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Cardanol-based benzoxazine-terminated graphene oxide-reinforced fluorinated benzoxazine hybrid composites for low K applications

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ABSTRACT

A novel fluorinated benzoxazine was prepared from bisphenol-AF, aniline and paraformaldehyde and was characterized by ¹H NMR, ¹⁹F NMR and FTIR. A benzoxazine-functionalized silane-coupling agent was synthesized using renewable resource cardanol, paraformaldehyde and aminopropyltriethoxysilane (APTES). Cardanol benzoxazine-functionalized graphene oxide (GO-C-aps)-reinforced fluorinated benzoxazine (BAF-a) hybrid composites poly(GO-BAF-a) have been developed through the facile one step copolymerization route. XRD and SEM analyses were used to ascertain the morphology of the composite materials developed. Data obtained from thermal, dielectric and surface studies infer that the hybrid cardanol-based benzoxazine composites possess the enhanced thermal stability, improved hydrophobic behaviour with lower value of dielectric constant according to the weight percentage concentration of functionalized graphene oxide than those of neat benzoxazine matrix. The hybrid cardanol benzoxazine composites developed in the present work can find application in the form of coatings, sealants and adhesives for interlayer low k dielectric insulation applications in microelectronics industries.

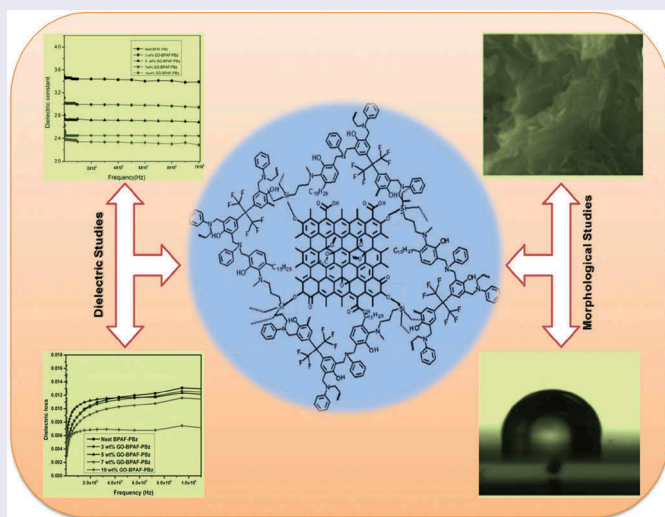
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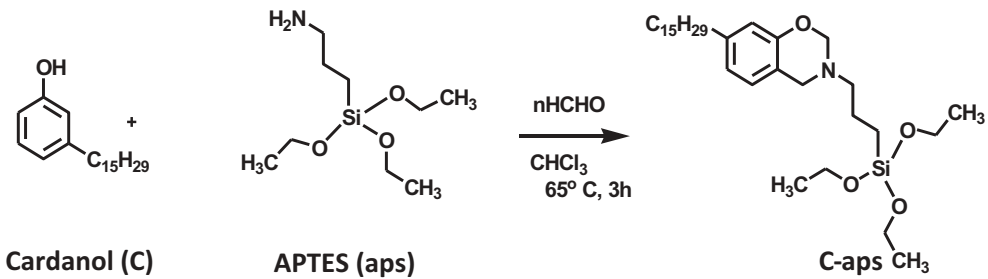
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Introduction

Ever since the invention of polybenzoxazines, they attracted more attention of researchers [1] due to their unique range of properties such as good thermal stability, degradation temperature, char yield, low water intake and low dielectric constant [2–5]. Due to these properties and other desirable advantages, benzoxazines found wide range of applications including the design of dielectric materials. The development of future high performance printed circuit boards requires materials with low thermal expansion, high thermal stability and dielectric behaviour. Since the signal propagation delay time and the signal propagation loss of integrated circuits (ICs) are proportional to the square root of dielectric constant, a material with dielectric constant will reduce both the delay time and propagation loss. Dielectric constant materials ($k < 2.0$) have the advantage of facilitating the production of high-performance IC devices with decreasing feature size of the chip [6]. Moreover, the proposed low k in prospective interlayer dielectrics must also satisfy a variety of requirements such as good thermal stability, chemical inertness, low moisture uptake, good adhesion to different substrates including semiconductors and metals [7,8].

An inorganic reinforcements such as mesoporous materials like MCM-41, SBA-15 and carbon-based material like GO and silica-based hybrid material like POSS have been used to attain the above requirements [9–15]. Synthesis of fluorinated benzoxazines from fluorine-containing monomers is also used to reduce the value of dielectric constant of the materials [16–19]. Earlier our research group have reported that the introduction of amine-functionalized mesoporous MCM-41 into the polyimide system substantially reduced the value of dielectric constant upto 2.21. [20] Graphene oxide (GO) has been used to develop polymer nanocomposites with substantially low k values [21–25]. Moreover, polymer composites containing carbon nanotubes (CNT) and reduced graphene oxides (rGO) show higher value of dielectric constant due to the conducting nature of CNT and rGO [26–30] whereas the GO incorporated polyimide composites exhibit the low value of dielectric constant of 2.1 [31] due to the insulating behaviour of GO.

