was cut into specimens of required dimensions, required for different testing and evaluation studies.

Test methods

The FT-IR spectra were recorded on a Perkin-Elmer 781 infrared spectrometer. ¹H NMR spectra was run on a Bruker 400 MHz spectrometer using CDCl₃ and DMSO as solvent and tetramethylsilane as internal standard proton decouple. Thermo gravimetric analysis of the polymeric matrices was carried out in TGA-Thermal Analyst Perkin Elmer (TA instrument USA) at a heating of 10°C per minute in an inert atmosphere to determine thermal degradation temperature and percentage weight loss. Differential scanning calorimeter NETZSCH DSC 200PC (TA instrument USA) was used to determine the glass transition temperature of the polymer matrices with a heating rate of 10°C/min. Dielectric strength was determined as per ASTM D149 in a dielectric strength tester and expressed in kV/mm. Arc resistance was measured as per ASTM D495 on a test specimen of thickness 3.17 mm. In order to assess the performance of the insulating material, the resistance offered by the polymeric material to electrical current along a 1-cm² surface or through the thickness was determined using a resistivity meter as per ASTM D257. In the comparative tracking index test, the specimen was exposed to either 50 or 100 drops of an aqueous contaminant solution of ammonium chloride and a wetting agent that produced tracking on the surface of the specimen. It was measured as per ASTM D3638.

Results and discussion

Spectroscopy analysis

FT-IR spectroscopy analysis

The FT-IR spectrum of TGDDS is shown in Fig. 1. The peaks corresponding to –S=O and –CH₂ group of TGDDS appear at 1,362, 1,184 and 2,900 cm⁻¹, respectively.

Scheme 3 Synthesis of amine functionalized POSS (POSS-NH₂)

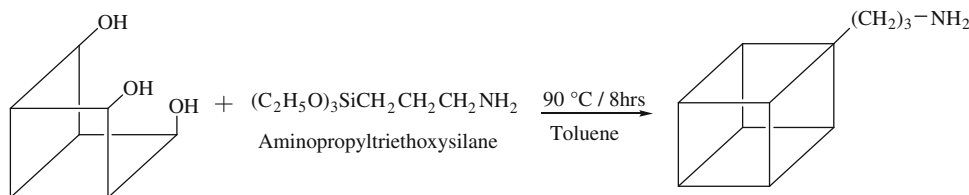


Table 1 Fabrication of neat resin laminates

Type of epoxy	Matrix name	Nanoreinforcement	Curing agent
TGDDS	BX	–	X
	BXN1	N1	X
	BXN2	N2	X
	BY	–	Y
	BYN1	N1	Y
	BYN2	N2	Y

Furthermore, absorption peaks which appear at 900–910 cm⁻¹ confirmed the presence of epoxy group in the prepared resin.

The FT-IR spectrum of bis(3-aminophenyl)phenylphosphine oxide (BAPPO) is shown in Fig. 2. The characteristic peaks that appear at 3,499 and 3,393 cm⁻¹ confirm the presence Ph-NH₂ group. The absorption band for P-O-Ph stretching appears at 1,093 cm⁻¹. The peak appearing at 1,277 cm⁻¹ confirms the presence of P=O group. Other FT-IR absorption band at 1,498 cm⁻¹ is attributed to the P-Ph stretching.

The FT-IR spectrum of POSS-NH₂ is depicted in Fig. 3.

The peaks corresponding to -NH₂ and -CH₂ group of POSS-NH₂ appear at 3,500 and 2,900 cm⁻¹, respectively. Furthermore, absorption peaks that appear at 1,200–1,300 and 1,500 cm⁻¹ confirm the presence of Si-O-Si linkage and -Si-CH₂, respectively.

¹H and ¹³C NMR spectrum analysis

The ¹H NMR spectrum of TGDDS is shown in Fig. 4. The signal at 6.5–7.5 ppm maybe due to the aromatic protons.

