



Blends of Chalcone Benzoxazine and Bio-benzoxazines Coated Cotton Fabrics for Oil–Water Separation and Bio-silica Reinforced Nanocomposites for Low-k Applications

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Abstract

In the present work, chalcone benzoxazine (Chal-Bz) was co-polymerized with two bio-based benzoxazines namely cardanol (CrAb) and eugenol (EuAb) benzoxazine and coated over cotton fabric. The Chal-Bz/CrAb and Chal-Bz/EuAb blends coated cotton fabrics show water contact angle values of 163° and 156° respectively and their oil–water separation efficiency were observed found to be 97 and 96% respectively. In addition, the glycidoxypropyltrimethoxysilane (GPTMS) functionalized bio-silica in varying weight percentages (1, 3, 5, 7 and 10 wt%) was also reinforced with two co-polymerized blended matrices to obtain respective composites. The developed composites were studied for their dielectric, thermal and morphological behaviours. The values of dielectric constant of 10 wt% bio-silica reinforced Chal-Bz/CrAb and Chal-Bz/EuAb composites were found to be 2.1 and 2.3, respectively. Similarly the values of contact angle of 10 wt% bio-silica reinforced chal-Bz/CrAb and Chal-Bz/EuAb composites were 137° and 116°, respectively. Data obtained from different studies suggest that these bio-silica reinforced benzoxazine composites can be used in the form of coatings, adhesives, sealants and encapsulants for high performance micro-electronics insulation applications under adverse environmental conditions.

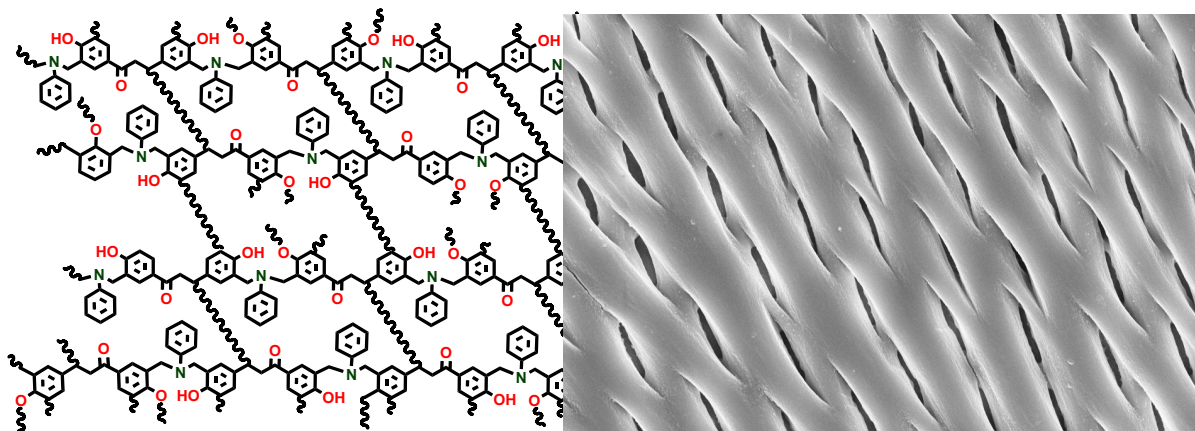
A. Hariharan and P. Prabunathan have contributed equally to this work.

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Graphic Abstract

Thermal assisted polymerization of chalcone based benzoxazine (Chal-Bz) with bio based benzoxazines cardanol-aniline based benzoxazine (CrAb) and eugenol-aniline based benzoxazine (EuAb)) for low k and oil–water separation application.



Keywords Bio-phenols · Polybenzoxazine · Hydrophobic/oleophilic nature · Oil–water separation · Dielectric constant

Introduction

Polybenzoxazines (PBZs) are phenolic resins, which possess attractive properties such as tunable dielectric constant (k) [1], excellent thermo-mechanical properties [2, 3], chemical stability [4], thermal stable [5], flame-retardancy [6, 7] and low moisture absorption [8, 9], etc., Tailor made properties can be achieved due to flexible molecular design of benzoxazine monomers. It is well known that fluorine atom build molecular structured polymer provides low-surface-free-energy, super hydrophobic surface because of their strong intermolecular hydrogen bonding after thermal polymerization [10]. Due to high cost substrates and tedious synthetic approach in building fluorine atom rich precursors, the need for the development of alternate cost competitive monomers are highly warranted. Thus, the introduction of long hydrocarbon chain into benzoxazine matrices can improve enhanced hydrophobicity, and are expected to replace fluorine based precursors [7, 8].

Cardanol and eugenol are naturally available phenolic derivatives and both have substituted alkyl and allyl groups in their molecular structure [11–13]. Reports suggest that cardanol based benzoxazine possess an enhanced hydrophobicity, lower values of dielectric constant, and good flexibility because of the long aliphatic chain present in the meta position [14]. Similarly, eugenol has two different substituents viz allyl and alkoxy group in ortho and meta positions [15]. However, replacing the conventional bis-phenol-A and bis-phenol-F based benzoxazines with the bio-precursors are limited because of their poor thermal stability and high curing temperatures [16]. Further, the existing conventional

bisphenol-A based materials are now slowly replaced due to environmental problems. While replacing bis-phenol-A with bisphenol-F involves higher cost. With the reason stated above and our continuous interest in developing variety of benzoxazines made us to proceed with the present work.

Earlier, our group and Lin et al. reported the development of chalcone based benzoxazines and their polymerization through photo-curing as well as thermal curing [17, 18]. Photo curing initially results in the cross-linking of α , β -unsaturated carbonyl functional groups and subsequent thermal curing results in ring opening polymerization of benzoxazine [19]. Earlier, we have reported the properties of MCM-41 as well as chalcone/Cyanate ester based composites [20], as well as the formation of thermal cross-linking behavior of α , β -unsaturated carbonyl functional groups with the olefin moiety of various co-substrates such as eugenol, cardanol, bismalimides [21]. In our previous study, thermal crosslink possibilities through various possible reactions such as Alder-ene, Wagner-Jauregg, Diels–Alder and Michel addition were discussed in detail [22–24]. Moreover, the resulted co-polymer of chalcone with eugenol, cardanol and bismalimides were found to show an excellent thermal stabilities as well as low curing behavior than those of conventional benzoxazines [21].

In continuation to our previous study, in the present work, an attempt has been made to develop GPTMS functionalized bio-silica reinforced biocomposites using the matrices derived by copolymerizing chalcone based benzoxazine with cardanol and eugenol based benzoxazines separately under appropriate experimental conditions. The molecular structure, thermal, morphology, dielectric and hydrophobic behavior of the

bio-based benzoxazine blended matrices and composites are studied in order to utilize them for high performance applications. Further, oil–water separation experiment was carried out with bio-based benzoxazine and chalcone-aniline benzoxazine blends coated superhydrophobic cotton fabrics. Data resulted from different studies are discussed and reported.

Experimental

Materials

Glycidoxypropyltrimethoxysilane (GPTMS) was purchased from Sigma Alrich, India. Analytical grades of p-hydroxy acetophenone, 4-hydroxybenzaldehyde, potassium hydroxide (KOH), ethanol, ethyl acetate, acetic acid, chloroform, sodium hydroxide (NaOH) were procured from SRL chemicals, India. Cardanol was obtained from Satya Cashew Products, Chennai. Eugenol, 1, 4-dioxane, aniline, paraformaldehyde, and anhydrous sodium sulfate (Na_2SO_4) were obtained from Spectrochem, India.

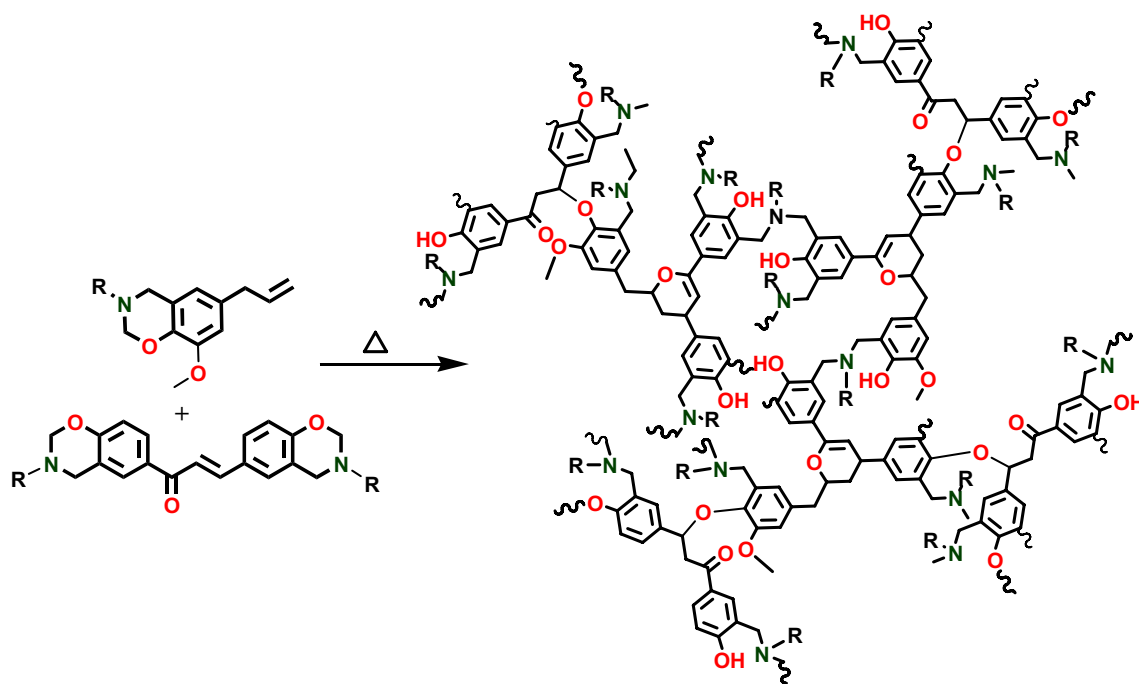
Synthesis of 1, 3-Bis (3, 4-dihydro-3-phenyl-2H-benzo [1, 3] oxazin-6-yl) prop-2-en-1-one (Chal-Bz) and Bio-based (cardanol/eugenol) Mono Functional Benzoxazines