Due to the above-mentioned desirable properties and considerable decrease in dielectric constant values by the incorporation of fluorine moiety in benzoxazines backbone and reinforcement with GO, the synthesis of polybenzoxazines received much focus compared to other hybrid polymers. Benzoxazine monomers have been synthesized by the condensation of phenols with primary amine and formaldehyde using Mannich mechanism and subsequently polymerized through ring opening and addition polymerization by thermal treatment in the absence of any catalyst with the release of no by-product. The performance of polybenzoxazines can be improved by reinforcing hydroxyl-terminated fillers such as SBA-15, MCM-41, POSS, GO, reduced GO and CNT. These fillers can be coupled with polymerizable alkenyl and methoxysilane groups like 3-aminopropyltrimethoxysilane (3-APTMS) or 3-aminopropyltriethoxysilane (3-APTES). These benzoxazine-terminated reinforcements can be copolymerized with polybenzoxazine matrix to form crosslinked networks with improved properties like high thermal stability, good water repellency and appreciably low dielectric properties. However, the reported works with the above contents are utilized only with conventional phenol and its derivatives and no significant approach has been yet made with bio-based derivatives.



Scheme 1. Synthesis of C-aps.

In the present work, an attempt has been to develop a novel hybrid cardanol-benzoxazine composites using GO modified with cardanol-based benzoxazine and fluorinated benzoxazine to obtain enhanced hydrophobic behaviour, high thermal stability and low dielectric constant to utilize them for high performance microelectronic applications. The hybrid composites developed are characterized by modern analytical methods and the data obtained from different studies are discussed and reported.

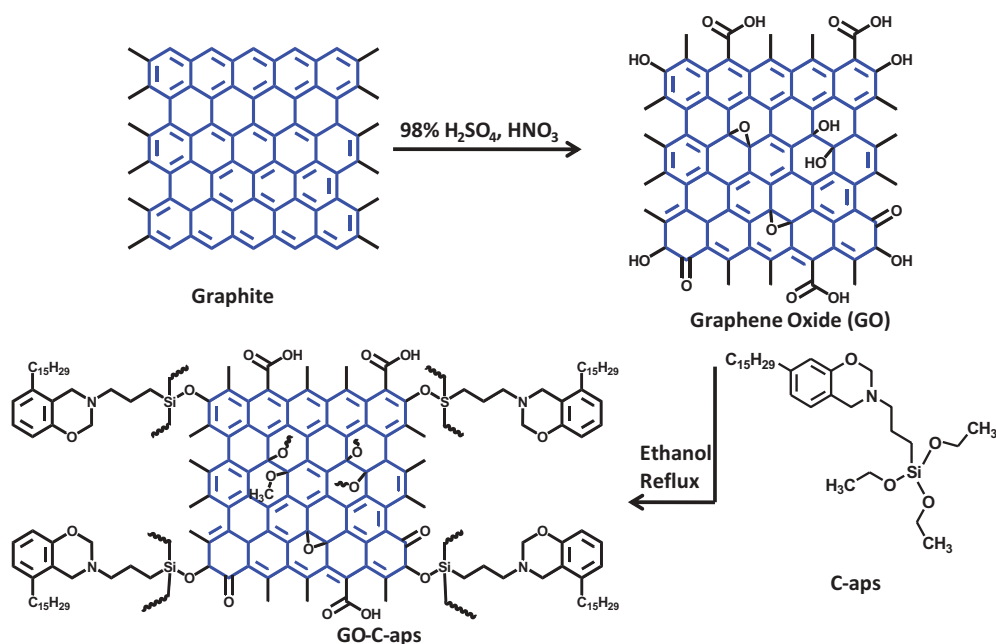
Experimental

Functionalization of cardanol with aminopropyltriethoxysilane (C-aps)

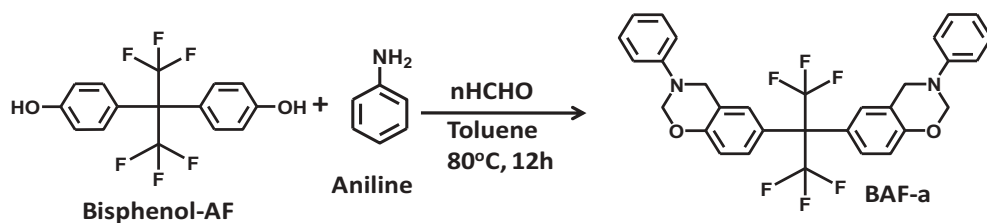
To a stirred solution of paraformaldehyde (0.06 mol) in chloroform (30 ml), calcium hydride was added under nitrogen atmosphere and the temperature was raised to 65°C and then 3-aminopropyltriethoxysilane (0.03 mol) was added to the reaction mixture with vigorous stirring followed by the addition of cardanol (0.03 mol) and stirred for 6 h at the same temperature. After that the product obtained was filtered and the filtrate was concentrated to get a transparent brownish viscous liquid with 90% yield (Scheme 1)

Preparation of GO

GO was prepared from natural graphite by the process of modified Hummers method using a mixture of sodium nitrate, sulfuric acid, and potassium permanganate. To a suspended solution of natural graphite (10 g) in concentrated sulfuric acid in an ice-cold condition, sodium nitrate (5 g) was added gradually and stirred for 10 min. Followed by, potassium permanganate was added slowly to the reaction mixture at the same temperature. Then, the solution was oxidized by thermal process, and the temperature was gradually raised and maintained at about 40°C for 24 h. After that, distilled water was added slowly to the reaction mixture under the controlled temperature of about below 100°C. Subsequently, 30% hydrogen peroxide and excess amount of distilled water were added for the termination of reaction and the obtained precipitate was centrifuged and washed several times with water until the pH of about 7 and dried in a vacuum oven at 70°C (Scheme 2) [32,33].



