



Cardanol-Imidazole Based Benzoxazine Blends and Bio-silica Reinforced Composites with Enhanced Surface, Thermal and Dielectric Properties

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Abstract

In the present work, imidazole core mono-amine (ima) was synthesized and used with cardanol (C) and bisphenol-F (BF) to obtain corresponding benzoxazines (C-ima and BF-ima) respectively. Similarly aniline (a) was used as amine precursor for synthesis of benzoxazines (C-a and BF-a) of cardanol (C) and bisphenol-F (BF) respectively for the purpose of blending and comparative studies with ima based benzoxazines. Benzoxazines (C-ima, C-a, BF-ima and BF-a) matrices and blends were prepared using both monofunctional and bifunctional benzoxazines in different weight percent (25/75 wt%, 50/50 wt% and 75/25 wt%) ratios and were characterized using different analytical techniques. From DSC analysis, it was observed that the curing temperature obtained for imidazole based benzoxazines (C-ima and BF-ima) was significantly lower than that of benzoxazines (C-a and BF-a) made using conventional aniline. Similarly, the blends prepared using ima based benzoxazine possess the lower curing temperature, with enhanced thermal stability and char yield than those of conventional cardanol-aniline benzoxazines to an appreciable extent. Hybrid blend composites were developed by reinforcing varying weight percentages (1, 3, 5, 7 and 10 wt%) of GPTMS functionalized bio-silica with selected blends (50:50) of imidazole based benzoxazines (C-ima and BF-ima) and their properties were studied. Data obtained from different studies, suggest that these hybrid composites possess an enhanced thermal stability, higher values of T_g , improved hydrophobic behavior, higher value of char yield and lower dielectric constant than those of neat matrices and blended matrices. It is concluded that the imidazole amine based benzoxazines (C-ima and BF-ima) blends and hybrid composites developed in the present work possess better properties than those of conventional benzoxazine based materials, hence it is suggested that these blends and composites can be used for high performance thermal and dielectric applications.

Keywords Cardanol · Imidazole · Benzoxazines · Hybrid blends and composites · Bio-silica · Thermal stability · Low dielectric constant · Hydrophobic behavior

Introduction

Polybenzoxazines are emerging as versatile thermoset resinous materials over the traditional epoxy resins and polyester resins [1–4]. Since, benzoxazines offer an excellent

mechanical properties, low water absorption, good chemical resistance, high thermal stability and good flame retardant behavior. They are prepared through the facile synthetic approach (Mannich condensation) using cost competitive phenols, formaldehyde and amines [5]. At present benzoxazines are prepared from conventional bisphenol-A which occupies major market share, because of its lesser cost as well as obtained from amenable synthetic process route to form different type of resins with varying range of properties [6]. However, the major problems associated with conventional bisphenol-A based benzoxazines are hazardous nature of bisphenol-A, high temperature curing and higher cross-linked density. Thus, in order to alleviate these problems, various skeletally modified benzoxazine monomers were developed in the recent past [7–9]. Recently, development

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of resinous material from bisphenol-F have been studied since, its structural similarity to bisphenol-A with less-toxic nature [10, 11]. However, the shortcomings such as brittleness due to higher cross-link density and high cure temperature are needed to be overcome to exploit wider range of applications.

Recently, much attention has been focused to utilize biomass precursors such as castor oil [12], cardanol [8, 13–15], eugenol [16–18], guaiacol [19], vanillin [20], catechol [21] etc. Since, the fast depletion of petroleum based precursors and their escalated cost. In this view, benzoxazine monomers from cardanol have recently been received a great importance and attention because of its sustainability and competitive cost. Even though large number of benzoxazine matrices have been synthesized using cardanol in combination with different amine as co-precursors [13, 22–29]. Still it needs improvement in thermal stability, low temperature cure behavior in order to facilitate efficient and economic processability suitable for commercial applications.

The major shortcoming observed in the case of benzoxazines prepared from both bisphenol-F and cardanol are high cure temperature around 250 °C [11, 13, 30]. Thus, an attempt has been made in the present work to prepare imidazole mono amine and its corresponding benzoxazines with cardanol and bisphenol-F in order to achieve low temperature cure and high thermal stability. Our group have continuously involved in the development of low temperature cure benzoxazines, in this context we have already reported novel imidazole core bisphenol based benzoxazines with low cure temperature ($T_p = 170$ °C) [7]. Further, it was observed that the caprolactum modified N,N, dimethylaminopropylamine and cardanol based benzoxazine cures ($T_p = 251$ °C) [13] at lower temperature than that of cardanol-aniline benzoxazine ($T_p = 275$ °C). These results refer that the nitrogen present in the amine (DMPA) as well as in the imidazole ring acts as built-in catalyst [31] and in turn reduces the curing temperature. Thus, the interesting results observed from previous work made us to perform the present work in the direction of low temperature cure imidazole ring containing mono and bifunctional benzoxazines. Further, the aniline based benzoxazines are also prepared and studied for comparison in order to explore the importance of imidazole core benzoxazines.

In order to improve the thermal stability of the cardanol based benzoxazines and to reduce the cure behaviour of the bisphenol based benzoxazines, an effective blending approach has been made in the present work using the combination of both cardanol and bisphenol-F based benzoxazine monomers. It is anticipated that the blending of cardanol and bisphenol-F benzoxazines to impart low temperature cure behavior and higher thermal stability than those of individual neat matrices. In addition, functionalized bio-silica was also reinforced with benzoxazine monomers

in order to achieve the enhanced thermal, surface, dielectric and mechanical properties through the formation of inorganic-organic hybrid network [32]. Data obtained for benzoxazine matrices and composites from different analytical studies are compared, discussed and reported.

Experimental

Materials

Cardanol was obtained from Satya cashew products, Chennai, India. Bisphenol-F was received from Anabond Limited, Chennai, India. Paraformaldehyde, tetrahydrofuran (THF) (99%), ethanol and methanol (99.8%), anhydrous sodium sulphate, hydrazine hydrate, ammonium acetate and acetic acid were obtained from Qualigens, India. Glycidoxypropyltrimethoxysilane (GPTMS), benzyl and 4-nitro benzaldehyde were purchased from Sigma Aldrich, India. Ethyl acetate and sodium hydroxide were received from SRL, India.

Synthesis

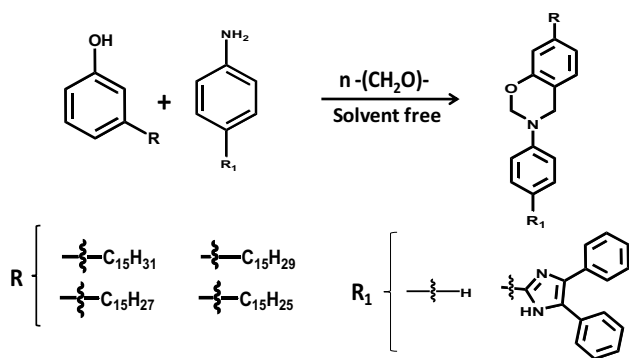
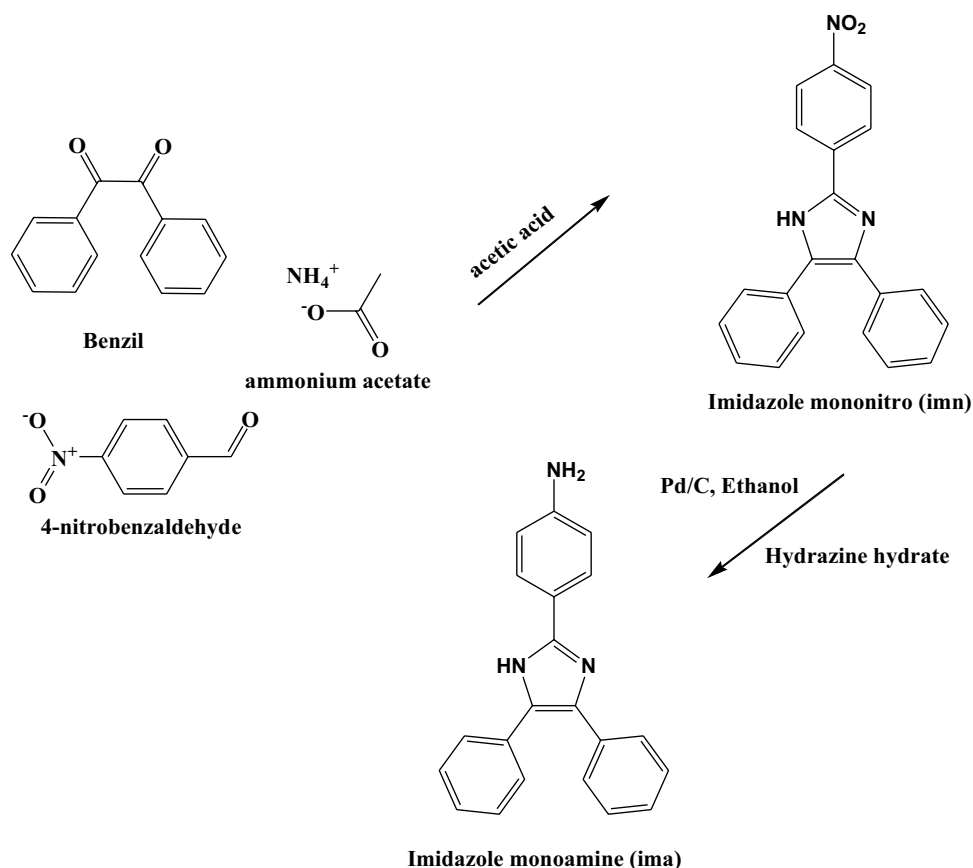
of 2-(4-Nitrophenyl)-4,5-diphenyl-1H-imidazole (imn)