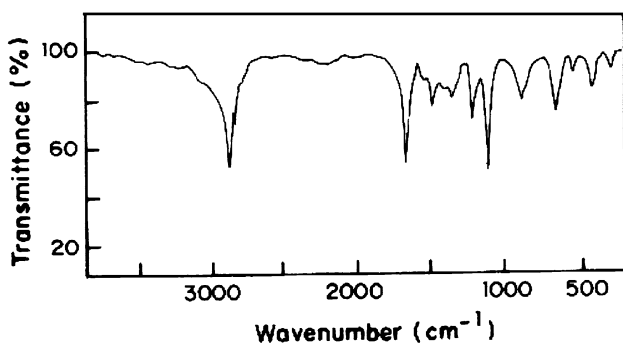


Fig. 1 FT-IR spectra of TGDDS

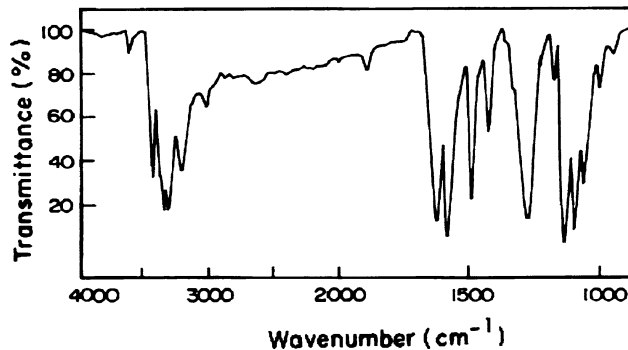


Fig. 2 FT-IR spectra of BAPPO

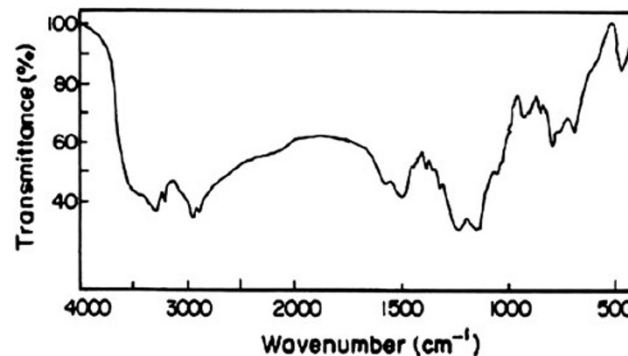


Fig. 3 FT-IR spectra of POSS-amine

The remaining oxirane and methylene protons adjacent to oxirane appear at 3.2–4.5 ppm.

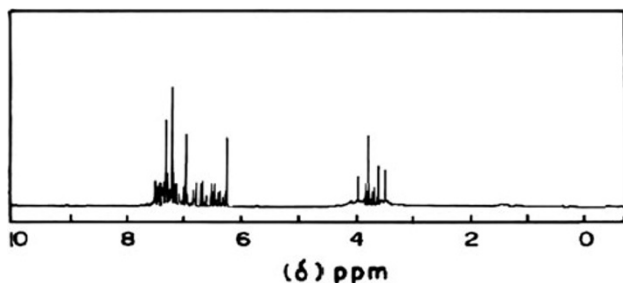
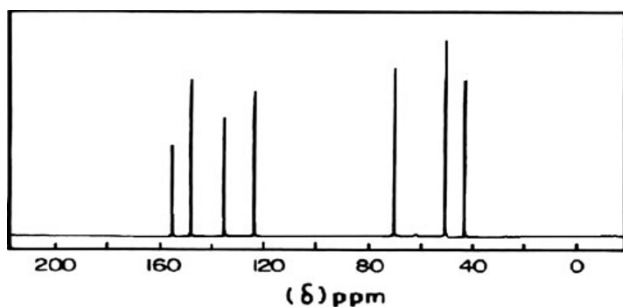
The ¹³C NMR spectrum of TGDDS is shown in Fig. 5.