Scheme 2. Synthesis of GO-C-aps.



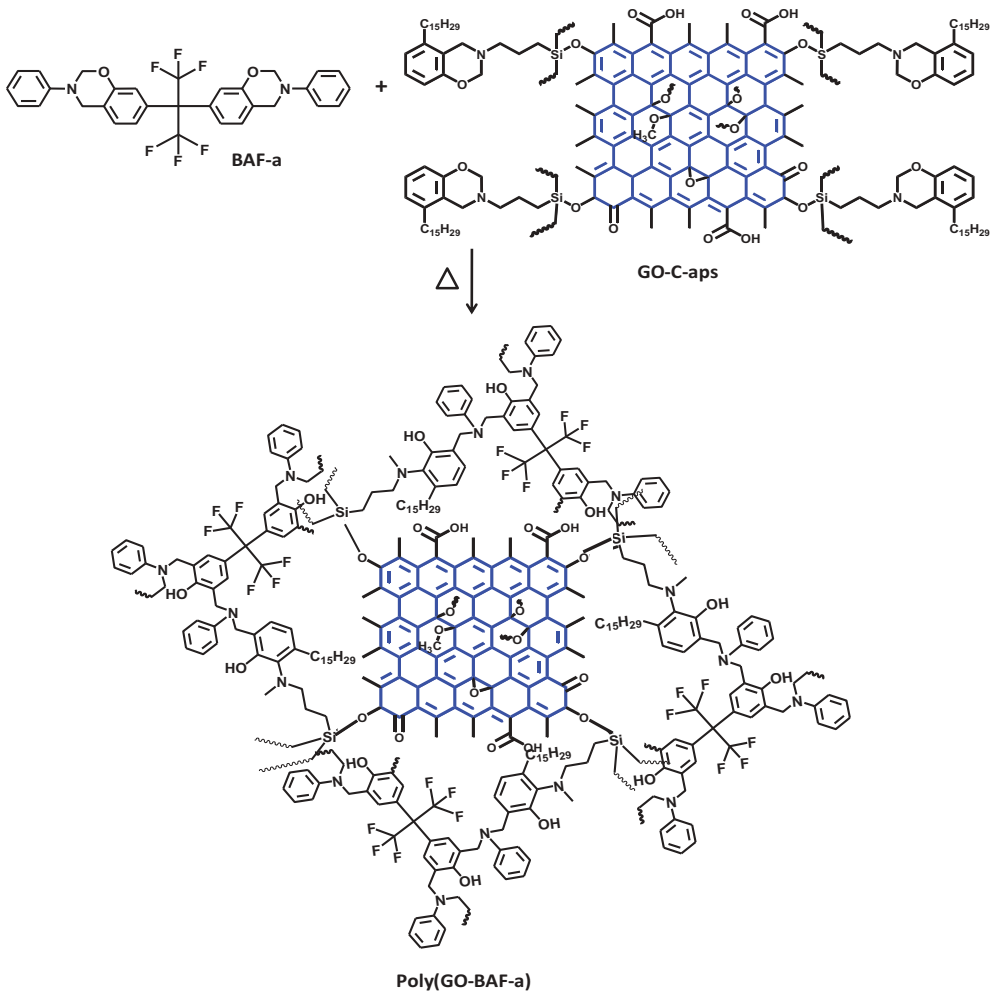
Scheme 3. Synthesis of BAF-a.

Preparation of benzoxazine-functionalized GO-C-aps

GO-C-aps was obtained by refluxing 1.0 g of GO and 4.0 g of C-aps in ethanol (100 ml) for 24 h. Then the product obtained was cooled and filtered, washed with ethanol and dried at 75°C under vacuum (Scheme 2).

Synthesis of bisphenol AF-based benzoxazine (BAF-a)

To a solution of aniline (2.76 g, 0.029 mol) in toluene, paraformaldehyde (1.83 g, 0.060 mol) was added and stirred for 30 min at 0°C. Subsequently, 5 g of bisphenol-AF was added to the reaction mixture and stirred at 80°C for 12 h. After that the reaction was monitored by TLC for its completion, then the reaction product was extracted with ethyl acetate and washed with 2N NaOH, water, brine solution and concentrated the organic layer to obtain yellow coloured solid with 95% yield (Scheme 3).



Scheme 4. Preparation of poly(GO-BAF-a) composites.

Preparation of neat polybenzoxazine poly(BAF-a) matrix

The monomer of bisphenol-F-based benzoxazine(BAF-a) was dissolved in tetrahydrofuran (THF) and stirred for 2 h to get a clear solution. After that the solution was transferred to glass mould and heated at 100°C for overnight to evaporate the solvent and then cured stepwise at 120, 140, 160, 180, 200 and 220°C for 1 h each to obtain yellowish brown film (Scheme 4).