Chalcone based bisphenol (1, 3-bis (4-hydroxyphenyl) prop-2-en-1-one) and its conversion to benzoxazine were carried

out as per our previous reported procedure [21]. In brief, 6 g of paraformaldehyde (0.2 mol) and 9.3 g of aniline (0.1 mol) were mixed in a 250 ml three-necked round bottomed flask under vigorous stirring in the presence of dioxane (60 ml) at 5 °C for an hour. After that 12 g of chalcone bisphenol (0.05 mol) was added to the mixture and the stirring was continued. The temperature was then gradually raised to 110 °C and maintained at this temperature until the completion of reaction. After the completion of the reaction, 50 ml of ethyl acetate was added to separate the organic phase. The obtained yellow product was washed several times with 2 N NaOH solution to remove the unreacted bisphenol. Then the crude product was purified and dried at 60 °C in a vacuum oven until the complete removal of solvent. The synthesis of cardanol and eugenol based benzoxazines (CrAb, and EuAb) using aniline as amine precursors were also prepared based on our earlier report [15, 21, 25].

Preparation and Functionalization of Bio-silica

Rice husk was washed with distilled water and dried at about 60 °C for 3 h. Dried rice husk was then bleached with conc. HCl to remove the unwanted contaminants and subsequently washed with water continuously till the pH become neutral. Then, the product was dried at 60 °C for 4 h and subsequently heated at 600 °C for 5 h in a muffle furnace, to obtain rice husk ash in which silica (SiO_2) is the major component (85%). Further, about 4 mL of GPTMS was mixed with 95% absolute ethanol and 5% deionized water and



Scheme 1 Thermal assisted polymerization of chalcone based benzoxazine (Chal-Bz) with eugenol-aniline based benzoxazine (EuAb)

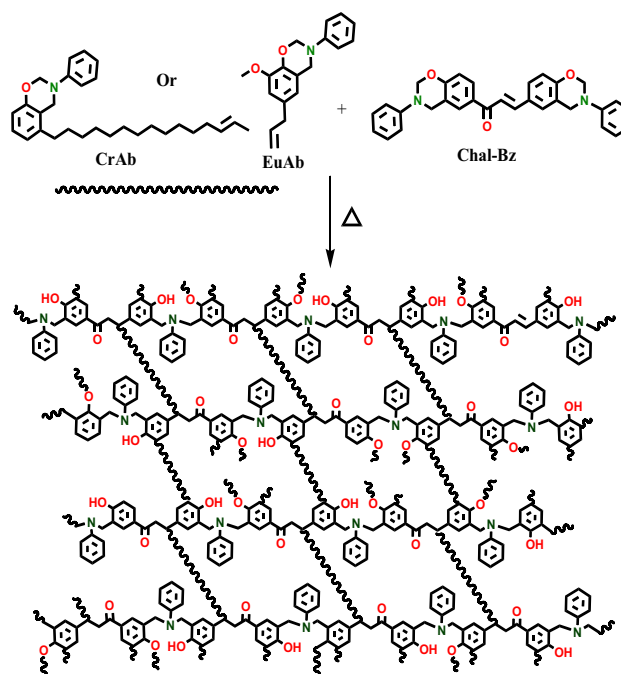
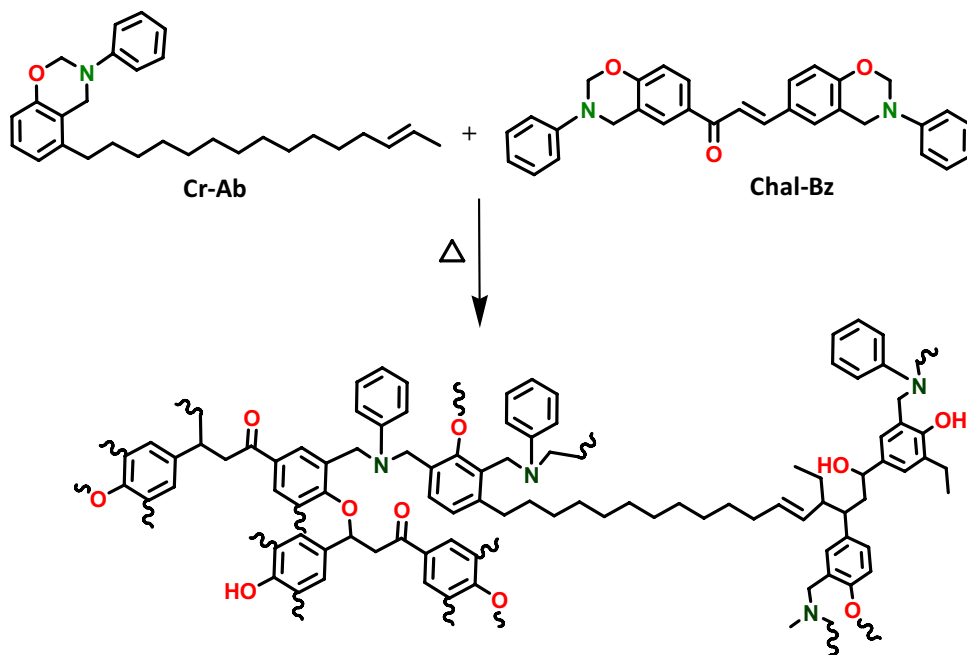
sonicated for 20 min. The solution pH was initially adjusted to 4.5 by using acetic acid and the sonication was continued for an hour. Subsequently, 10 g of bio-silica was added and the resulting mixture was sonicated for another 2 h and then refluxed for 24 h at 80 °C. The obtained product was then centrifuged and washed with water followed by ethanol and hexane. The GPTMS functionalized bio-silica was further dried in hot air oven at 80 °C in order to remove the moisture and then preserved in a desiccator for further use. [15, 26–28].

Preparation of Neat Benzoxazine Copolymer and Composites

The copolymerization of chalcone based benzoxazine (Ch-Bz) and bio-based mono functional benzoxazines (CrAb and EuAb) was carried out separately via thermal ring opening polymerization. Chalcone based benzoxazine (Chal-Bz) and bio-based benzoxazine monomers are taken in the ratio of 1:0.5. The chalcone based benzoxazine (Chal-Bz) and eugenol as well as cardanol benzoxazines blended separately in order to attain homogeneity. Further, before curing the blends were subjected to heating at 80 °C for 8 h to stabilize and to remove the traces of moisture if present any. After the stabilization, the temperature was raised to 230 °C at a heating rate of 20 °C per hour. The temperature is maintained for another 3 h in order to achieve the completion of curing. Schemes 1, 2 and 3 explain about the formation of co-polymerization of polybenzoxazine with cross linked network.