The signal at 50 ppm may be due to the presence of -CH- of epoxy group. The signal which appears at 44 ppm may be due to the -OCH₂- of epoxy group. The signal at about 70 ppm may be due to the presence of -N-CH₂- carbons. The remaining signal that appears at around 120–140 ppm may be due to aromatic carbons.

The ¹H NMR spectrum of BAPPO is shown in Fig. 6. The resonance signal at 3.45 ppm confirms the presence of -NH₂ group. The signal at 6.62–7.13 ppm may be due to the aromatic amine proton (C₆H₄-NH₂). The remaining signal that appears at 7.4–7.9 ppm is due to aromatic protons.

The ¹³C NMR spectrum of BAPPO is shown in Fig. 7.

The signal at 40 ppm is due to the presence of -C-P group. The signal at about 30 ppm may be due to the -CH-NH₂- of group. The remaining signal appearing at

Fig. 4 ¹H-NMR spectra of TGDDSFig. 5 ¹³C-NMR spectra of TGDDS

around 120–150 ppm is due to aromatic carbons. The single signal in the ³¹P spectra at around 30 ppm as seen in Fig. 8 confirms the structure of BAPPO.

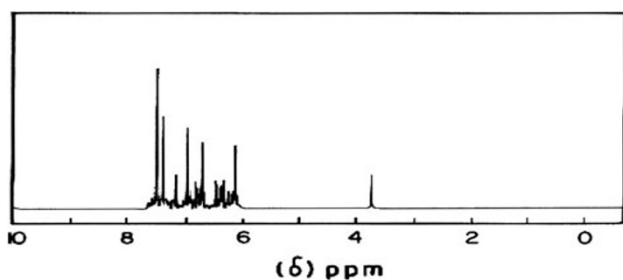
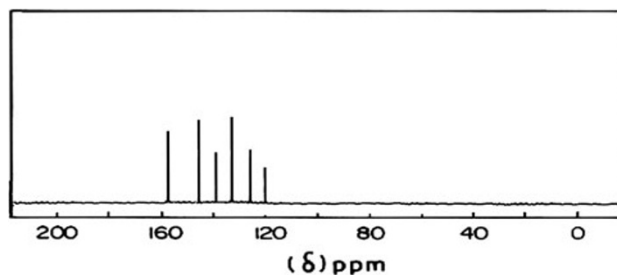
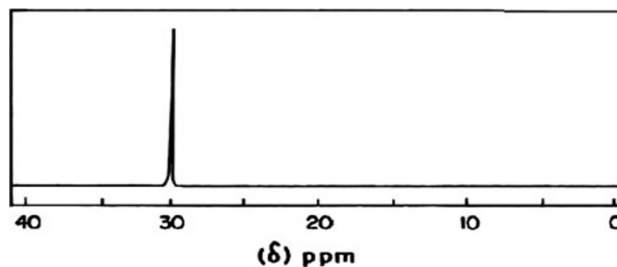
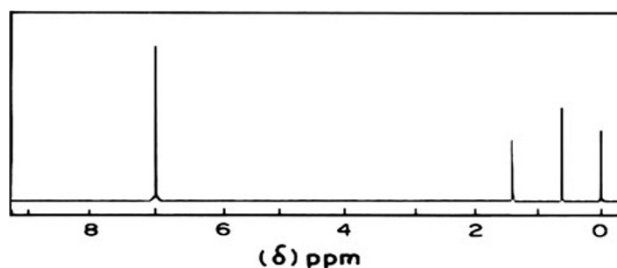
The ¹H NMR spectrum of POSS amine is shown in Fig. 9. The signal at 0.64 ppm is due to the Si-CH₂ protons. The signal at 1.4 ppm corresponds to C-NH₂ protons.

Discussion on thermal stability

Thermogravimetric analysis (TGA)

The thermal analyses of the resins were studied by thermogravimetric analysis and from the data the thermal degradation temperature of the resins could be found. The char yield and LOI of the resins were found by TGA. The data obtained from the TGA studies is shown in Table 2 and the Figs. 10, 11.