Preparation of GO-C-aps reinforced (3, 5, 7 and 10 wt %) poly(GO-BAF-a) composites

The varying weight percentages of GO-C-aps (3, 5, 7 and 10 wt %) were separately added to a solution of BAF-a (2 g) in 10 ml THF and stirred for 30 min at ambient temperature. The solutions were poured into respective glass moulds and heated at 100°C for

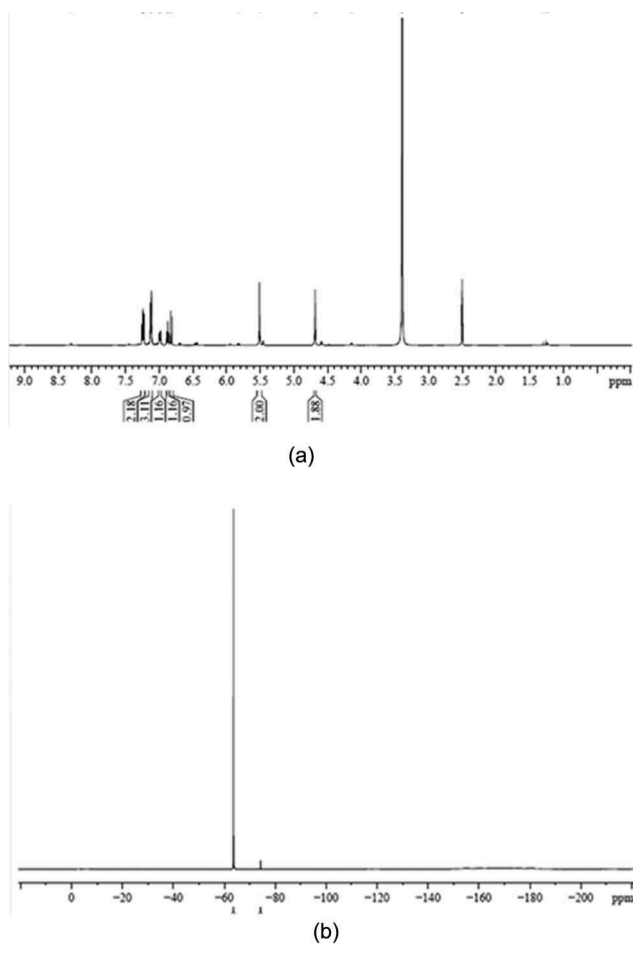


Figure 1. (a) ^1H NMR spectrum of BAF-a. (b) ^{19}F NMR spectrum of BAF-a.

overnight to evaporate the solvent and then cured stepwise at 120, 140, 160, 180, 200, 220 and 240°C for 1 h each to obtain dark brown hybrid composite films (Scheme 4).

Results and discussion

Spectral analysis

The ^1H NMR (Figure 1(a)) of monomer BAF-a delivers a series of proton shift, which are attributed to the presence of symmetric protons, 7.25–6.80 ppm (m, 8H, Ar), 5.10 ppm (s, 2H, O-CH₂-N), 4.68 ppm (s, 2H, Ar-CH₂-N). The presence of fluorine moiety has been confirmed through the ^{19}F NMR (500 MHz, DMSO) (Figure 1(b)) in which the peak at 63.60 ppm corresponds to the 6F of CF₃-C-CF₃. Figure 1S presents the FTIR spectra of both monomer BAF-a and silane coupling agent C-aps. The peak appeared at 1107 cm⁻¹ in C-aps spectrum, represents to the Si-O-C stretching vibration. The appearance of peak at 956 cm⁻¹ infers the stretching vibration of N-C-O group present in the oxazine ring.

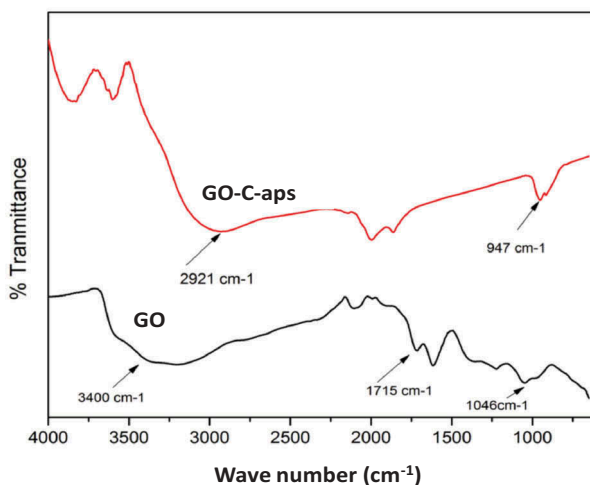


Figure 2. FTIR spectra of GO and GO-C-aps.