Scheme 4 illustrates the formation of GPTMS functionalized bio-silica reinforced chalcone based benzoxazines

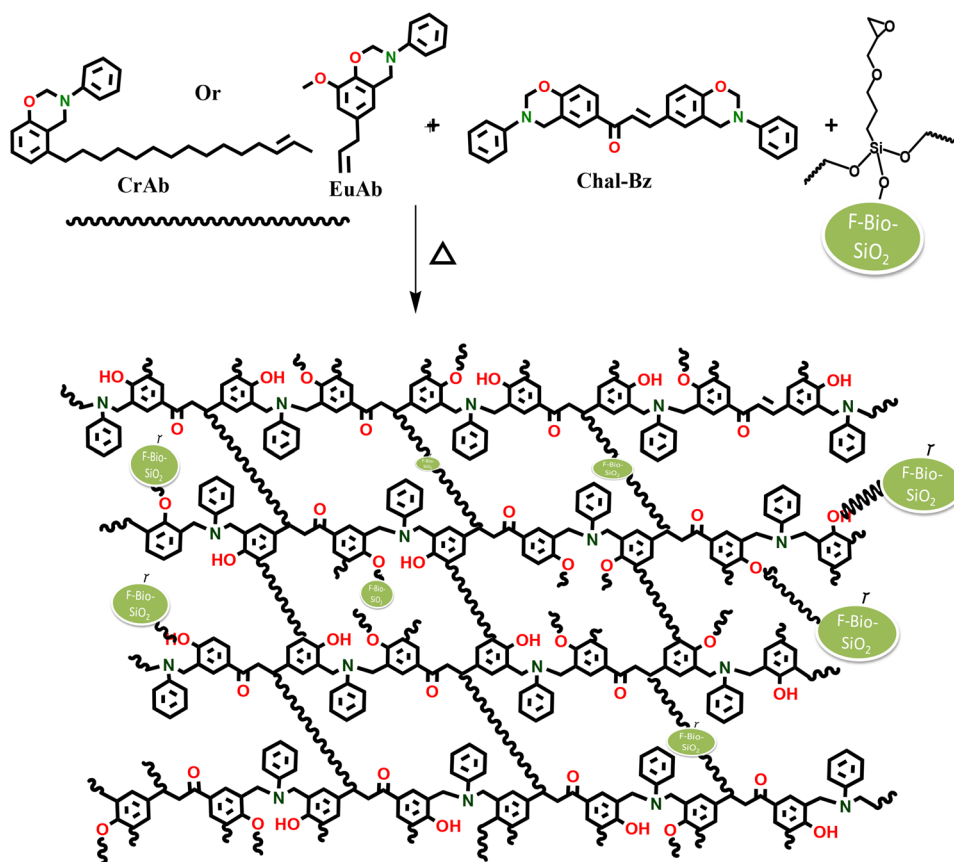
Scheme 2 Thermal assisted polymerization of chalcone based benzoxazine (Chal-Bz) with cardanol-aniline based benzoxazine (CrAb)



Scheme 3 Thermal assisted polymerization of chalcone based benzoxazine (Chal-Bz) with cardanol-aniline based benzoxazine (CrAb) and eugenol-aniline based benzoxazine (EuAb) with assumed weaving mechanism

copolymer with CrAb and EuAb. In brief, 1, 3, 5, 7, 10 wt% of bio-silica were separately mixed with Chal-Bz/CrAb, Chal-Bz/EuAb benzoxazines and stirred for 1 h to get the homogeneous product. The resulting copolymer blends were cured as similar to the process carried out for neat matrices.

Scheme 4 Schematic representations of model structural of bio-silica reinforced chalcone based benzoxazine (Chal-Bz) blended with cardanol-aniline based benzoxazine (CrAb) and eugenol-aniline based benzoxazine (EuAb)



Characterization

FT-IR spectra were recorded on a Perkin Elmer 6X FT-IR spectrometer using KBr as reference. NMR spectra were obtained with Bruker (400 MHz) using dimethylsulfoxide (d6-DMSO) as a solvent and tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded with Agilent mass spectrometer. DSC measurements were recorded using NETZSCH STA 449F3 under N_2 purge (60 mL min^{-1}) at scanning rate of $10 \text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was carried out using NETZSCH STA 449F3 taking 5 mg of sample under N_2 flow (260 mL min^{-1}) and controlling the heating rate at $20 \text{ }^\circ\text{C min}^{-1}$. X-ray diffraction patterns were recorded at room temperature, by monitoring the diffraction angle 2θ from 10 to 80° on a PANalytical X'pert3 powder—Netherlands. The surface morphology of the samples were studied using FESEM ZEISS Zigma Gemini 0336—USA, attached with EDX—Bruker nano X flash—German. Flame retardancy was analyzed based on UL-94 standards. HR-TEM images were captured using TECNAI G2 S-Twin high resolution transmission electron microscope. The dielectric constant was determined with help of an impedance analyzer (Solartron impedance analyzer 1260, UK) at room temperature using platinum electrode from 1 Hz to 1 MHz. Contact angle measurements

were carried out using a DMs 200, Kwoya goniometry, Japan with $5 \mu\text{l}$ of water as probe liquid.

Results and Discussion

The molecular structure of the chalcone based benzoxazine (Chal-Bz) cardanol-aniline (CrAb) and eugenol-aniline (EuAb) based benzoxazines were studied through spectral analysis. The FTIR spectra of chalcone (chal-Bz), cardanol-aniline (CrAb) and eugenol-aniline (EuAb) based benzoxazines are presented in Figure S1. The bands appeared at 1220 and 1090 cm^{-1} were attributed to the asymmetric and symmetric stretching vibrations of C–O–C bond in the benzoxazine respectively. The band appeared at 1174 cm^{-1} ascertains the presence of asymmetric stretching of C–N–C. Similarly, the appearance of bands at 930 and 1500 cm^{-1} correspond to a tri-substituted benzene ring which confirms the formation of benzoxazine ring structure. Further, the band appeared at 3009 cm^{-1} corresponds to C–H stretching vibration of the benzene ring. Characteristic absorption bands appeared at around 2925 and 2853 cm^{-1} represent the asymmetric and symmetric stretching vibrations of CH_2 of oxazine ring respectively as well as alkyl side chain of cardanol moiety.

In addition, the proton NMR spectra of chalcone (chal-Bz), cardanol-aniline (CrAb) and eugenol-aniline (EuAb) based benzoxazines are presented in Figures S2, S3, S4. The formation of benzoxazine ring was confirmed by the appearance of resonance peaks around 4.6 (Ar-CH₂-N) and 5.6 ppm (O-CH₂-N) in ¹H-NMR spectroscopy (Figures S2, S3 and S4).

The curing temperature of the covalently bonded copolymeric benzoxazine blends were studied by DSC technique. The DSC data resulted are presented in Fig. 1. The exothermic peak appeared at 206 °C corresponds to the curing temperature of the neat Chal-Bz matrix. Further, bio-based CrAb and EuAb benzoxazines are blended with chalcone benzoxazine are subjected to curing analysis. From the DSC data (Fig. 1), it was ascertained that the copolymerization of chal-Bz and CrAb proceeds at 196 °C and that of Chal-Bz and EuAb occurs at 205 °C. These cure temperature data are significantly lower when compared with that of conventional benzoxazines [29]. During thermal treatment, the olefinic group present in bio-based phenolic benzoxazine will undergo Alder-ene reaction with the unsaturated carbonyl group of chalcone and results in a highly cross-linked polybenzoxazine network [21]. Further, the solid state ¹³C-NMR (Figure S5, Supporting Information) illustrates formation of Alder-ene as well as Michael addition reaction. After the copolymerization of Chal-Bz/EuAb, the appearance of a broad signal at 205 ppm confirms the presence of carbonyl group. The appearance of signals at 47 and 39 ppm confirm the presence of methylene group of carbonyl neighboring and aryl substituted tertiary methyl group respectively. Similarly, the presence of alkene neighboring methylene group was

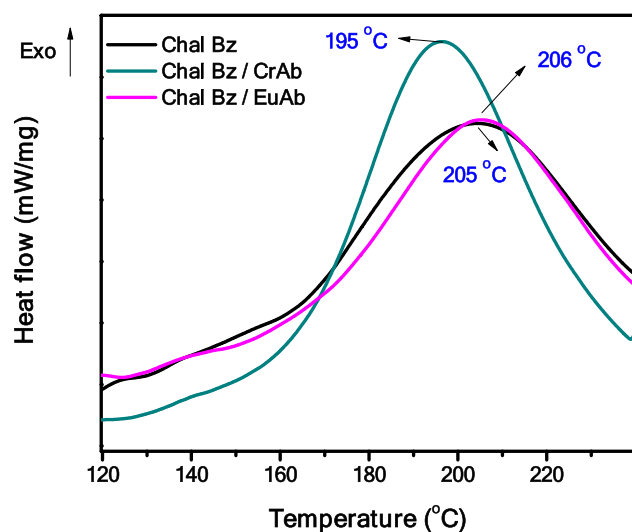


Fig. 1 DSC curves of neat Chal-Bz, bio based Chal-Bz/CrAb and Chal-Bz/EuAb matrices

ascertained from the appearance of a signal at 33 ppm. From the results, it is concluded that the formation of the Alder-ene adduct. In addition, both CrAb and EuAb can act as reactive diluents as well as a co-cross linking agents in the curing reaction [21].