The synthesis of 2, 4, 5-trisubstituted imidazole based nitro compound (imn) is shown in Scheme 1. In brief, 0.1 mol of both benzil, 4-nitrobenzaldehyde and 0.3 mol of ammonium acetate were stirred vigorously at 110 °C for 8 h in the presence of acetic acid medium [33]. Then the reaction mixture was cooled to room temperature and poured into ice cold water and repeatedly washed with water until the acetic acid was removed. The crude nitro product obtained was washed twice with ethanol and dried under vacuum for overnight and filtered. The molecular structure of 2-(4-nitrophenyl)-4,5-diphenyl-1H-imidazole (imn) was confirmed by spectroscopy technique such as IR and NMR (Fig. S1).

Synthesis of 4-(4,5-Diphenyl-1H-imidazol-2-yl)benzenamine (ima)

The synthesis of imidazole core mono amine (ima) is presented in Scheme 1. In brief, imidazole nitro compound was reduced by 10% palladium on activated carbon (10%Pd/C) dispersed in ethanol. The suspension solution was heated to reflux condition with slow addition of required amount of hydrazine monohydrate, which was stirred continuously for 5 h. Then, the hot reaction mixture was filtered to remove Pd/C, and the filtrate was cooled to precipitate 4-(4,5-diphenyl-1H-imidazol-2-yl)benzenamine [7]. The molecular structure of imidazole based mono amine (ima) was confirmed by FT-IR and ¹H-NMR spectroscopic techniques (Fig. S2, Supporting Information).

Scheme 1 Synthesis of 4-(4,5-diphenyl-1H-imidazol-2-yl)benzenamine (ima)



Scheme 2 Synthesis of mono functional benzoxazines

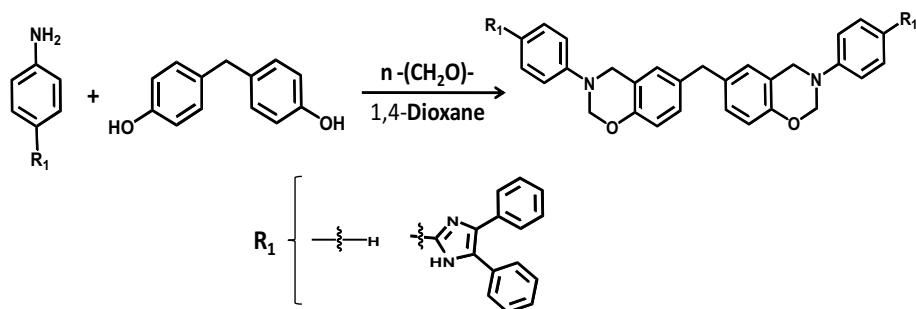
Synthesis of Monofunctional Benzoxazines (C-ima and C-a)

The syntheses of cardanol based monofunctional benzoxazine using amines [imidazole core mono amine (ima) and aniline] are shown in Scheme 2. About 0.2 mol of paraformaldehyde and 0.1 mol of cardanol were mixed under vigorous stirring and then, 0.1 mole of amines [imidazole core mono amine (ima) or aniline] were added separately without solvent and the temperature was raised slowly to 110

°C. The stirring was continued until the completion of the reaction monitored using TLC. Then, the resulted products were poured into 2N sodium hydroxide in order to remove the unreacted phenols and then extracted with chloroform solvent. The separated organic layers were dried over anhydrous sodium sulphate and filtered. Finally the solvent was removed under reduced pressure in order to obtain two types of cardanol benzoxazine monomers from respective experiments namely (C-a) Bz and (C-ima) Bz. The obtained monofunctional monomers and are studied for their chemical structure using FTIR and NMR spectroscopic techniques (Fig. S3, Supporting Information).

Synthesis of Difunctional Benzoxazines [BF-a and BF-ima]

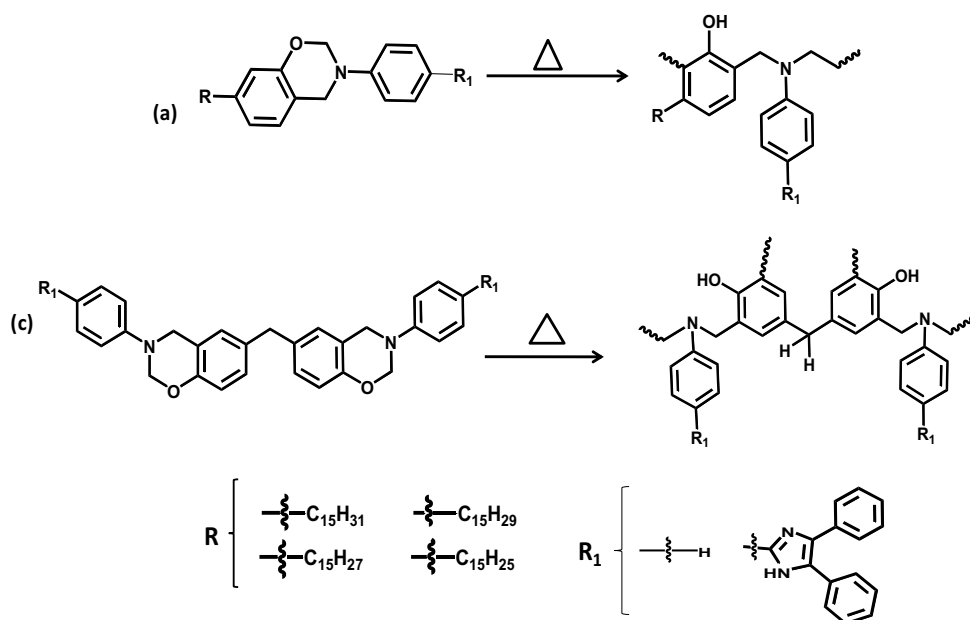
The synthesis of difunctional benzoxazines of bisphenol-F using imidazole core mono amine and aniline are shown in Scheme 3. About 0.4 mol of paraformaldehyde were mixed with 0.2 mol of amines (ima and aniline) under vigorous stirring in the presence of 1,4-dioxane solvent. Then, 0.1 mol of bisphenol-F was added separately and the temperature was raised slowly to 110 °C. The stirring was continued until the reaction completes. Then, the resulted products were poured into 2N sodium hydroxide and followed by extraction

Scheme 3 Synthesis of difunctional benzoxazine monomers

with chloroform solvent. The separated organic layer was dried over anhydrous sodium sulfate and filtered. Finally, the solvent was removed under reduced pressure. The obtained benzoxazine monomers namely BF-a and BF-ima are studied for their chemical structure using FTIR and NMR spectroscopic techniques (Fig. S4, Supporting Information).

Ring Opening Polymerization of Neat Benzoxazines

Thermal ring opening polymerization of cardanol and bisphenol-F based benzoxazines were carried out as presented in Scheme 4. The benzoxazine monomers were placed in an air oven at 80 °C for 8 h to remove the moisture and traces of solvent. After stabilization, the temperature was raised slowly to suitable temperature for the completion of curing process.

Scheme 4 Ring opening polymerization of neat benzoxazines

Preparation of Mono and Difunctional Benzoxazine Reactive Blends

The benzoxazine blends were mixed separately in different weight ratios as presented in Table 1. The preparation of copolymer blends of C-a/BF-a is illustrated in Scheme 5. The blended benzoxazine monomers were heated at 80 °C and subsequently cured thermally at 220 °C and then post-cured at 250 °C for 3 h. The products obtained were cooled to room temperature and subsequently removed from the petri dish and characterized.