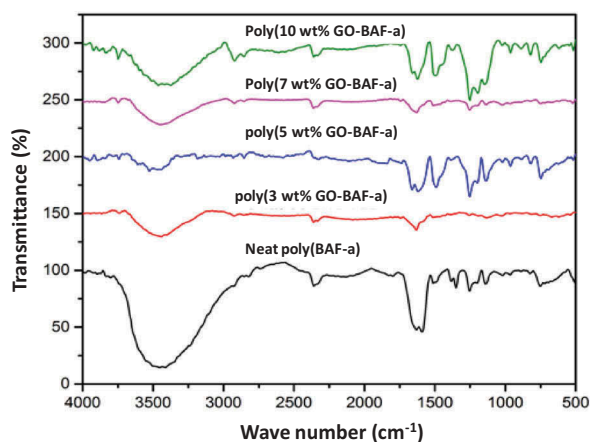


Figure 3. FTIR spectra of BAF-a and poly(GO-BAF-a) composites.

The broad peak appeared at 2926 cm^{-1} indicates the presence of alkyl side chain of cardanol. However, the peaks appeared at 2908 , 2853 and 820 cm^{-1} are assigned to the symmetric and asymmetric stretching C-H bonds, and para-substituted benzene rings, respectively of the BAF-a spectrum (Figure 1S). The associated bands to N-C-O and C-O-C of benzoxazine ring can be seen at 922 and 1242 cm^{-1} , respectively [34–36].

Figure 2 details about the FTIR spectra of prepared GO and GO-C-aps. The peaks appeared at 3400 , 1715 , and 1046 cm^{-1} indicate the presence of the hydroxyl, carbonyl, and C-O stretching frequencies of GO, respectively. The FT-IR spectrum of GO-C-aps shows a peak at 2921 cm^{-1} , which represents the alkyl side chain of cardanol. The peak appeared at 947 and 1233 cm^{-1} , corresponds to vibration of N-C-O and C-O-C respectively. Scheme 2 shows the schematic representation of formation of poly(GO-BAF-a)

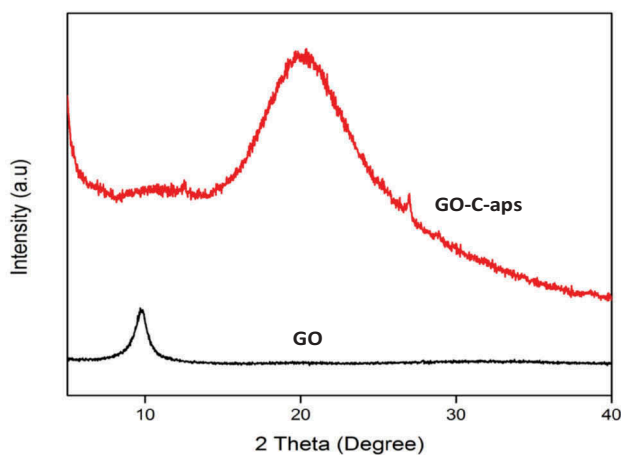


Figure 4. XRD pattern of GO and GO-C-aps.

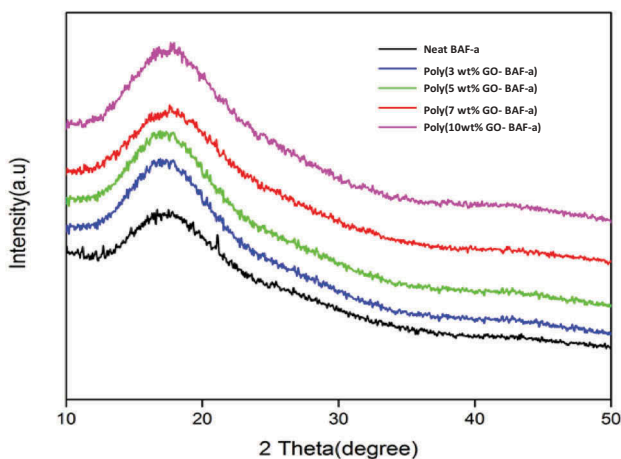


Figure 5. XRD pattern of neat poly(BAF-a) and poly(GO-BAF-a) composites.

composites. The formation has been confirmed through the disappearance of bands related to N-C-O bond at 947 cm^{-1} (Figure 3). The ring opening of benzoxazines moiety leads to the formation of hybrid composite GO-BAF-a

Morphological studies of BAF-a and poly(GO-BAF-a) films

Figure 4 illustrates the XRD patterns of GO and GO-C-aps, in which the peak appeared at 9.7° (GO) and the disappearance of peak at 26.5° infer that the graphite has been oxidized and completely converted into GO. The diffraction patterns obtained for both GO and FGO (Figure 4) illustrate a sharp reflection at 9.7° and confirm the existence of the crystalline nature of the synthesized GO and GO-C-aps. However, the peak intensity gets lowered for GO-C-aps, which may be due to the presence of organic moiety on the surfaces