The formation of bio-composites using bio-silica reinforced bio-benzoxazine copolymerized Chal-Bz nanocomposites are studied using FTIR and the results obtained are presented in Figs. 2 (bio-silica/Chal-Bz/CrAb) and 3 (bio-silica/Chal-Bz/EuAb). The appearance of band at 930 cm⁻¹ corresponds to the disappearance of oxazine. The appearance of band at 1250 cm⁻¹ suggests that the formation of ether bonds through Michael addition reaction. In addition the bands appeared at 1095 and 817 cm⁻¹ confirm the presence of Si-O-Si- linkages, which ascertained

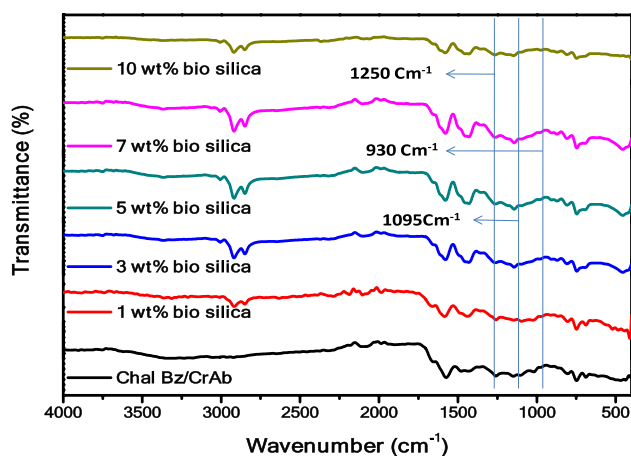


Fig. 2 FT-IR spectra of bio silica reinforced Chal-Bz/CrAb composites

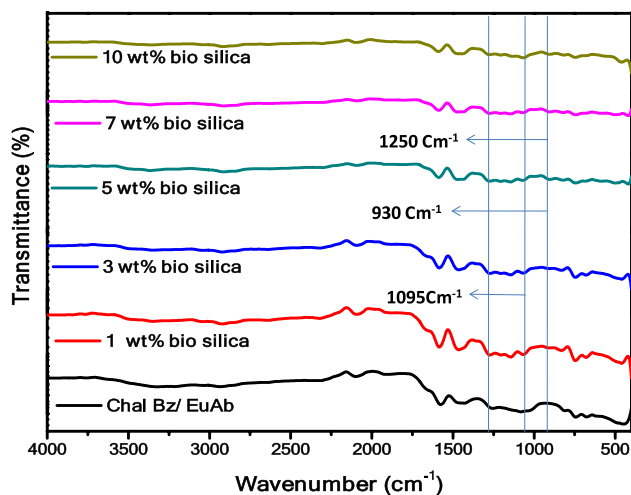


Fig. 3 FT-IR spectra of bio-silica reinforced Chal-Bz/EuAb composites

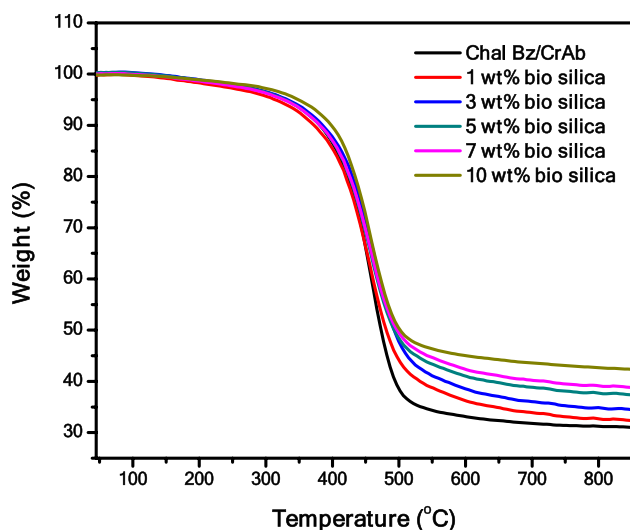


Fig. 4 TGA Profile of bio-silica reinforced with Chal-Bz/CrAb composites

the asymmetric stretching and symmetric stretching vibrations of bio-silica respectively.

Thermal Behavior of Bio-silica Reinforced Benzoxazine Copolymers

TGA profile for the binary blends of Chal-Bz with varying weight percentages (100:25, 100:50, 100:75 and 100:100) of CrAb and EuAb are reported earlier [21]. Among which the blend of Chal-Bz/EuAb with 100:50 wt% ratio possesses a better char yield and higher degradation temperature than those of neat chalcone benzoxazine system. This may be explained due to the formation of ether linkages as a result of Michael addition reaction and Alder-ene reactions occurred between the hydroxyl group and an olefinic group of bio-based phenolic benzoxazine with unsaturated carbonyl functionality of chalcones. Further, it was noticed that the cardanol based benzoxazine blends possess the lower thermal stability than that of neat chalcone based benzoxazine, though it is equivalent to that of conventional benzoxazine [21]. However the addition of CrAb found to reduce the

thermal stability of Chal-Bz. This might be due to the presence of thermally weak aliphatic chain.

Figure 4 and Table 1 present the TGA data for the copolymers of Chal-Bz/CrAb polybenzoxazine and bio-silica reinforced Chal-Bz/CrAb polybenzoxazine nanocomposites. The neat copolymeric matrix of Chal-Bz/CrAb and bio-silica reinforced Chal-Bz/CrAb polybenzoxazine nanocomposites show similar degradation behavior. It was noticed that the initial weight loss was associated with the removal of traces of moisture present in the sample as well as the degradation of aliphatic moieties. The value of T_{max} was found to be 455 °C for neat matrix, whereas the value of T_{max} was increased with increase in weight percentage of silica and reached to 469 °C for 10 wt% bio-silica reinforcement. The values of percentage char yield of copolymeric matrix of Chal-Bz/CrAb was found to be 30% for neat Chal-Bz/CrAb, whereas the values of char yield obtained for 1 wt%, 3 wt%, 5 wt%, 7 wt% and 10 wt% bio-silica reinforced Chal-Bz/CrAb polybenzoxazine nanocomposites are 32% and 34%, 37%, 38% and 40% respectively.

The TGA data obtained for the copolymeric matrix of Chal-Bz/EuAb and bio-silica reinforced Chal-Bz/CrAb polybenzoxazine nanocomposites are presented in Fig. 5 and Table 2. It was also observed that both the neat matrix of Chal-Bz/EuAb and bio-silica reinforced Chal-Bz/EuAb polybenzoxazine nanocomposites show similar degradation behavior as noticed in the case of Chal-Bz/CrAb. Initial weight loss is associated with the removal of traces of moisture present as well as the degradation of aliphatic chains. The value of T_{max} was found to be 471 °C for neat matrix, whereas that of the T_{max} increased with increase in weight percentage of bio-silica and reached to 485 °C for 10 wt% bio-silica reinforcement. The value of percentage char yield of copolymeric matrix of Chal-Bz/CrAb was found to be 36.3% and that of reinforced with 1 wt%, 3 wt%, 5 wt%, 7 wt% and 10 wt% bio-silica obtained are 48% and 51%, 53%, 55% and 56%, respectively.

Data obtained from thermal studies suggest that the cardanol based benzoxazine copolymeric blend and its composites possess the lower thermal stability than that of eugenol benzoxazine based copolymer composites. This may

Table 1 Thermal and dielectric behavior of (Chal-Bz)/CrAb benzoxazine matrix and composites

Samples	Temperature (°C)			Char yield % at LOI 800 °C	Dielectric constant	
	T_g	$T_{10\%}$	T_{max}			
Neat chal-Bz/CrAb	207	371	455	30	29.5	3.9
1 wt% biosilica/chal-Bz/CrAb	207	373	460	32	30.3	3.6
3 wt% biosilica/chal-Bz/CrAb	209	383	464	34	31.1	3.2
5 wt% biosilica/chal-Bz/CrAb	212	382	467	37	32.3	3.1
7 wt% biosilica/chal-Bz/CrAb	213	382	468	38	32.7	2.5
10 wt% biosilica/chal-Bz/CrAb	214	399	469	40	33.5	2.1

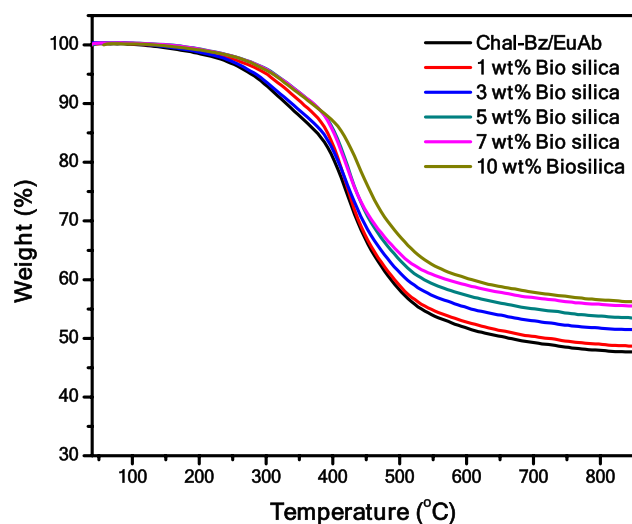


Fig. 5 TGA Profile of bio-silica reinforced with Chal-Bz/EuAb composites

be explained due to the inferior thermal stability behavior of long aliphatic chain of cardanol. However, when the weight percentage concentration of bio-silica increases, the stability of the resulting composites also increased accordingly. This may be explained due to the intercalation of bio-silica with the PBZ matrices, which induces the formation of the intercross linked three dimensional hybrid network structure. Thus, the formed hybrid network acts as a heat barrier and provides more thermal permanence to the resulted composites. Further, it is more interesting to note that the stability of copolymeric matrices are higher than that of conventional benzoxazines of bisphenol-A and bisphenol-F aniline based benzoxazines. This may be explained due to the formation of ether linkages as a result of Michael addition reaction and Alder-ene reactions occurred between the hydroxyl group and an olefinic group of bio based phenolic benzoxazine with unsaturated carbonyl functionality of chalcones, which has been reported by our group earlier [16]. Further the same have been confirmed through the morphological studies discussed in the later part of the manuscript.