Preparation of Hybrid Nanocomposites

The detailed procedure for the preparation of silane functionalized biosilica is given in supporting information [34] (Scheme S1). Different weight percentages of silane functionalized bio-silica were added and agitated into the THF solution containing 50:50 weight percentages of benzoxazine monomers of C-ima/BF-ima. Then the resulted homogeneous hybrid blends were transferred into respective silane coated glass plates and left to evaporate slowly at 50 °C

Table 1 Blending ratio of benzoxazine monomers

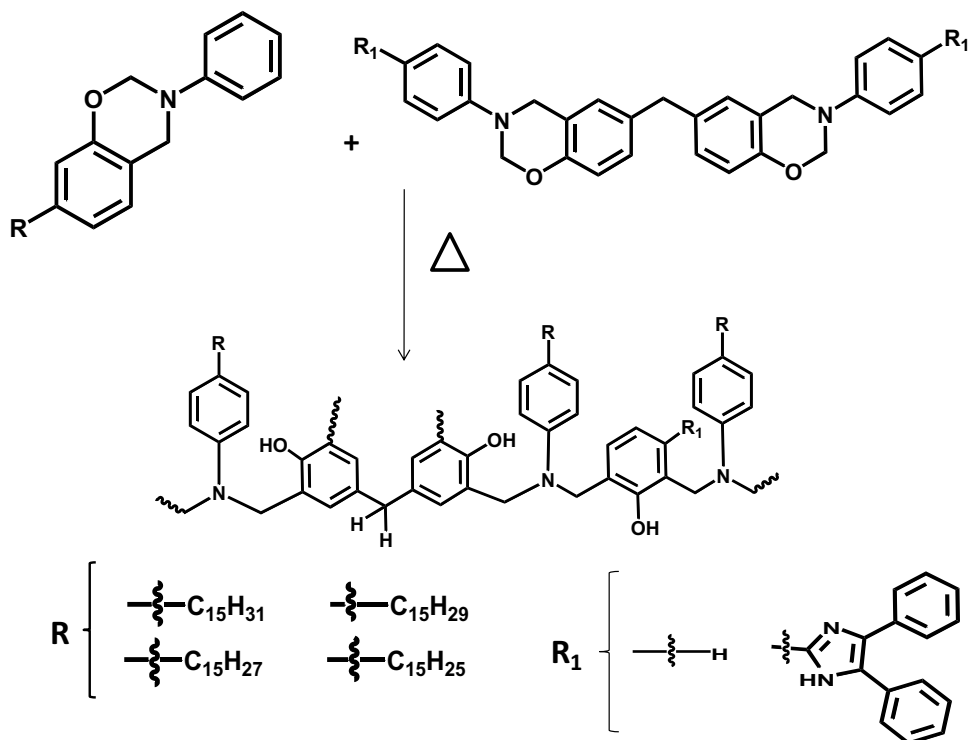
S. no.	Blended matrices	Monomers			
		C-ima	C-a	BF-ima	BF-a
1.	Poly(C-ima/BF-a)	100	–	–	0
2.		75	–	–	25
3.		50	–	–	50
4.		25	–	–	75
5.		0	–	–	100
6.	Poly(C-ima/BF-ima)	100	–	0	–
7.		75	–	25	–
8.		50	–	50	–
9.		25	–	75	–
10.		0	–	100	–
11.	Poly(C-a/BF-a)	–	100	–	0
12.		–	75	–	25
13.		–	50	–	50
14.		–	25	–	75
15.		–	0	–	100
16.	Poly(C-a/BF-ima)	–	100	0	–
17.		–	75	25	–
18.		–	50	50	–
19.		–	25	75	–
20.		–	0	100	–

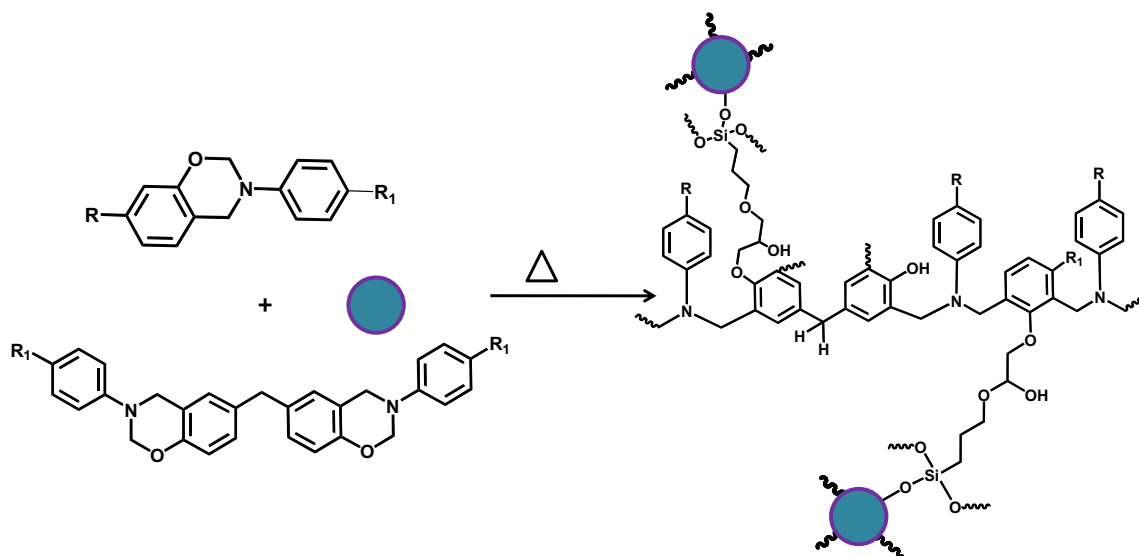
for overnight. Subsequently cured at suitable temperature at the heating rate of 20 °C per hour and the obtained light brown colored thin hybrid composite films were characterized (Scheme 6).

Characterization

FTIR spectra measurements were carried out with Agilent Cary 630 FTIR Spectrometer. NMR spectra were obtained with Bruker (400 MHz) using dimethylsulfoxide (d₆-DMSO) as a solvent and tetramethylsilane (TMS) as an internal standard. DSC measurements were recorded using NETZSCH STA 449F3 under N₂ purge (60 mL min⁻¹) at scanning rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was carried out from room temperature to 850 °C using NETZSCH STA 449F3 using 5 mg of sample under N₂ flow (60 mL min⁻¹) at heating rate of 20 °C min⁻¹. The dielectric constant of the samples was determined from impedance analyzer (Numeric LCR meter, UK) at room temperature from 1 Hz to 1 MHz. The morphology of the blended matrices and composites were analyzed from an FEI QUANTA 200F high-resolution scanning electron microscope (HRSEM). HR-TEM images were also recorded to ascertain the dispersion of silica using TECNAI G2 S-Twin high resolution transmission electron microscope, with an acceleration voltage of 150 kV. Contact angle measurements were obtained using a Kwoya goniometer with 5 μL of water as probe liquid.

Scheme 5 Preparation of mono and difunctional benzoxazine reactive blends





Scheme 6 Preparation of hybrid blend composites

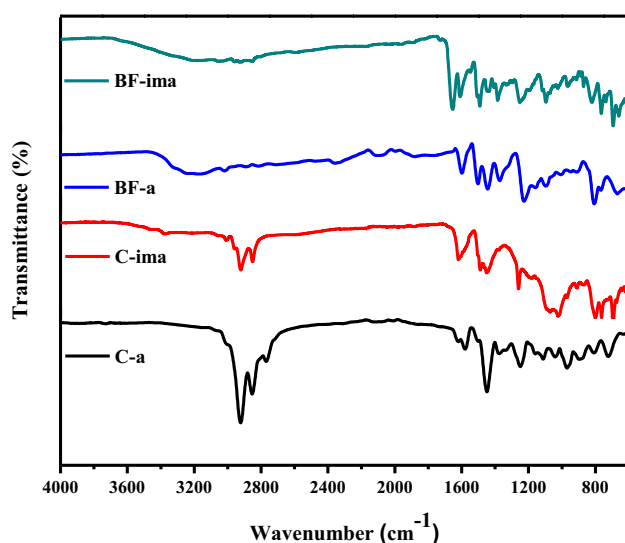


Fig. 1 IR spectra of benzoxazine monomers

Results and Discussion

The molecular structure of synthesized benzoxazine monomers (C-a, C-ima, BF-a and BF-ima Bz) were ascertained using FTIR. Figure 1 presents the FTIR spectra of benzoxazine monomers. The appearance of bands at 1215 cm^{-1} and 1088 cm^{-1} correspond to C–O–C asymmetric stretching and symmetric stretching respectively and 916 cm^{-1} represents C–H (out of plane) which confirms the presence of benzene ring attached to a heterocyclic moiety. Similarly, the appearance of the absorption band at 1514 cm^{-1}

corresponds to aromatic in-plane vibration of disubstituted benzene, which also confirms the formation of benzoxazine monomers. The presence of presence of C=N in the imidazole ring was also confirmed through the appearance of band at 1600 cm^{-1} .