It was observed that the TGDDS systems performed slightly better than the TGDDM systems. The initial

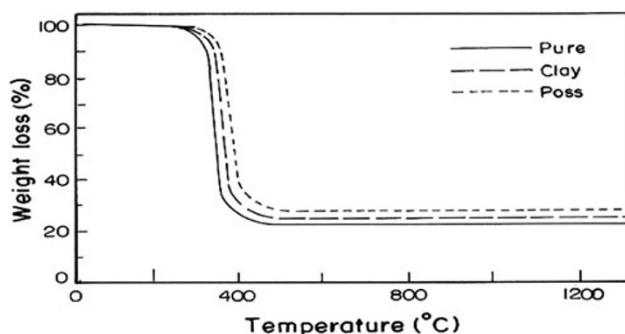
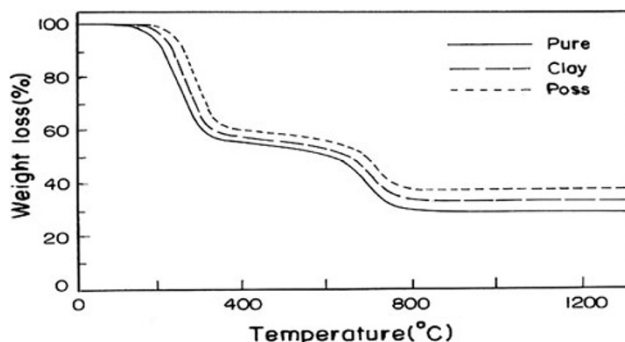
Fig. 6 ¹H-NMR spectra of BAPPOFig. 7 ¹³C-NMR spectra of BAPPOFig. 8 ³¹P-NMR spectra of BAPPOFig. 9 ¹H-NMR spectra of POSS-amine

decomposition temperature, char yield and LOI were higher for the TGDDS systems as seen from the Table 2.

For example, the initial decomposition temperature of BX system was enhanced to 295°C (Fig. 10). The Y cured systems (BY, BYN1 and BYN2) showed a similar double decomposition pattern. In contrast to this observation, the X-cured resin systems (BX, BXN1 and BXN2) showed a single decomposition pattern. The initial degradation temperature of the Y-cured system was lower than that of the X-cured systems, which was due to the decomposition of P-O-C bond at lower temperature. It was interesting to note that the char yield and LOI of the tetraglycidyl systems cured with Y were found to be higher than those of X-cured systems. For example as seen from Table 2, the char yield of BX was 22% and LOI was 27, whereas the char yield of BY was 30% (Fig. 11) and LOI was 31. The higher char yield observed for Y-cured systems may be due to the formation of a protective char layer formed as a result of the degradation that occurred at a lower temperature, thereby protecting the underlying matrix from further degradation.

Table 2 Data of thermogravimetric analysis (TGA)

Resin System	Initial decomposition temperature (°C)	Char yield (%)	LOI
BX	295	22	27
BY	195	30	31
BXN1	310	25	29
BYN1	220	33	33
BXN2	330	28	30
BYN2	235	37	34

**Fig. 10** TGA of BX based systems**Fig. 11** TGA of BY based systems

The addition of nanoreinforcements produced a significant improvement on the thermal stability, char yield and LOI of all tetra functional epoxy resin systems. For example the initial decomposition temperature of BX system was 295°C, while the initial decomposition temperatures of BXN1 and BXN2 systems were significantly improved to 310 and 330°C, respectively, as seen from the Table 2 and Fig. 10. Similarly the char yield for the BX system was 22% and that for the BXN1 and BXN2 systems was 25 and 28%, respectively, leading to an enhanced LOI values. Incorporation of POSS-amine significantly enhanced the thermal stability of the epoxy resin due to the formation of an inert silica layer on the surface of materials when decomposition takes place and prevented further

oxidation of the inner part of the epoxy matrices. POSS molecules having silica like Si–O–Si structure led to higher inorganic components in the cured materials, resulting in higher char yields (Zhang et al. 2007). This Si–O–Si linkage prevented the underlying polymeric matrix from further degradation. On the other hand, the clay nanolayers acted as barriers by preventing the evolution of volatile degradation products from the epoxy matrices (Leszczyńska et al. 2005). Between the two nanoreinforcements, the best results of thermal stability and flame retardancy were given by POSS amine-reinforced system, namely BYN2.