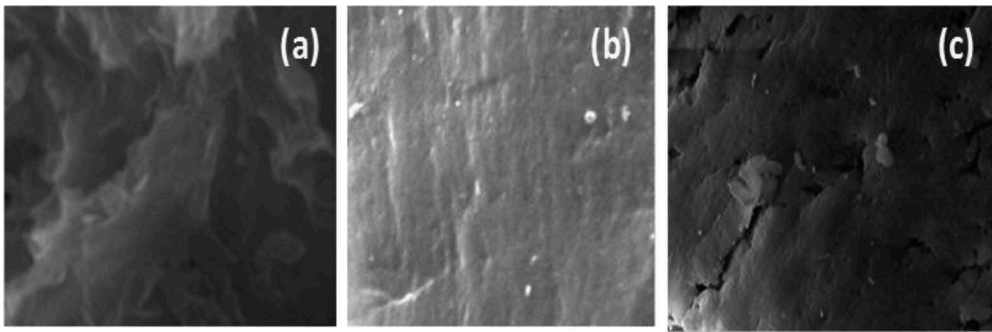


Figure 6. SEM images of (a) GO, (b) neat poly(BAF-a) and (c) 10 wt% poly(GO-BAF-a) composites

of GO. Further, the broad peak from 12° to 24° (GO-C-aps) corresponds to the presence of benzoxazines moiety. XRD diffractograms shown in Figure 5 that the material is completely amorphous and there is no evidence for crystalline/aggregates of GO in polymer matrix. The absence of aggregation may be due to the complete exfoliation of GO. It can be inferred that as the percentage weight of GO-C-aps increases, the intensity of composite pattern also increases, which indicates the enhancement of interlayer distance. Moreover, the existence of small voids as the interlayer distance increases which can be filled by air or vacuum, which contributes to reduction in the values of dielectric constant.

The surface morphologies of GO, neat BAF-a and poly(GO-BAF-a) composites were obtained using scanning electron microscope and the images are presented in Figure 6. The wrinkle sheets indicate the formation of complete oxidation of graphite, which in turn forms GOs. The microstructure of neat BAF-a shows the smooth, dense morphology without voids, whereas, 10 wt% poly(GO-BAF-a) composites shows a crack penetrated voids happened because of GO reinforcement, which clearly shows the existence of GO sheets in the polybenzoxazine system.

Thermal studies of BAF-a and poly(GO-BAF-a) films

Thermal curing character of BAF-a monomer was examined by differential scanning calorimetry (DSC). Thermal polymerization of benzoxazine monomer taking place by heating benzoxazine and then the ring gets opened by the cleavage of C-O bond; there by the benzoxazine molecule is transformed from a closed-ring structure to a linear open chain structure. Figure 2S shows the typical DSC graph of BAF-a monomer which shows the polymerization was initiated at 197°C , a peak maxima (Curing temperature) was found at 218°C and the polymerization was completed at 279°C , which confirms the occurrence of exothermic polymerization reaction. From DSC analysis, it was also observed that the value of an apparent enthalpy change (ΔH) of 277.4 J/g during curing.

The thermal stability of neat polybenzoxazines (BAF-a), and GO/polybenzoxazine hybrid composites poly(GO-BAF-a) were analysed using thermogravimetric analysis (TGA) (Figure 7). Thermal stability of the materials is one of the most important criteria considered in device fabrication. In the present work, TGA technique is used to evaluate the thermal behaviour of poly(GO-BAF-a) hybrid composite materials and the quantity

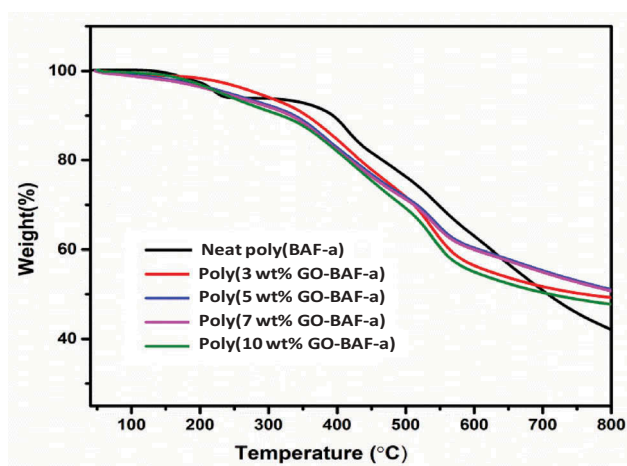


Figure 7. TGA spectra of neat poly(BAF-a) and poly(GO-BAF-a) composites.

Table 1. Thermal and dielectric properties of neat poly(BAF-a) and poly(GO-BAF-a) composites.

Sample	T_{10} (°C)	Char Yield (Yc)% at 800°C	LOI at 800°C	Dielectric Constant (K) at 1MHz	Dielectric loss at 1MHz	Water contact angle values (°)
Poly(BAF-a)	393.8	42.06	34.32	3.38	0.0130	96.9
Poly(3 wt % GO-BAF-a)	355.5	49.26	37.20	2.94	0.0126	100.5
Poly(5 wt % GO-BAF-a)	337.6	51.04	39.92	2.68	0.0123	110.7
Poly(7 wt % GO-BAF-a)	332.4	50.75	37.80	2.44	0.0115	116.9
Poly(10 wt % GO-BAF-a)	318.6	47.75	36.60	2.28	0.0073	125.4

of removal of organic substances which can be determined by weight loss, because the covalent bond exist between the graphene moiety and its organic substituent are thermally stripped off in the higher temperature. [15] Moreover in the present system, the presence of epoxy, hydroxyl and carboxyl functional groups present in GO expected to undergo cleavage and leads to decomposition at lower temperature. To compensate the thermal stability of GO and to strengthen the less stable aliphatic C-H bond, the introduction of bisphenol-AF skeleton which is having strong C-F bond was introduced. The introduction of fluorine atoms not only increases the thermal stability but also contributes to reduce the value of dielectric constant, which is a very important factor in designing interlayer dielectric materials. [37]