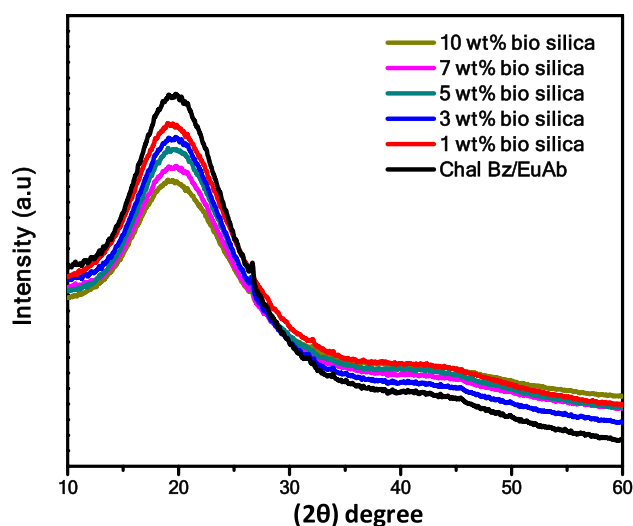


Fig. 6 XRD Profile of bio-silica 1, 3, 5, 7, 10 wt% reinforced with Chal-Bz/EuAb composites

Flame Retardant Property

The flame retardant behavior of the materials can be accessed from the value of Limiting Oxygen Index (LOI). The values of LOI are calculated using the Van Krevelen and Hoftyzer relation. $LOI = 17.5 + 0.4 CR$ [5, 30, 31]. The percentage char yield (CR) of the samples were obtained from TGA analysis at 800 °C (Tables 1 and 2). It is experimentally proved that the materials with higher LOI values possess an enhanced flame retardant property. The values of LOI of polymer systems should be above threshold value of 26 and above, to render them self-extinguishing and for their suitability for many applications requiring good flame resistance [32–40]. From the data resulted, the values of LOI Chal-Bz/CrAb and Chal-Bz/EuAb copolymers were found to be higher than or equal to that of conventional benzoxazines. The calculated LOI value of Chal-Bz/CrAb is 29.6 and that of Chal/EuAb is 36.3. LOI values of 1, 3, 5, 7, 10 wt% bio-silica reinforced Chal-Bz/CrAb benzoxazine copolymer composites are 30.3, 31.1, 32.3, 32.7 and 33.5, respectively,

Table 2 Thermal and dielectric behavior of (Chal-Bz)/EuAb benzoxazine matrix and composites

Samples	Temperature (°C)			Char yield % at 800 °C	LOI	Dielectric constant
	T _g	T _{10%}	T _{max}			
Neat chal-Bz/EuAb	251	328	471	47	36.3	4.1
1 wt% biosilica/chal-Bz/EuAb	253	359	475	48	36.7	3.6
3 wt% biosilica/chal-Bz/EuAb	253	338	476	51	37.9	3.2
5 wt% biosilica/chal-Bz/EuAb	254	370	476	53	38.7	2.7
7 wt% biosilica/chal-Bz/EuAb	256	370	478	55	39.5	2.4
10 wt% biosilica/chal-Bz/EuAb	257	371	485	56	39.9	2.3

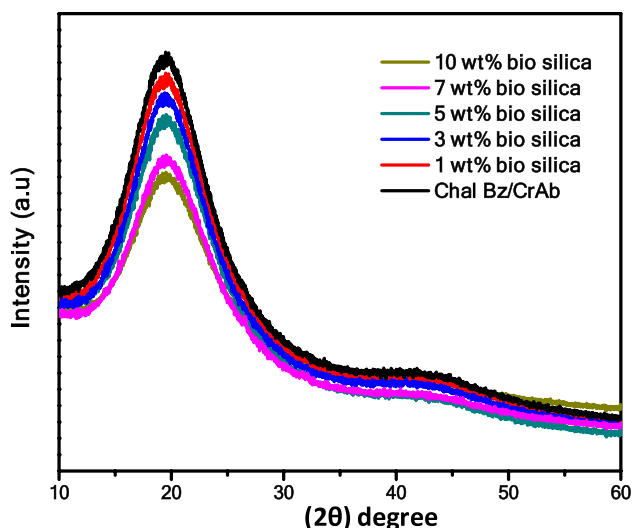


Fig. 7 XRD Profile of bio- silica 1, 3, 5, 7, 10 wt% reinforced with Chal-Bz/CrAb composites

whereas the LOI values of similar weight percentages of bio-silica reinforced Chal-Bz/EuAb benzoxazine copolymer composites are 36.7, 37.9, 38.7, 39.5 and 39.9, respectively.

Morphological Properties

Figures 6 and 7 illustrate the XRD patterns of bio-silica reinforced Chal-Bz/CrAb and Chal-Bz/CrAb benzoxazine composites along with their neat matrices. The appearance of a broad peak at $2\theta = 20^\circ$ ascertains the amorphous nature. Further, it also confirms that the existence of homogeneous distribution of silica within the polymer matrices without any aggregation, which in turn that contributes to an enhanced thermal stability and improved flame retardant behavior as discussed earlier. Also, the morphological behaviour of both the bio-silica and functionalized bio-silica were analyzed using XRD and presented in Figure S6 (Supporting Information). The broad diffraction patterns observed at $2\theta = 21^\circ$ suggest that both the bio-silica and functionalized bio-silica were found to be in amorphous state.

Further, the morphology of the developed polymer matrices of Chal-Bz/CrAb and Chal-Bz/EuAb along with their respective bio-silica reinforced composites are presented in Figs. 8a–d and 9a–d respectively. It is interesting to note that both the polymer matrices of Chal-Bz/CrAb and Chal-Bz/EuAb are appeared to be weaved network with continuous weft and warp structures of a fabric. The neat matrices in both cases show a smooth fibrous structure whereas, the

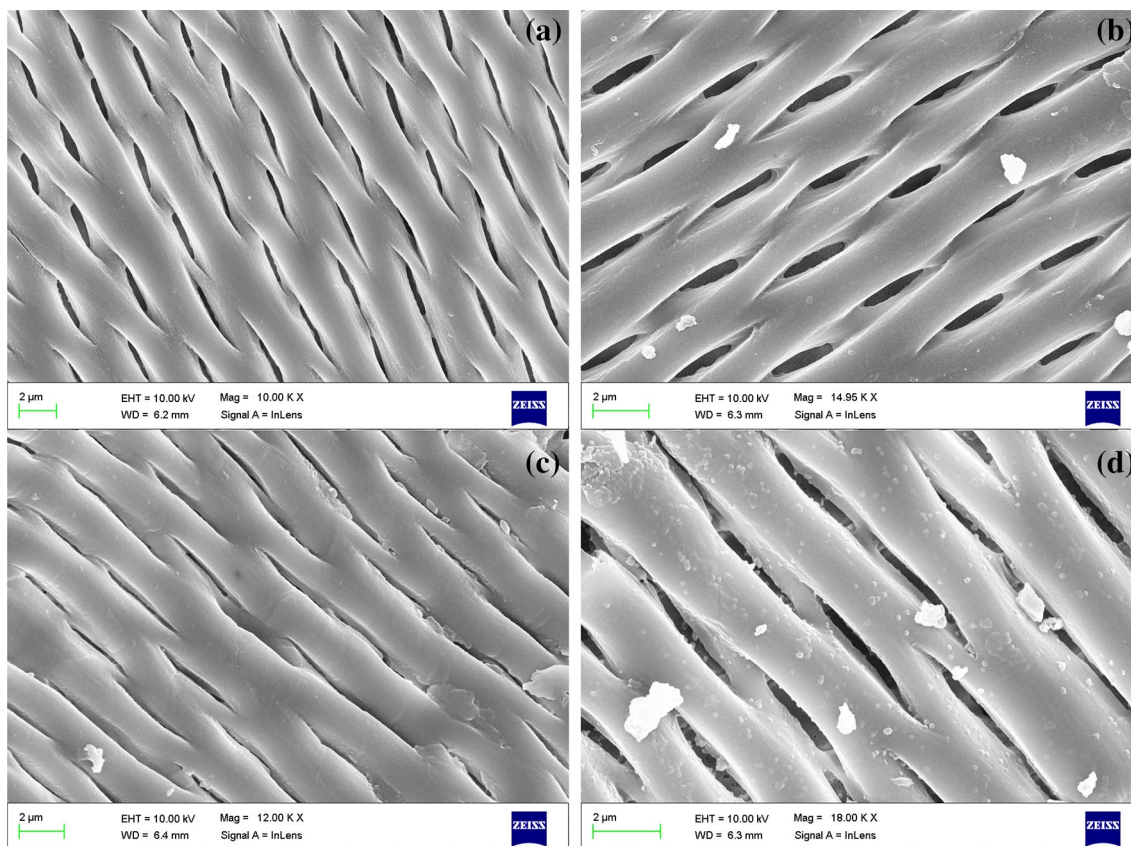


Fig. 8 Scanning electron microscopy (SEM) images of **a** neat Chal-Bz/CrAb, **b** 3 wt%, **c** 5 wt%, **d** 10 wt% bio-silica incorporated Chal-Bz/CrAb