Curing Behavior of Benzoxazine Monomers

The thermal polymerization behavior of different benzoxazine monomers are observed through DSC analysis at the heating rate of 10 °C min^{-1} under nitrogen atmosphere. The DSC thermograms of C-a, C-ima, BF-a, and BF-ima are shown in Fig. 2a. The curing of C-a monofunctional benzoxazine monomer was observed to occur at 288 °C , whereas that of C-ima monomer cures at 218 °C . The curing of bifunctional benzoxazine monomers namely BF-a and BF-ima occurs at $T_p = 226$ and 202 °C respectively. The curing temperature (T_p) obtained for imidazole containing cardanol and bisphenol-F based benzoxazines (C-ima and BF-ima) were significantly lowered when compared with that of benzoxazines (C-a and BF-a) prepared using aniline (Fig. 2a; Table 2). This might be due to the presence of nitrogen atom with acidic proton in the benzoxazine moiety. The mechanism that favors low cure ring-opening polymerization through the presence of imidazole is presented in Scheme 7. Due to the catalytic nature of imidazole, the curing occurs at relatively lower temperature, which supports the built-in catalytic nature of imidazole moiety. Further, the imidazole behaves as an amphoteric nature because 1-H of imidazole attached with nitrogen was more acidic, whereas the double bonded nitrogen atom is basic in nature like pyridine. However, the nitrogen attached acidic proton (N–H) influences

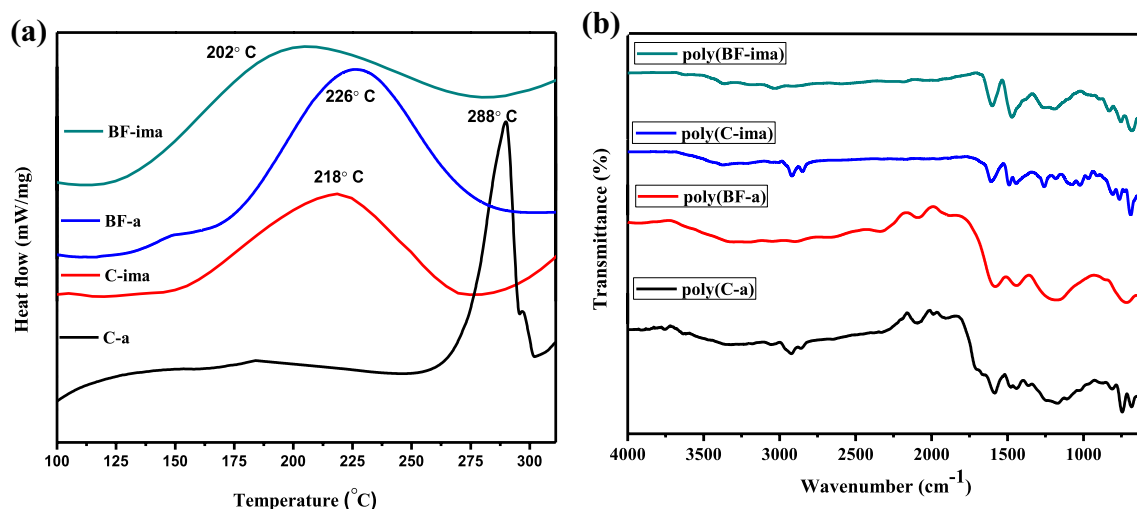
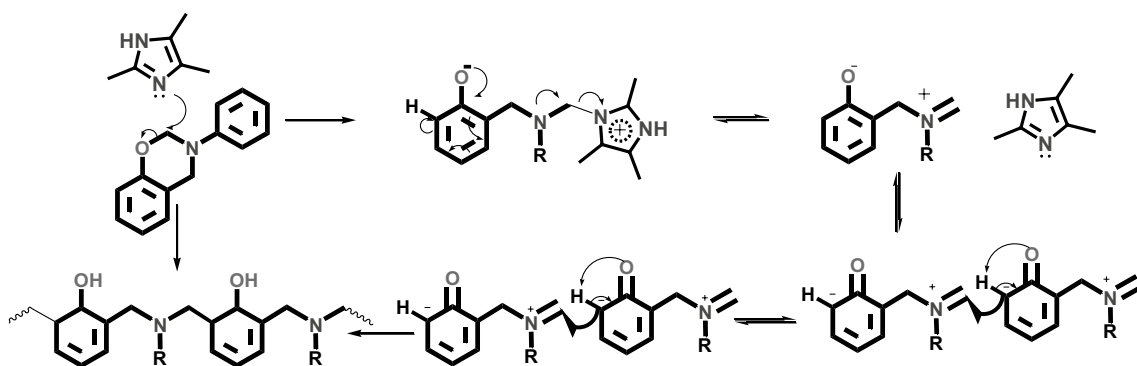


Fig. 2 a DSC thermogram of benzoxazine monomers and **b** FTIR spectra of neat matrices



Scheme 7 Mechanism for the ring-opening polymerization process with built-in catalytic imidazole core

the formation of zwitter ion (Scheme 7) through its catalytic behavior. The curing reaction of monomers and the formation of neat matrices were also confirmed through the absence of oxazine band in the FTIR presented in Fig. 2b.

The thermal polymerization (T_p) behavior of different benzoxazine blends with 50/50 weight % are also observed through DSC analysis is presented in Fig. 3 and Table 2. The exothermic peaks (polymerization temperature, T_p) observed in DSC thermograms of blends such as C-a/BF-a, C-ima/BF-a, C-a/BF-ima and C-ima/BF-ima are appeared at 228, 217, 212 and 202 °C, respectively (Fig. 3a). Comparatively, the blends with imidazole based benzoxazine monomers are found to possess lower curing temperature than that of aniline based benzoxazine monomers due to synergistic effect of copolymerization as well as catalytic activity of imidazole as discussed earlier. The apparent heat of polymerization (ΔH) is listed in Table 2. It was noticed that the heat of polymerization if imidazole based benzoxazine blends exhibit lower values than

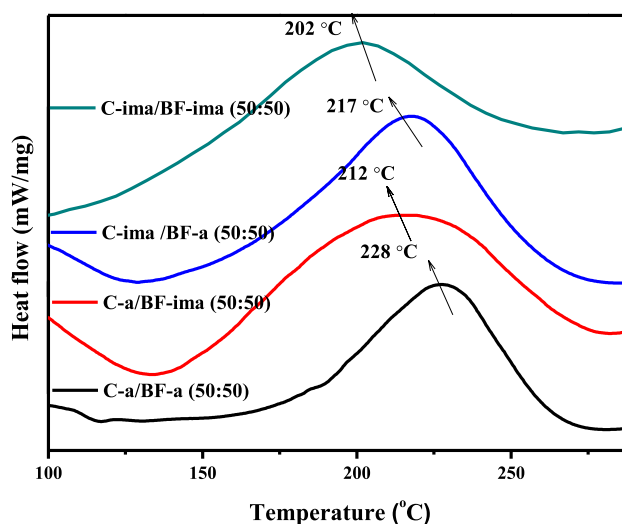
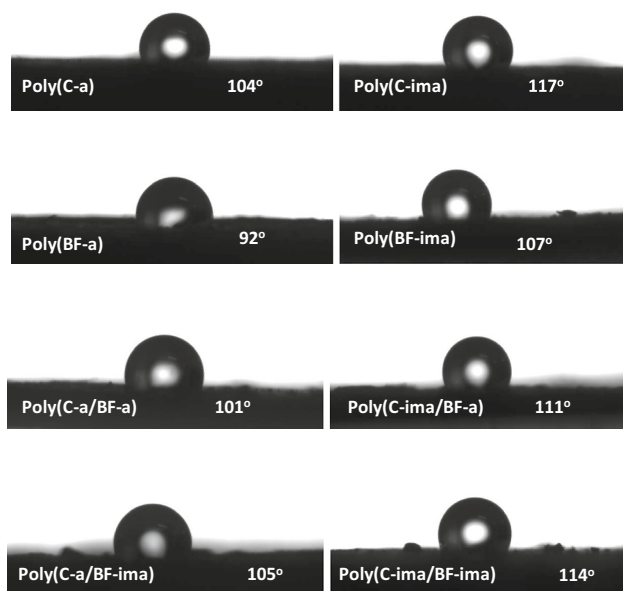