In the present study, it was observed that the neat BAF-a exhibits marginally higher thermal stability and lower char yield than those of the poly(GO-BAF-a) hybrid composites (Table 1). The increase in weight percentage of GO also increases the char yield of the composites which in turn contributes to an improved the thermal stability and to reduce the flammability. It was also ascertained that the reinforcement of GO with polybenzoxazine matrix restricts the chain mobility of polymer matrix near the GO surfaces. [38] The results obtained from TGA, it has been inferred that the incorporation of fluorine moiety and GO into polybenzoxazine matrix is considered as versatile method in designing high performance composites for inter layer dielectric (ILD) applications.

Thermogravimetric analysis provides the valuable information about flame retardant behaviour, in addition to thermal stability. The Limiting Oxygen Index (LOI) value can be calculated using the value of char yield from TGA and applying it in Van Krevelen's equation. [39]

$$LOI = 17.5 + 0.4 CR - \text{Van Krevelen's equation.}$$

where CR is the percentage char yield of polymer remaining at 800°C. In general, the polymer with more than 21 LOI value is considered as a good flame retardant material, and it is experimentally proved that the materials with highest LOI values possess the superior flame retardant property. The LOI values of the neat and hybrid composites were calculated from their respective char yield. These values are found to be higher than that of the conventional benzoxazines, which suggest that the hybrid composites developed in the present work are expected to function as better flame retardant behaviour. The LOI values calculated are presented in Table 1. The incorporation of fluorine atoms into the benzoxazine structure was able to achieve materials with high thermal stability as the C-F bond is stronger than that of the C-H bond and also contributes to higher char yield for all the poly(GO-BAF-a) composites.

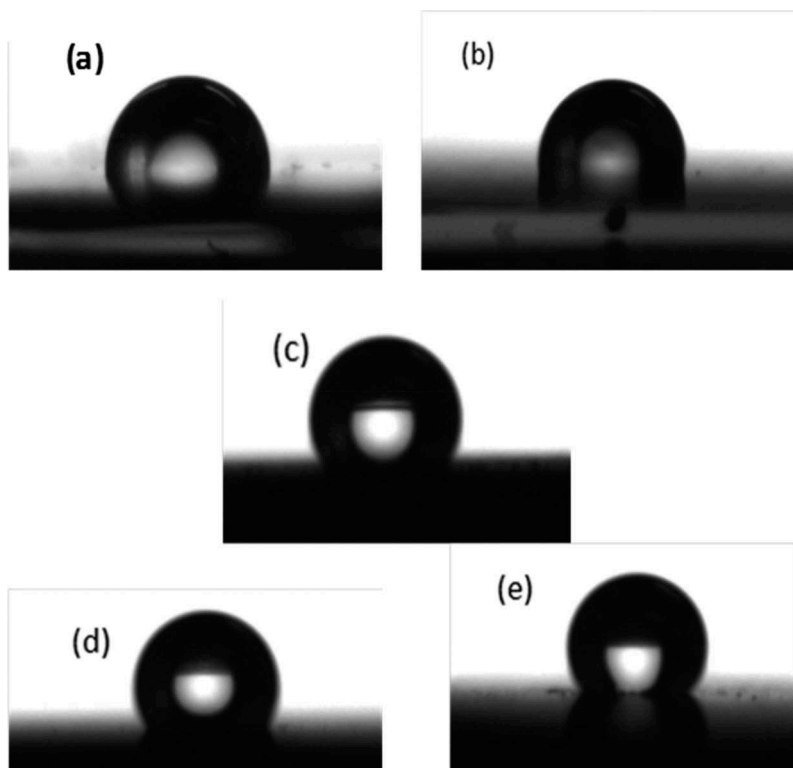


Figure 8. Water contact angle images of a) neat poly(BAF-a), b) poly(3 wt % GO-BAF-a), c) poly(5 wt % GO-BAF-a), d) poly(7 wt % GO-BAF-a) and e) poly(10 wt % GO-BAF-a) composites.

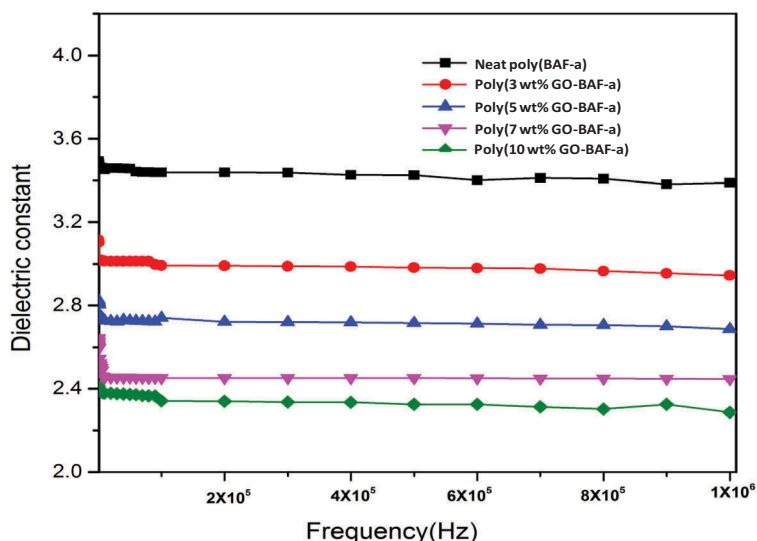


Figure 9. Dielectric constant spectra of neat poly(BAF-a) and poly(GO-BAF-a) composites.