Discussion on electrical properties

The results of the various electrical studies are shown in Table 3.

As seen from the Table 3, the Y-cured systems were found to show better electrical properties than the X-cured systems. For example, the dielectric properties of the X-cured system BX was 14.1 kV/mm while that of the Y-cured system BY was 15.1 kV/mm. This could be due to the presence of rigid aromatic groups of Y which might have enhanced the hydrophobic behaviour and may also be due to the formation of insulative char layer that contributed to better electrical properties. The incorporation of nanoreinforcements (nanoclay and POSS-amine) was found to enhance the electrical properties significantly. The nanoreinforced epoxy composites yielded breakdown strength values as high as that of the base resin indicating their insulative behaviour required for electrical application. For example surface resistivity of BX system was 3.02×10^{12} Ohm, whereas for the system BXN1 and BXN2 the surface resistivity was enhanced to 5.16×10^{12} and 7.24×10^{12} Ohm, respectively. Similar observation was noticed for the dielectric strength and arc resistance measurements of nanocomposites. This could possibly be due to the presence of the siloxane linkages present in the nanoreinforcements that may be responsible for the enhanced insulative properties.

Conclusion

The present work deals with the development and characterization of high-functionality epoxy resin, namely TGDDs. These epoxies were cured with DDM and BAP-PO, respectively, with and without the incorporation of nanoclay (Nanomer 1.30 E) and nanoreinforcement (POSS amine) to get matrix materials to be utilized for high-performance applications. The developed materials were characterized by spectral studies to ascertain their structures. The polymerization of these resins was carried out in

Table 3 Electrical properties of various systems

Systems	Dielectric strength (kV/mm)	Surface resistivity (Ohm)	Volume resistivity (Ohm)	Arc resistance (s)	Comparative tracking index (Volts)
BX	14.1	3.02×10^{12}	$>10^{14}$	80	>600
BY	15.1	4.22×10^{12}	$>10^{14}$	88	>600
BX N1	16.3	5.16×10^{12}	$>10^{14}$	89	>600
BY N1	17.4	6.35×10^{12}	$>10^{14}$	100	>600
BX N2	18.2	7.24×10^{12}	$>10^{14}$	99	>600
BY N2	19.4	8.18×10^{12}	$>10^{14}$	108	>600

the presence and absence of nanoclay and nanoreinforcement to get nanocomposites with improved properties ideally suited for advanced engineering applications.

The thermal studies of these materials were carried out by means of TGA and the results obtained from this study clearly indicate that BAPPO (Y) cured tetra epoxies, irrespective of nanoclay and nanoreinforcement showed better char yield and LOI values in spite of their degradation at a lower temperature. The incorporation of nanoclay and nanoreinforcement to both the epoxy improved the IDT, char yield and LOI values. The Y-cured systems were found to show better electrical properties than that of X-cured systems. This could be due to the presence of rigid aromatic groups which enhanced the hydrophobic behaviour and also due to the formation of insulative char layer that contributed to improved electrical properties. The addition of nanoreinforcements (nanoclay and POSS-amine) was found to significantly enhance the electrical properties. For example the arc resistance value of the neat system BX was found to be 80 s, while for the nanocomposites BXN1 and BXN2 the values were enhanced to 89 and 99 s, respectively. This could be attributed to the presence of the siloxane linkages present in the nanoreinforcements that enhanced the insulative properties.

From the data obtained from different studies, it can be concluded that the novel organic–inorganic nano hybrid composites synthesized in the present study, having improved mechanical, thermal properties being self extinguishable, heat resistant at the same time with excellent dielectric properties can very well be used for automotive, electronics and advanced aerospace applications for improved performance and longevity than the materials that are currently in use.

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