Fig. 3 DSC curves of blends of monomers in 50:50 ratio

Table 2 Curing profile of monomers and blends

Monomers	Curing behavior				Blends	Curing behavior			
	T _i (°C)	T _p (°C)	T _f (°C)	ΔH (mJ/mg)		T _i (°C)	T _p (°C)	T _f (°C)	ΔH (mJ/mg)
C-a BZ	254	288	302	35	C-a Bz/BF-a	153	228	279	127
C-ima Bz	150	218	271	68	C-a Bz/BF-ima	132	212	281	110
BF-a Bz	167	226	280	130	C-ima / BF-a	136	217	277	136
BF-ima Bz	120	202	228	83	C-ima /BF-ima	119	202	226	98

Heat of polymerisation—ΔH, initial polymerisation temperature—T_i, polymerisation maxima temperature—T_p, onset (final) polymerisation temperature—T_f

**Fig. 4** Contact angle images of neat matrices and 50:50 blended matrices

that of aniline based benzoxazine blends. The presence of imidazole core also influences the low cure behavior and reduced heat of polymerization (ΔH) in the blended matrices. Further, curing of blends was ascertained from the FTIR analysis presented in Fig. S5. The absence of bands at 1215 cm⁻¹, 1088 cm⁻¹, and 929 cm⁻¹ after curing confirm the occurrence of ring opening reaction of benzoxazine monomers (Fig. S5). The reactive methylene group abstracts the ortho hydrogen present in the neighboring

oxazine ring and initiates the polymerization reaction (Scheme 4).

Wettability Studies

Figure 4 illustrates the contact angle images of neat matrices. The neat matrix surfaces are observed to be hydrophobic in nature. The cardanol based monofunctional benzoxazines are having higher values of contact angle because of the presence of long aliphatic hydrocarbon side chain. Thus, contact angle value of poly(C-a) was observed to be 104°, whereas that of poly(C-ima) was observed to be 117°. Comparatively, imidazole amine and cardanol based benzoxazine matrix possesses the higher value of contact angle, which contributes to the hydrophobic behavior. After blending, there was no significant change in the value of contact angle, which confirms that the blended matrices retain the hydrophobic behavior.

Thermal Behavior of Neat Matrices

The values of glass transition temperature (T_g) observed for neat benzoxazine matrices from DSC analysis are presented in Table 3. The value of T_g obtained for poly(C-a, C-ima, BF-a and BF-ima) are 61 °C, 137 °C, 182 °C and 197 °C respectively. It was observed that the value of T_g of bifunctional benzoxazine monomers (BF-a and BF-ima) are higher than that of monofunctional benzoxazine monomers (C-a and C-ima) due to the restricted chain mobility, molecular entanglement and enhanced network structure brought by bifunctional monomers. It was also noticed that

Table 3 Thermal behavior of neat benzoxazines matrices

Neat matrices	Thermal behavior					LOI
	T _g (°C)	5% weight loss (°C)	10% weight loss (°C)	T _{max} (°C)	Char yield at 850 °C (%)	
Poly(C-a)	61	377	407	468	9	21.1
Poly(C-ima)	137	358	383	453	23	26.7
Poly(BF-a)	182	361	402	483	45	35.5
Poly(BF-ima)	198	405	442	491	61	41.9

the benzoxazines prepared using imidazole based amine possess the higher value of T_g than that of aniline due to rigid complex aromatic imidazole moiety. The low cure temperature and high T_g value are desirable for matrices those intended for high temperature applications.

Further, the thermal properties of cured benzoxazines [poly(C-a), poly(C-ima), poly(BF-a) and poly(BF-ima)] were studied using TGA analysis under inert condition and the data obtained are presented in Fig. 5 and Table 3. There was no weight loss observed below 150 °C which suggests that there are no volatiles and moisture present in the samples. The temperature corresponds to 5/10% weight losses were observed at 377/407 °C for poly(C-a PBz), 358/383 °C for poly(C-ima), 361/402 °C for poly(BF-a) and

405/442 °C poly(BF-ima) respectively. The decomposition maxima (T_{max}) for poly(C-a), poly(C-ima), poly(BF-a) and poly(BF-ima) were observed at 468, 453, 483 and 491 °C, respectively. The occurrence of major weight losses were observed in the temperature range between 450 and 500 °C. The residual char yields at 850 °C observed for poly(C-a), poly(C-ima), poly(BF-a) and poly(BF-ima) are 9%, 23%, 45% and 61% respectively. The thermogram results suggest that the matrices of monomers with imidazole ring moieties have higher thermal stability than that of matrices built with benzene ring of aniline. Thus, in addition to low cure temperature and high T_g value, the thermal stability of benzoxazines are also enhanced to an appreciable extent due to the presence of imidazole moiety.

Thermal Behavior of Blended Matrices

Cardanol and its derivatives are conventionally used as diluents for processing of high viscous resins such as epoxy, benzoxazines. It was noticed that the blending of monofunctional (C-a and C-ima) benzoxazine monomers with bifunctional (BF-a and BF-ima) (Scheme 5) monomers imparts higher values of T_g than that of the neat monofunctional benzoxazine matrices (Table 4). For example, blending of monofunctional C-a/C-ima with BF-a and BF-ima matrices with 50:50 ratio offers T_g values as 106 °C/162 °C and 156 °C/176 °C respectively. The blending of monofunctional benzoxazines with bifunctional benzoxazines alter the resulting network structure of the cured copolymeric blends of benzoxazines, according to the nature of complexity of molecular structure, which influences the value of T_g . It was also noticed that the value of T_g of blends obtained are higher than that of neat monofunctional benzoxazines and lower than that of neat bifunctional benzoxazines (Table 4).

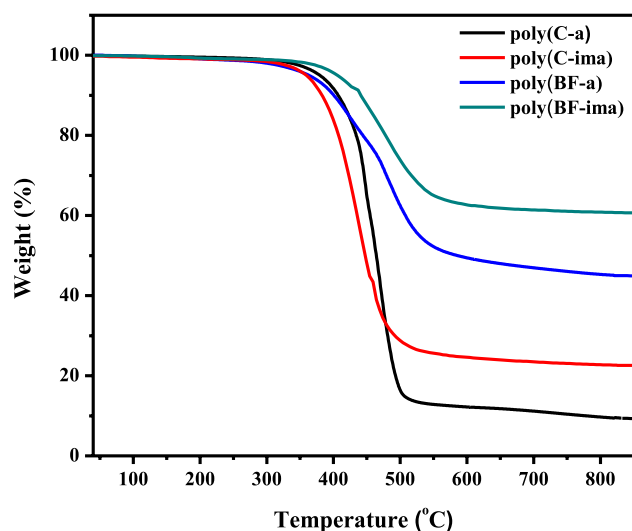


Fig. 5 TGA thermogram of neat benzoxazine matrices

Table 4 Thermal behavior of neat blended matrices

Blended matrices	Blend ratio	Thermal behavior					LOI
		T_g (°C)	5% weight loss (°C)	10% weight loss (°C)	T_{max} (°C)	Char yield at 850 °C (%)	
Poly(C-a Bz/BF-a)	75:25	86	387	410	472	18	24.7
	50:50	106	381	412	475	24	27.1
	25:75	141	379	414	481	34	31.1
Poly(C-a Bz/BF-ima)	75:25	136	376	405	478	20	25.5
	50:50	162	377	403	480	30	29.5
	25:75	174	376	403	485	41	33.9
Poly(C-ima/BF-a)	75:25	149	365	385	462	26	27.9
	50:50	156	341	382	470	31	29.9
	25:75	169	344	380	478	37	32.3
Poly(C-ima/BF-ima)	75:25	155	370	398	465	36	31.9
	50:50	176	378	412	468	45	35.5
	25:75	188	382	408	476	53	38.7

This may be explained due to the synergistic effect of cardanol skeleton with long alkyl chain moiety and rigid heterocyclic imidazole moiety, which contributes to an average value of T_g of resulting copolymeric benzoxazine blends.

Thermograms of blended matrices and the degradation temperatures obtained are presented in Fig. 6a–d and Table 4. Among the developed blended matrices, the blends with higher ratio of bifunctional benzoxazines (BF-a and BF-ima) show an improved thermal stability. For example, C-a and C-ima blends with ratio greater than 50% of BF-a and BF-ima shows higher thermal stability. The 5% weight loss temperatures obtained for the blends of poly(C-a/BF-a) for 25/75 ratio is 379 °C, whereas that of the poly(C-a/BF-ima) shows 376 °C. Similarly 5% weight loss temperatures of poly(C-ima/BF-a) and poly(C-ima/BF-ima) were observed at 344 °C and 382 °C respectively. It was also observed that the degradation temperatures observed for 10% weight losses are higher for the blends having higher weight percentage of both BF-a and BF-ima (Table 4). For example, the blends namely C-a/BF-a, C-a/BF-ima, C-ima/BF-a and C-ima/BF-ima having ratio of 25/75 possess the

value of char yield of 34%, 41%, 37% and 53% respectively, which are significantly higher than that of same blends having 50/50 or 75/25 weight percentage composition (Table 4).