Hydrophobic and dielectric studies of BAF-a and poly(GO-BAF-a) films

Figure 8 and Table 1 show the contact angle images and value of contact angle obtained for neat polybenzoxazines poly(BAF-a) and hybrid benzoxazine composites poly(GO-BAF-a). From the images, it was clear that the value of contact angle increases with increasing weight percentages of GO-C-aps, the highest value of 125.4 was obtained for 10 wt% GO-BAF-a composites. This may be explained due to the incorporation of fluorine atoms in the polymer backbone, which in turn induces a non-polar nature as well as hydrophobic character with decreased moisture absorption. In addition, an increasing wt% of reinforcement poly(GO-C-aps) enhances the hydrophobic behaviour of hybrid composites due to the increased concentration of GO and long aliphatic chain present in the cardanol moiety. [40] The contact angle is strongly influenced by the incorporation of GO. The surface roughness caused by the GO particles embedded right beneath the polybenzoxazine surface may expect to contribute to the extent possible superhydrophobic nature to the nanocomposite surface.

Figure 9 presents the dielectric spectra of neat polybenzoxazine (BAF-a) and hybrid benzoxazine composites poly(GO-BAF-a). The values of dielectric constant obtained are presented in Table 1. From the table, it can be inferred that the reinforcement of varying weight percentages of GO-C-aps bring down the value of dielectric constant according to the concentration. The reduction in the values of dielectric constant may be explained due to the enhanced concentration of cardanol benzoxazine moiety with long chain and the presence of graphene oxide, which in turn significantly reduces the polarization. In addition, the presence of sp and sp^2 carbons in GO also influences the reduction in polarization behaviour and thereby contribute to lower the value of dielectric constant.

In addition to dielectric constant values, dielectric loss is also plays vital role in the design of interlayer dielectric materials the higher values of as more dielectric loss leads to

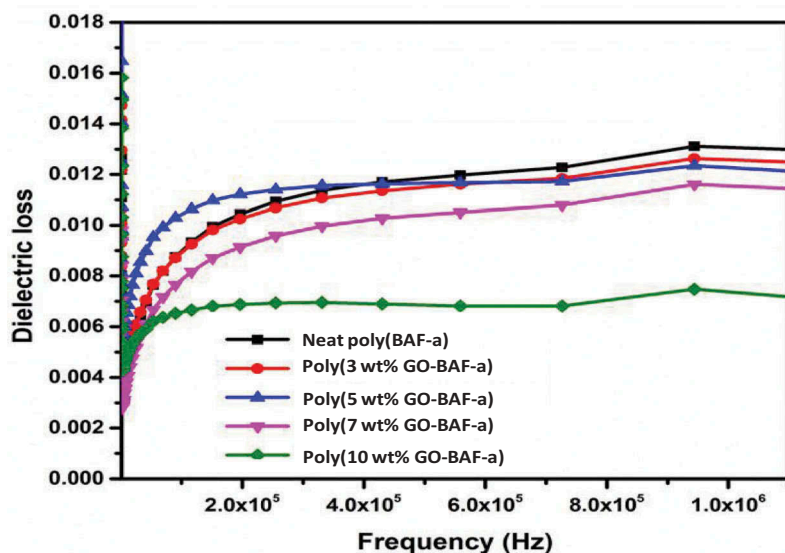


Figure 10. Dielectric loss spectra of neat poly(BAF-a) and poly(GO-BAF-a) composites.

more power consumption. Consequently, the lower dielectric loss or almost negligible value of dielectric loss is desirable for practical applications. Dielectric loss spectra of neat BAF-a and poly(GO-BAF-a) hybrid systems are shown in Figure 10. Trend similar to the values of dielectric constant was also observed in the case values of dielectric loss. The dielectric loss values follow the decreasing trend from neat BAF-a to poly(GO-BAF-a). The poly (10 wt% GO-BAF-a) hybrid composites exhibit the lowest value of dielectric loss (Table 1).

Conclusion

In the present work, a novel type of GO-functionalized, cardanol-based benzoxazine reinforced with fluorine moiety containing benzoxazine hybrid poly(GO-BAF-a) composites have been developed and characterized using modern analytical methods. It was observed that the varying weight percentages of reinforcement of GO-C-aps into benzoxazine significantly improved the thermal stability, value of contact angle and substantially reduced the value of dielectric constant, due to the graphitic nature of reinforcement and the presence of thermally stable low polarisable fluorine atom and silane moiety in the hybrid benzoxazine composites. Data resulted from different thermal and dielectric studies indicate that these hybrid composites can be used in the form of adhesives, sealants, encapsulents and matrices in the field of fabrication of microelectronic devices for high performance applications with improved longevity.

Disclosure statement

No potential conflict of interest was reported by the authors.

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