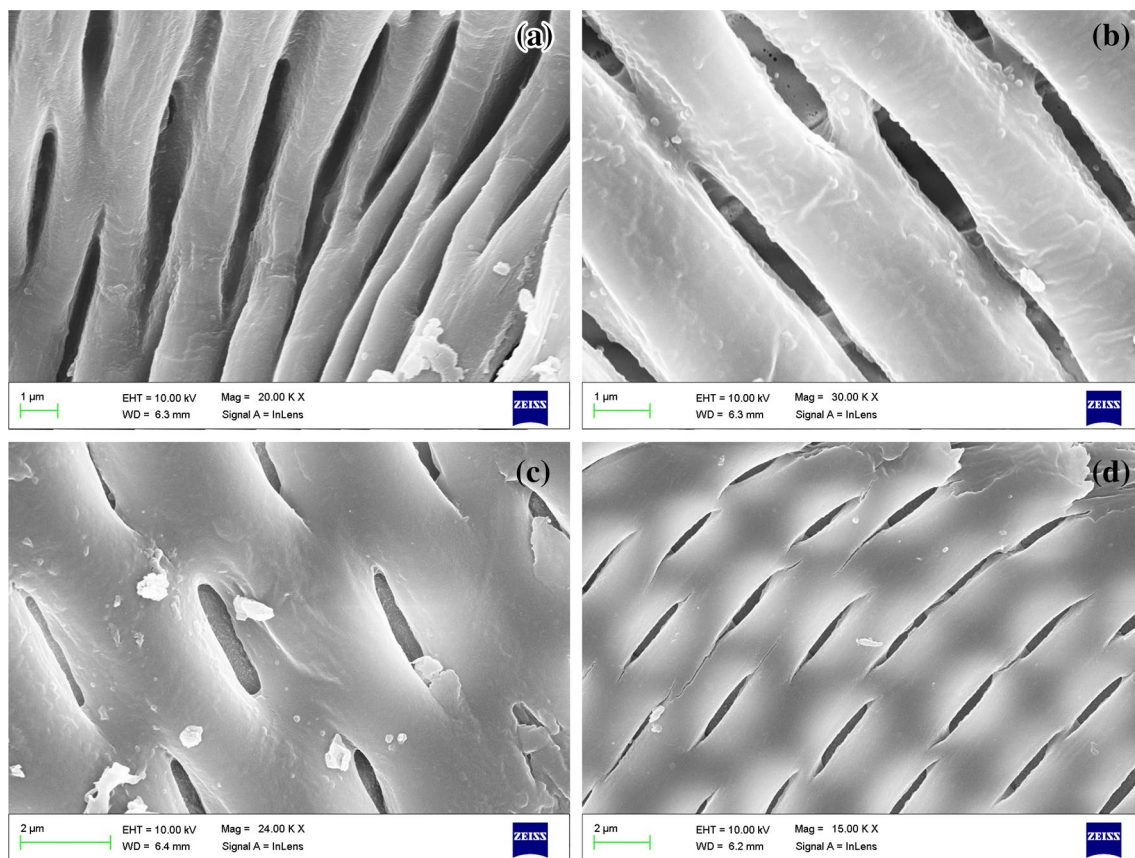


Fig. 9 Scanning electron microscopy (SEM) images of **a** neat Chal-Bz/EuAb, **b** 3 wt%, **c** 5 wt%, **d** 10 wt% bio-silica incorporated Chal-Bz/EuAb

bio-silica reinforced composites exhibit rough surfaces with clusters of nano-silica. Further, in between the fibrous network the pores are noticed, which was measured to be around 420 nm for 10 wt% bio-silica reinforced cardanol based copolymer composites. In case of 10 wt% bio-silica reinforced eugenol based copolymer composites the pores structures with nearly 380 nm was noticed. In addition to SEM micrographs, the distribution of bio-silica within the composites was analyzed using TEM and the images are presented in Figs. 10 and 11. From the TEM images, the dark regions indicate the presence of silica layer. TEM micrographs clearly show the occurrence of effective interfacial interaction between the bio-silica and benzoxazine matrix, which became more intense as the concentration of silica increases.

The dielectric constant (K) of varying weight percentages (0, 1, 3, 5, 7 and 10 wt%) of bio-silica reinforced Chal-Bz/CrAb copolymer nanocomposites at 1 MHz are presented in Table 1. The value of dielectric constant obtained for neat matrix is found to be 3.9, whereas the value of dielectric constant is decreased with increasing weight percentages of silica reinforcement. Thus, 1 wt% of bio-silica reinforced Chal-Bz/CrAb benzoxazine is 3.6 at 1 MHz. Similarly, 3 and

5 wt% of bio-silica reinforced Chal-Bz/CrAb composites are found to be 3.2 and 3.1, respectively. Upon further addition of silica the value of dielectric constant tends to decrease to 2.5 and 2.1 for 7 wt% and 10 wt% bio-silica reinforced Chal-Bz/CrAb composites respectively. Similarly, the values of dielectric constant obtained for neat matrix and 1, 3, 5, 7 and 10 wt% of bio-silica reinforced Chal-Bz/EuAb nanocomposites are 4.1, 3.6, 3.2, 2.7, 2.4 and 2.3 respectively. The reduction in the value of dielectric constant with increasing weight percentage concentration of bio-silica reduces the dipole-dipole interaction within the composites and contributes to the effective reduction in the value of dielectric constant. Further, the presence of pores and voids in the cases of both copolymeric (Chal-Bz/CrAb and Chal-Bz/EuAb) composites as ascertained from the morphological studies support the low k values [41]. In addition the contact angle values obtained for the bio-silica reinforced composites are also strengthen the low k behavior and in turn suggest that these bio-based silica reinforced composites can be conveniently used in the form of adhesives coatings, and sealants for high performance microelectronics applications.

The contact angle images of neat matrix, 1, 3, 5, 7 and 10 wt% bio-silica reinforced Chal-Bz/CrAb and Chal-Bz/

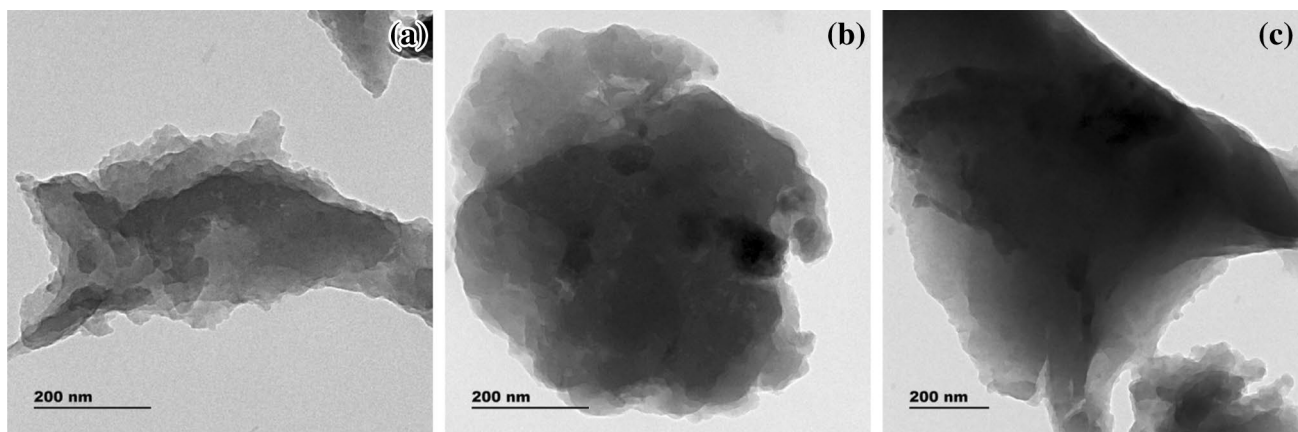


Fig. 10 TEM micrograph of a 3 wt%, b 5 wt%, c 10 wt% bio-silica reinforced Chal-Bz/CrAb nanocomposites