Further, it was interesting to note that the values of char yield obtained for the blends of all the combinations studied in the present work are higher than that of conventional cardanol-aniline based benzoxazine, indicating the enhanced behavior of thermal stability and flame retardancy. From the results obtained from thermogravimetric analysis, it is explained that the blends with bisphenol-F and imidazole moieties influence to retard the heat transfer and protects the benzoxazine blends from thermal degradation and also contributes to flame retardant character. This is one of the prime objectives of the present work in addition to reducing the cure temperature of conventional cardanol benzoxazine to widen the area of applications.

Preparation of Hybrid Bio-silica Composites

In addition to the preparation of blends, the present work extends with the development of organic-inorganic hybrid

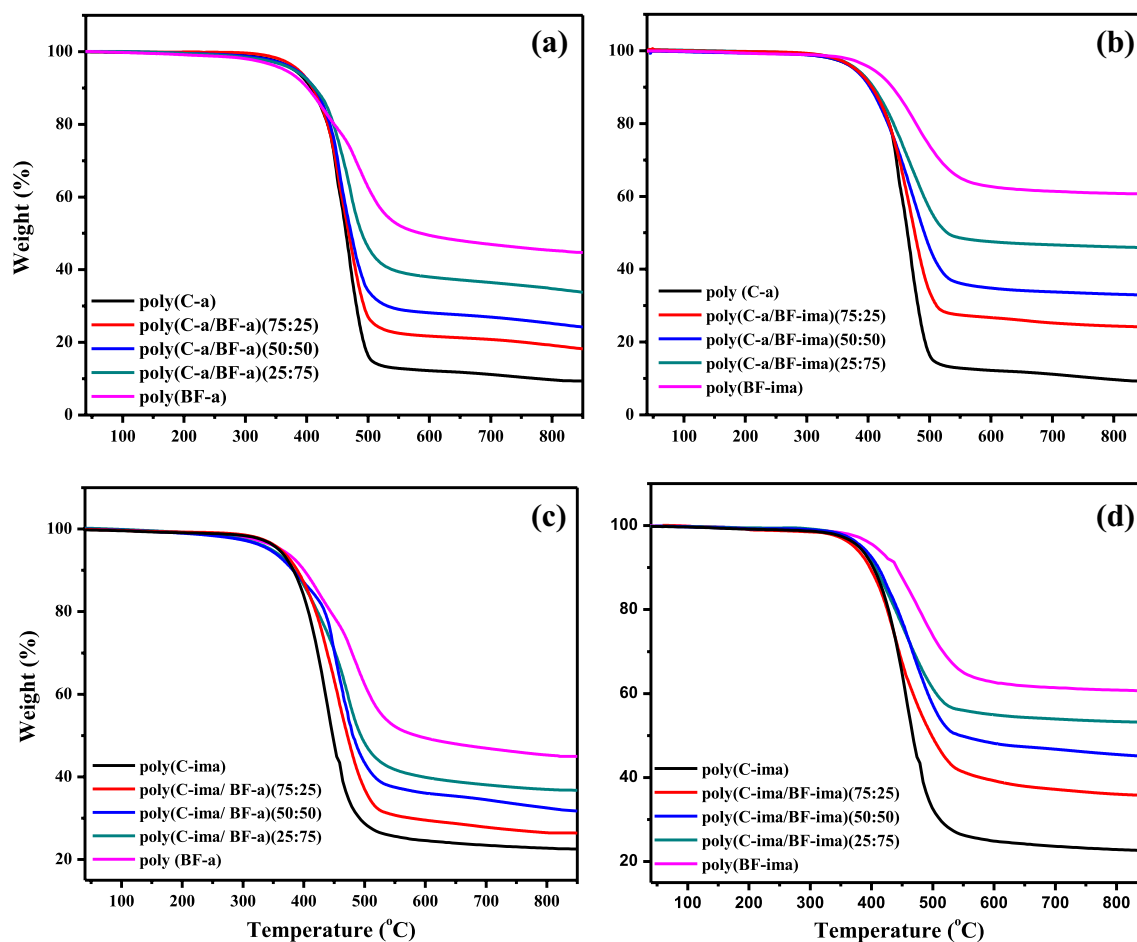


Fig. 6 TGA thermogram of blended matrices

composites. The matrices with imidazole moieties are found to possess lower cure temperature, higher T_g , better higher

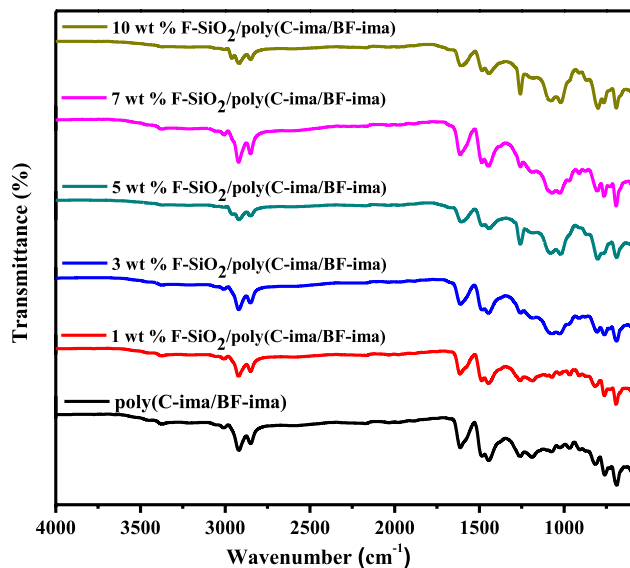


Fig. 7 FTIR spectra of F-SiO₂ incorporated poly(C-ima/BF-ima) composites

thermal stability and hydrophobic behavior. Hence, blend based on C-ima and BF-ima (50/50) matrices are selected for the preparation of hybrid organic-inorganic composites by reinforcing with varying weight percentages of functionalized bio-silica. The formation of hybrid blend (C-ima/BF-ima: 50/50) with biosilica (1, 3, 5, 7 and 10 wt%) reinforced composites were ascertained from spectral and morphological data obtained from respective analysis.

Figure 7 illustrates the FTIR spectra of bio-silica F-SiO₂ reinforced poly(C-ima/BF-ima) hybrid nanocomposites. The appearance of new band at 1050 cm⁻¹ corresponds to the Si–O–Si stretching vibration mode. The intensity of band became stronger with increase in the weight percentage concentration of bio-silica. In addition to the FTIR, the SEM analysis was made and resulted images of neat matrices of C-ima/BF-ima and F-SiO₂ reinforced poly(C-ima/BF-ima) nanocomposites are presented in Fig. 8. The morphology of neat blended matrices illustrates in Fig. 8a shows uniform and smooth surfaces without any cracks. This infers the effective and efficient compatibility exist between the benzoxazines, which contributes to homogenous morphology. However, F-SiO₂ reinforced matrices show rough crack propagated surfaces (Fig. 8b). Upon increase in the

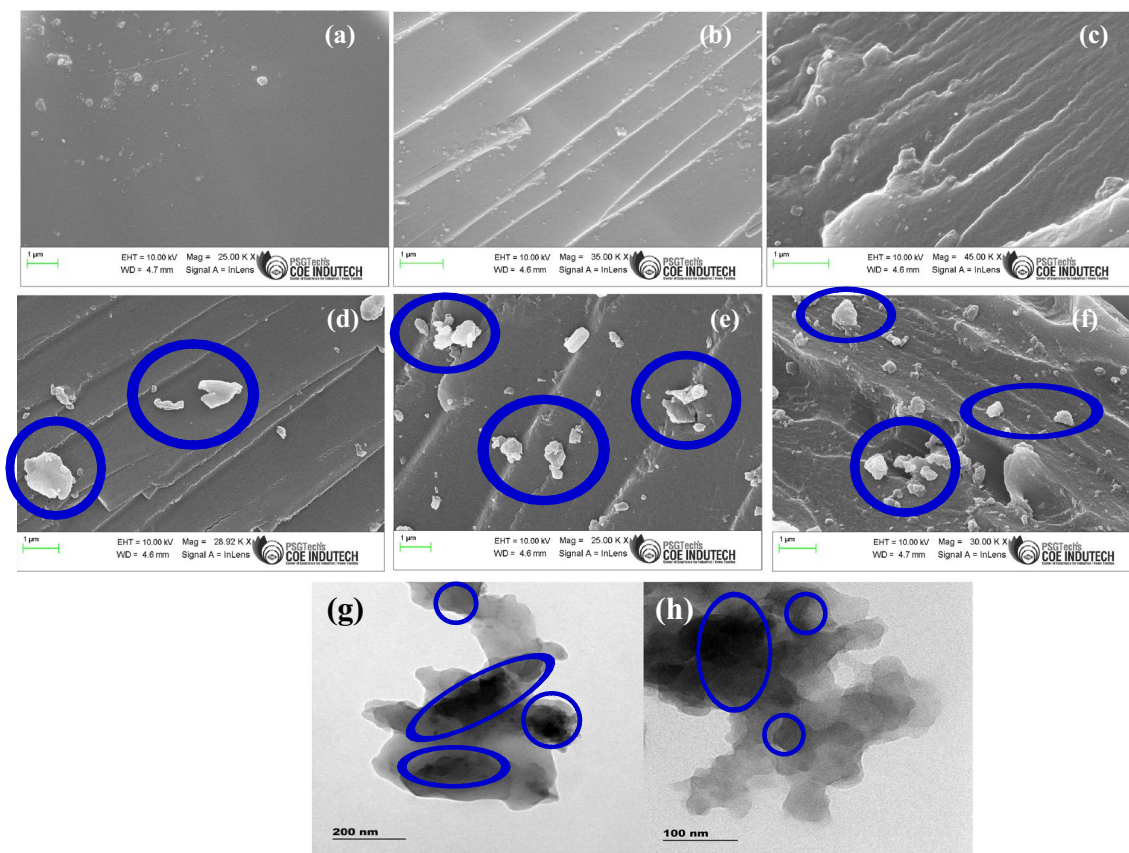


Fig. 8 SEM images of **a** neat, **b** 1 wt%, **c** 3 wt%, **d** 5 wt%, **e** 7 wt%, **f** 10 wt% F-SiO₂ reinforced benzoxazine composites, **g**, **h** TEM images of 10 wt% F-SiO₂ reinforced benzoxazine composites

concentration, the roughness also increases along with the propagated cracked surfaces with heterogeneous morphology as presented in Fig. 8c–f. Further, the dispersion of bio-silica (F-SiO₂) within the blended matrix (C-ima/BF-ima 50:50) was ascertained from the images obtained from TEM analysis, which are presented in Fig. 9a, b. The dark region in the TEM images correspond to the presence of dispersed silica, which confirms the formation of nanocomposites. Further, the dispersed silica particles are observed to be in the range of 30 to 50 nm (highlighted with blue ring). The GPTMS functionalized bio-silica became an integral part of the matrices with uniform distribution with formation of rough surfaces.

Further, to confirm the interaction of bio-silica (F-SiO₂) with the benzoxazine matrices the XPS analysis was carried out and presented in Fig. 9a, b. The interaction between polybenzoxazine and silica ascertained from the XPS binding energy curve presented in Fig. 9a, b. The 10 wt% F-SiO₂/polybenzoxazines shows the presence of silica in addition to the presence of carbon, nitrogen and oxygen elements. The carbon, oxygen, nitrogen and silica shows binding energy signals at 282, 530, 397 and 100 eV respectively. Also, the elemental profiles are found as carbon 84.53%, oxygen 6.3%, nitrogen 6.74% and rest of silica 2.52%. In addition, the formation of hybrid composites was ascertained from the change in binding energy value of oxygen. Thus, the deconvoluted curve of O 1s peak is presented in Fig. 9b in which two binding energy signals are observed. The peak observed at 530.5 eV corresponds to the presence of Si–O–Si groups. Further, the signal appeared at 529.5 eV corresponds to the presence of Si-O-C groups. The results obtained both from XPS and TEM analysis infer that the formation of hybrid nanocomposites (Fig. 8g, h).

The XRD analysis was also performed in order to ascertain the uniform dispersion of bio-silica and morphology

of the blended matrices and composites. The XRD diffractogram of neat blended matrices and F-SiO₂ reinforced benzoxazine composites (C-ima/BF-ima) are presented in Fig. 10. The appearance of diffraction peaks at $2\theta = 20^\circ$ infer the amorphous nature of both blended matrices and composites. Due to uniform dispersion of F-SiO₂ in C-ima/BF-ima blended benzoxazine matrix, no distinct phases are observed. Thus, the XRD patterns confirm the effective compatibility resulted between the F-SiO₂ and blended benzoxazine hybrid composites.

Data obtained from thermogravimetric analysis of functionalized bio-silica (F-SiO₂) reinforced benzoxazine blend (C-ima/BF-ima) composites are presented in Fig. 11 and Table 5. As shown in Fig. 11, the 5% weight loss of 1, 3, 5, 7 and 10 wt% of F-SiO₂ reinforced nanocomposites were

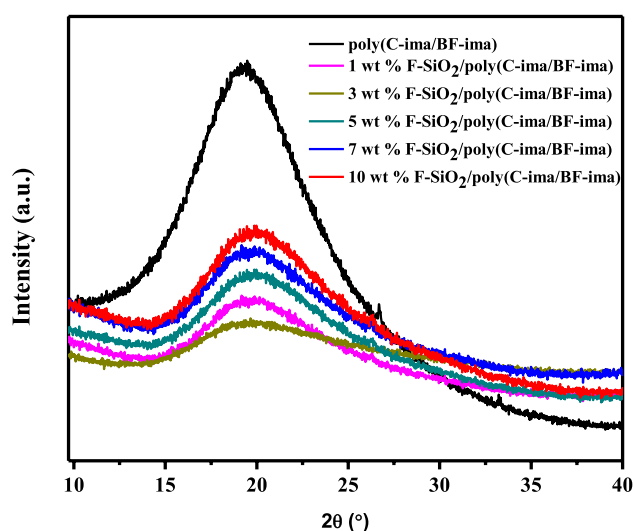


Fig. 10 XRD patterns of F-SiO₂ reinforced C-ima / BF-ima nanocomposites

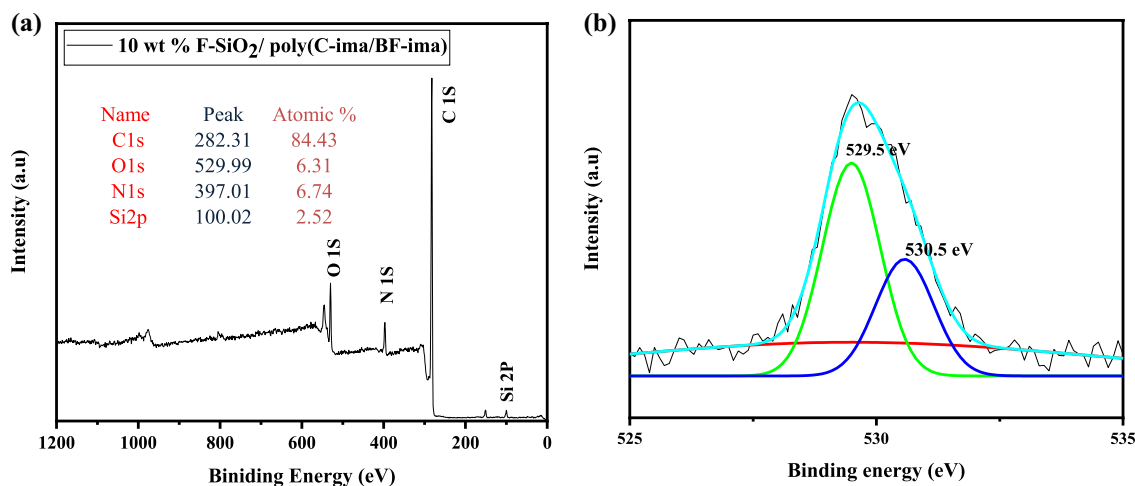


Fig. 9 XPS profile of 10 wt% F-SiO₂ reinforced benzoxazine composites

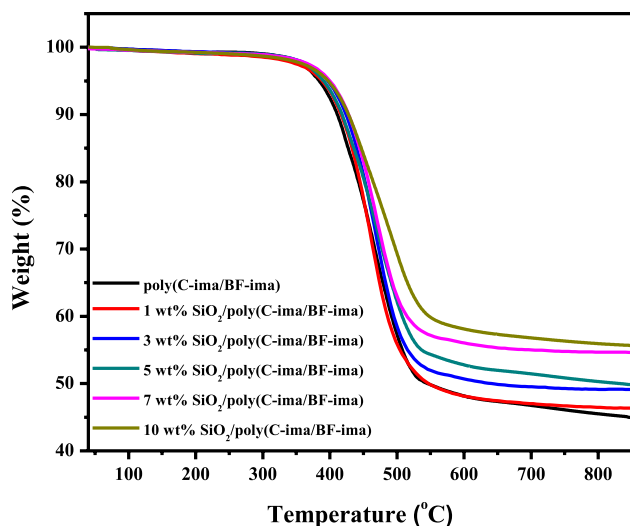


Fig. 11 TGA thermogram of F-SiO₂ reinforced C-ima/BF-ima nanocomposites

observed at 365, 389, 387, 401 and 400 °C, respectively. Similarly, the 10% weight losses were observed at 413, 424, 416, 425 and 428 °C, respectively. The maximum degradation temperatures (T_{max}) of nanocomposites with 1, 3, 5, 7 and 10 wt% of F-SiO₂ reinforced C-ima/ BF-ima nanocomposites were observed at 471, 473, 476, 483 and 493 °C respectively. Further, the char yield obtained for 1, 3, 5, 7 and 10 wt% F-SiO₂ reinforced C-ima/BF-ima nanocomposites were 46, 48, 50, 54 and 55% respectively (Fig. 11). The values of char yield obtained for bio-silica reinforced blended benzoxazine composites are appreciably higher than that of conventional benzoxazines indicate that these hybrid composites can be considered for thermally stable adhesives, coatings and sealants for microelectronic applications.