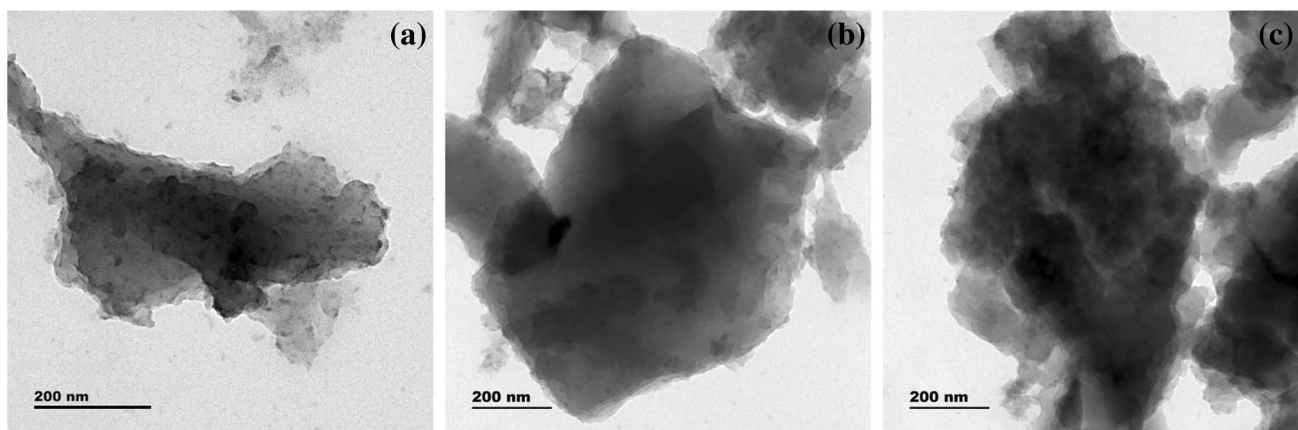


Fig. 11 TEM micrograph of a 3 wt%, b 5 wt%, c 10 wt% bio-silica reinforced Chal-Bz/EuAb nanocomposites

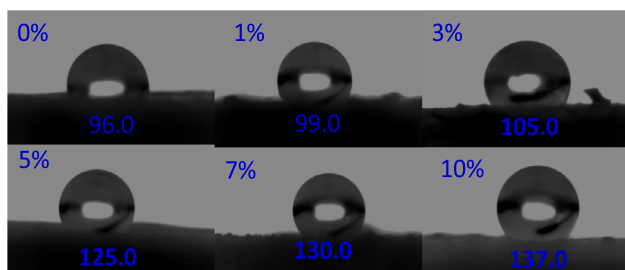


Fig. 12 Contact angle images of bio-silica reinforced Chal-Bz/CrAb composites

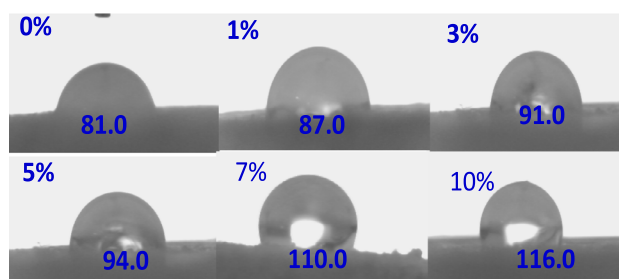


Fig. 13 Contact angle images of bio-silica reinforced Chal-Bz/EuAb composites

EuAb composites are presented in Figs. 12 and 13 respectively. It can be observed that the reinforced composites possess the higher values of contact angle when compared to that of neat copolymerized polybenzoxazines, due to the lower affinity resulted between surface of the composites and water, which in turn enhances the hydrophobic behavior. It

may be explained that the reinforcement of silica contributes to the lower surface free energy due the presence of (-Si-O-Si-) linkage in the copolymerized matrix. In comparison between the Chal-Bz/CrAb and Chal-Bz/EuAb composites, the former possesses the higher values of contact angle than that of the latter. This may be explained due to

the presence of long aliphatic chain in cardanol moiety and less polar nature of bio-silica which enhances the value of contact angle. In addition, the formation and existence of intra-molecular hydrogen bonding in the composite network results in enhanced water contact angle. Thus, it is suggested that the developed composites with enhanced hydrophobic behavior can be used as an effective insulation material under humid environmental conditions.

Preparation of Benzoxazine Coated Fabric

Cotton fabric was washed in order to remove any impurities present in it with distilled water. Further the washed and dried fabric was treated with hexane solvent to remove any organic impurities like fats, wax, etc. Then the fabric was soaked with 5 wt% NaOH for 3 h at room temperature for surface activation and to remove any greasy material if any present and dried. Further the cotton fabric was treated with 1% acetic acid for neutralization and then washed with distilled water followed by drying the fabric at 60 °C for 12 h. Now the dried fabric was separately soaked with 4 wt% solution of Chal Bz/CrAb and Chal Bz/EuAb dissolved in THF solvent at room temperature for 1 h. Further, the soaked fabrics from the respective benzoxazine solutions were removed and dried at 60 °C for 2 h and then placed in a hot air oven at 240 °C for 5 min for thermal curing of benzoxazines. The schematic representations of the preparation of benzoxazines coated cotton fabric are presented in Fig. 14.

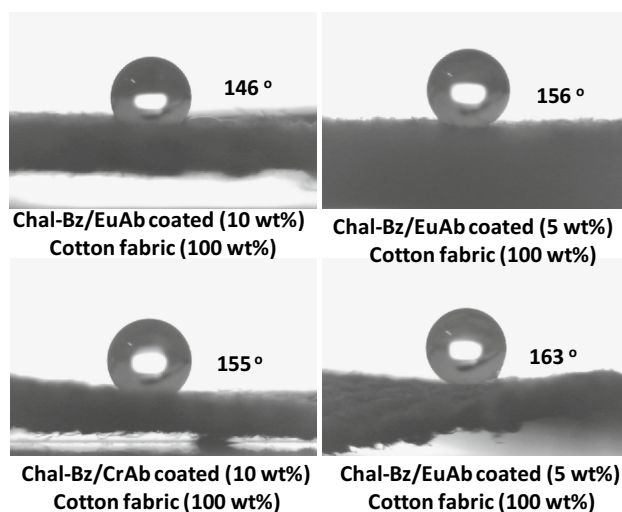


Fig. 15 Water contact angle of benzoxazines coated cotton fabrics

Oil–Water Separation Studies of Benzoxazine Coated Fabrics

The thermally cured cotton fabric coated with benzoxazines viz., chal Bz/CrAb and chal Bz/EuAb possess the values of contact angle (Fig. 15) against water are 163° and 156°, respectively, which is higher than that of cotton fabric coated with benzoxazine obtained from bisphenol-A and aniline (132°) [42]. The higher values of contact angle obtained for cardanol and eugenol benzoxazines coated fabrics may be explained due to the presence of long alkyl chain in cardanol

Preparation of benzoxazine coated fabric.

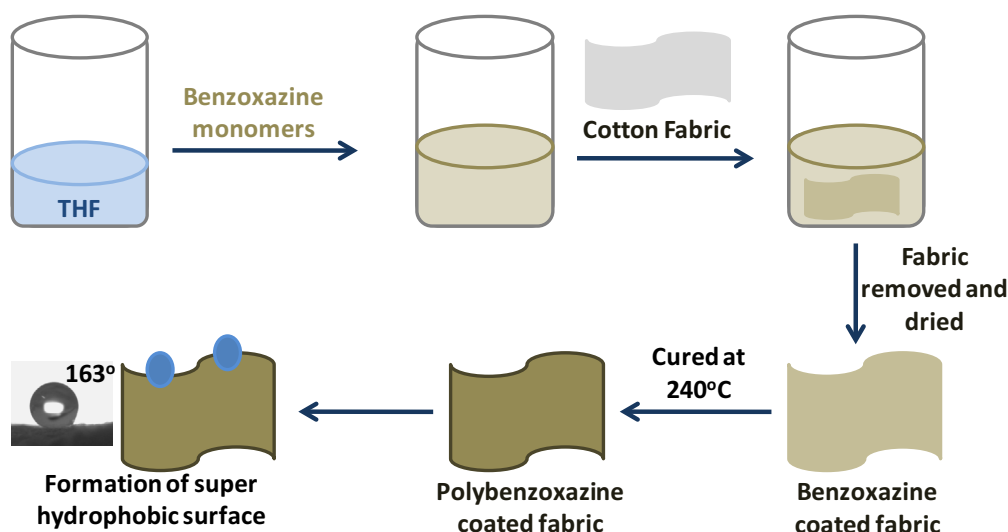


Fig. 14 Preparation of benzoxazines coated cotton fabrics

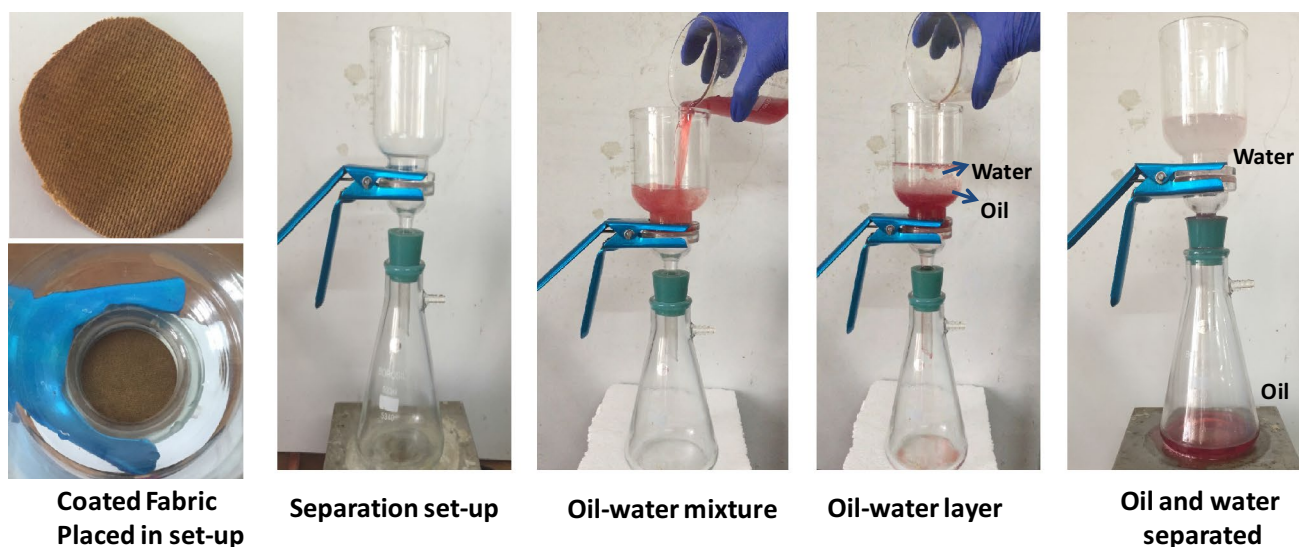


Fig. 16 Oil-water separation by benzoxazine coated cotton fabrics

and allyl and methoxy groups present, in the case of eugenol skeleton. Further the cotton fabrics coated with benzoxazine viz., Chal Bz/CrAb and Chal Bz/EuAb have been tested for their oleophilic behavior by utilizing them as filtration substrate for the separation of oil–water mixture. The oil–water mixture was prepared by mixing the engine oil (20W40, density = 0.88 g.cm^{-3}) and distilled water in equal volumes. In order to bring the oil phase down, a high density non-polar solvent dichloromethane (density 1.325 g.cm^{-3}) has been added to oil–water mixture. Then the separation of oil was carried out using benzoxazine coated fabrics at room temperature without applying any external force as per the experimental set-up presented in Fig. 16.

From the oil–water separation experiments using benzoxazines viz., chal Bz/CrAb and chal Bz/EuAb coated cotton fabrics, the separation efficiency was found to be 97 and 96% respectively according to the Eq. 1.

$$\text{Separation Efficiency (\%)} = \frac{\text{Volume of the oil after separation}}{\text{Volume of the oil before separation}} \times 100 \quad (1)$$

Similarly the flux values calculated from the experiments for benzoxazines viz., chal Bz/CrAb and chal Bz/EuAb coated cotton fabrics are 476 and 471 respectively according to the Eq. 2.

$$\text{Flux} = \frac{\text{Volume of the permeated oil}}{\text{Area of the fabric} \times \text{time for separation}} \quad (2)$$

Further, the oil–water separation efficiency of cotton fabric coated with benzoxazine viz., Chal Bz/CrAb and Chal Bz/EuAb are repeated 10 times after washing and drying the fabrics at end of the each experiment. From the oil separation experiments carried out after 10 cycles using the fabrics, it was found to be the separation efficiency of fabrics are about 93 and 92% respectively (Fig. 17). Similarly the flux values obtained after 10 cycles are 429 and 428 $\text{L/m}^2\text{h}$ respectively (Fig. 17).

Conclusion

Cardanol and eugenol benzoxazine based co-polymers of chalcone benzoxazine matrices were developed. The chal Bz/CrAb and chal Bz/EuAb co-polymer matrices coated cotton fabric delivers hydrophobic surfaces which was evidenced from their contact angle values against water as 163° and 156° , respectively. The observed values are higher than that of cotton fabric coated with benzoxazine obtained from bisphenol-A and aniline (132°). Subsequent oil–water separation studies suggest that the separation efficiency of chal Bz/CrAb coated fabric was found to be shows comparatively higher efficiency (97%) than that of chal Bz/EuAb coated fabric (96%). Also, the separation efficiency and flux values are reasonably maintained up to 10 cycles.

Further, the blended matrices were subsequently reinforced with varying weight percentages of (1, 3, 5, 7 and

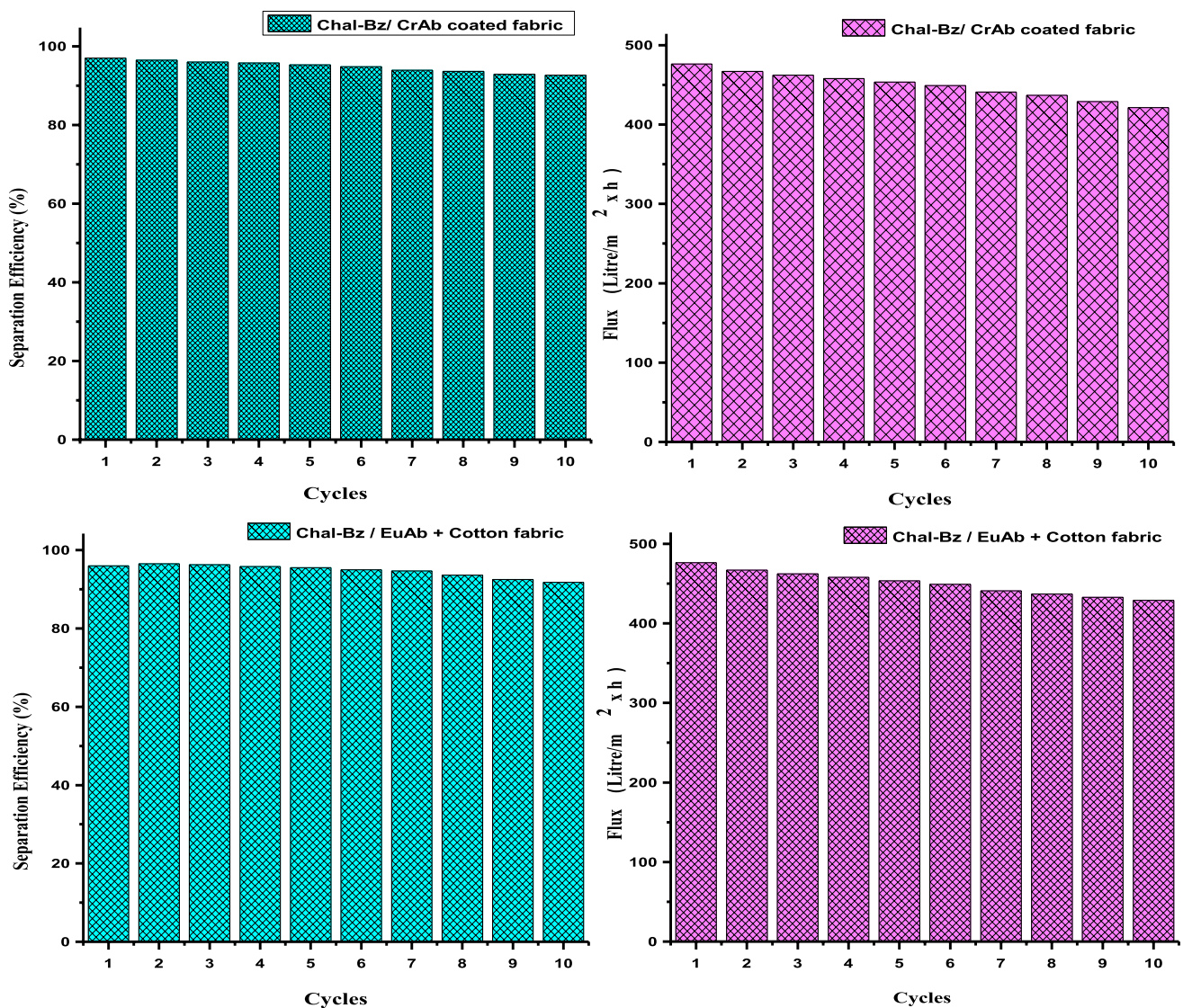


Fig. 17 Oil-water sample separation efficiency and flux of Chal Bz/CrAb and Chal Bz/EuAb coated cotton fabrics

10 wt%) of GPTMS functionalized bio-silica to obtain composites and were characterized using different analytical techniques. Composites obtained from 10 wt% bio-silica and co-polymer of chalcone benzoxazine with monofunctional cardanol benzoxazine results enhanced hydrophobicity (137°) and lower dielectric constant (2.1) than those of the composites of chalcone eugenol co-polymeric composites. The presence of long aliphatic chain moiety in cardanol contributes to better water repulsion and creates more free space in the matrices, which alter the surface morphology as well as dielectric properties. However, the chalcone benzoxazine copolymerized eugenol benzoxazine composites possess higher thermal stability and thus delivers higher char yield (56%).

Thus, it is suggested that the developed matrices and composites can be used in the form of adhesives, sealants,

encapsulants and coatings for high performance micro-electronics insulation applications under adverse environmental conditions.

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