Flame Retardant Property

In addition, the flame retardant properties of the neat matrices, blends and composites in terms of limiting oxygen index (LOI) values were studied using the char yield percentage from the equation of Van Krevelen [35] (Eq. 1). The values of LOI calculated are presented in Tables 3, 4 and 5.

$$LOI = 17.5 + (0.4 \times \theta) \quad (1)$$

where θ is the percentages of char yield remain at 850 °C. The calculated LOI values are presented in Tables 3, 4 and 5. These LOI values are significantly higher when compared with that of conventional benzoxazines. Thus, the blended matrix of C-ima/BF-ima was calculated to be 35.5%, whereas that of the 10 weight % F-SiO₂ reinforced matrices possesses the value of 39.5%. Further, the LOI values infer that these materials can be effectively used as non-halogen and non-phosphorus flame retardant materials in the form of sealants, encapsulants and coatings for different industrial and engineering applications.

Dielectric Behavior and Water Contact Angle of Composites

The dielectric constant (k) behavior of varying weight percentages (1, 3, 5, 7 and 10 wt%) of F-SiO₂ reinforced C-ima/BF-ima benzoxazine nanocomposites are determined along with the neat blended matrix. The values of dielectric constant obtained at 1 MHz are presented in Table 4 and Fig. 12. The value of dielectric constant observed for neat C-ima Bz/BF-ima blended matrix of benzoxazine is 4.6 at 1 MHz, whereas that of 1, 3, 5, 7 and 10 wt% of F-SiO₂ reinforced C-ima Bz/BF-ima Bz composites are found to be 4.2, 3.6,

Table 5 Thermal, dielectric, and surface properties of hybrid blended bio-silica composites

Composites	Thermal stability				LOI	Dielectric constant (1 MHz) (k)	Contact angle (°)
	5% weight loss (°C)	10% weight loss (°C)	T_{max} (°C)	Char yield at 850 °C (%)			
Neat poly(C-ima/ BF-ima)	378	412	468	45	35.5	4.6	114
1 wt% F-SiO ₂	383	414	470	46	35.9	4.2	117
3 wt% F-SiO ₂	389	424	473	48	36.7	3.6	118
5 wt% F-SiO ₂	387	416	476	50	37.5	2.9	121
7 wt% F-SiO ₂	401	425	483	54	39.1	2.7	124
10 wt% F-SiO ₂	400	428	493	55	39.5	2.3	127

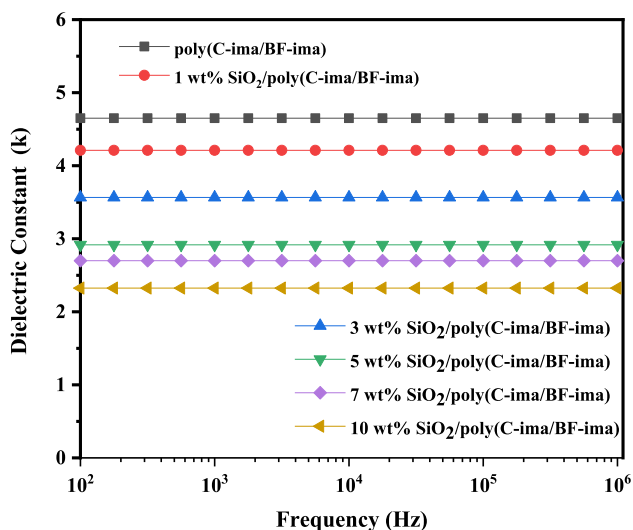


Fig. 12 Dielectric profile F-SiO₂ reinforced benzoxazine composites

2.9, 2.7 and 2.3 respectively. The hybrid composites with formation of network structure having –Si–O–Si linkages effectively reduced the dipole–dipole interaction and consequently, lowers value of dielectric constant to an appreciable extent [36]. Thus, the F-SiO₂ reinforced benzoxazine composites with low values of dielectric constant can be considered as an effective insulation material for high performance microelectronics applications in the form of adhesives, sealants and encapsulants.

The contact angle images of blended composites with 1, 5, and 10 wt% F-SiO₂ reinforced poly(C-ima/BF-ima) composites are presented in Fig. 13. It was observed that the functionalized bio-silica reinforced composites possess the higher values of contact angle when compared to that of neat blended matrices. The value of contact angle of neat poly(C-ima/BF-ima) is 114°, whereas that of values of 1, 3, 5, 7 and 10 wt% of F-SiO₂ incorporated C poly(C-ima/

BF-ima) are 117°, 118°, 121°, 124° and 127° respectively. The enhanced value of water contact angle indicates the improved hydrophobic behavior and is incorporated by the (Si–O–Si) non-polar network present in the hybrid composites [36, 37]. In addition to the non-polar nature of the bio-silica, its reinforcement also increases the roughness of the polymer surface as observed from the SEM images (Fig. 8). Consequently, the developed composites with higher values of contact angle and enhanced surface roughness make the material surface become more hydrophobic behavior indicating their usefulness for insulation applications.

Conclusion

In the present work, new types of mono and difunctional benzoxazines were synthesized using cardanol and bisphenol-F respectively with imidazole mono amine. The molecular structure of benzoxazines was characterized by FT-IR and ¹H-NMR. Data obtained from DSC analysis, suggest that the benzoxazines with imidazole moiety influences the lowering of cure temperature to an appreciable extent. Blends developed using higher weight percentage of imidazole amine based benzoxazines possess significantly higher values of T_g, thermal stability and char yield than those of conventional cardanol-aniline benzoxazines. Further, functionalized bio-silica reinforced C-ima/BF-ima hybrid composites possess an improved thermal stability with lower value of dielectric constant and enhanced values of contact angle. Data resulted from different studies such as thermal, dielectric, surface and morphological analysis suggest that the developed C-ima/BF-ima blended matrix and F-SiO₂ reinforced composites can be used in the form of adhesives, sealants and encapsulants for microelectronics insulation applications under humid environment with improved performance and enhanced longevity.

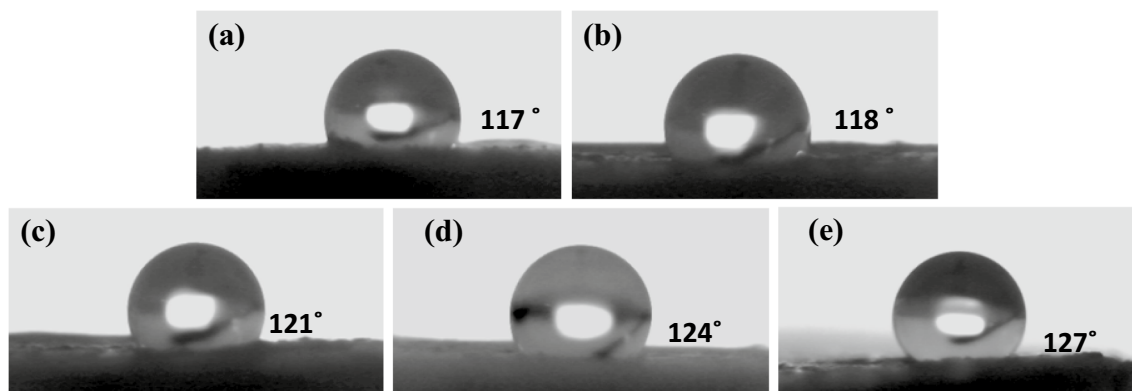


Fig. 13 Water contact angle image of a 1 wt% F-SiO₂, b 3 wt% F-SiO₂, c 5 wt% F-SiO₂, d 7 wt% F-SiO₂, e 10 wt% F-SiO₂ reinforced benzoxazine composites

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