



Eco-friendly fully bio-based polybenzoxazine-silica hybrid materials by sol–gel approach

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Abstract

In the present work, a high thermal and flame-retardant polybenzoxazine-silica hybrid material has been synthesized using renewable raw materials (including eugenol and furfurylamine) via a greener sol–gel-based approach. Inorganic component tetraethoxysilane (TEOS) was introduced into eugenol benzoxazine (BZ–E–F) with the help of (3-mercaptopropyl) trimethoxysilane (MPTMS) as a coupling agent viz thiol-ene click approach among the mercapto group (–SH) of MPTMS and allyl functional group in the eugenol. The developed BZ–E–F monomer and PBZ–E–F hybrids are characterized to check the molecular structures, curing behaviour, thermal stability and flame-retardant properties. The thermal studies reveal that the char yield increases to 67.54 from 41.32 and LOI increased to 44.52 from 34.03 for PBZ–E–F silica hybrid. The thermal and flame-resistant studies strongly suggest that the prepared sustainable and eco-friendly PBZ silica hybrid can be used to replace the petroleum-based polymeric materials for better thermal and flame-resistant applications.

Keywords Bio-based benzoxazine · Renewable raw materials · Thiol-ene click · Silica hybrid · Flame retardant

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Introduction

Polybenzoxazines (PBZs) emerges as a new class of phenolic resins owing to their collective thermal and mechanical stability with vast molecular flexibility, which allows overcoming numerous shortcomings of traditional phenolics [1–4]. Thus, polybenzoxazines extend an enormous interest in the high-performance thermoset polymer resins. The remarkable properties of polybenzoxazines including high glass transition temperature, higher char yield, good flame retardant, better mechanical properties, lower moisture absorption, minimal shrinkage, and no side product formed during polymerization etc. make these types of materials unique and unparallel than the other polymeric materials, used for similar applications [5–12].

In the recent years, due to the economic and environmental concerns, research efforts are being increasingly devoted to the development of polymer materials from renewable materials instead of petroleum founded materials [12–25]. In this concern, PBZs cannot be an exception. Actually, many academic and industrial efforts have promised for the development of renewable, sustainable and eco-friendly PBZs. Generally, BZs are synthesized using primary amine, phenol and formaldehyde through Mannich reaction. Among sustainable phenolic alternatives to replace the traditional phenolic moieties, eugenol emerges as one of the best impending materials for the green production of PBZs due to its, high abundance and less production cost. Eugenol is naturally available phenolic material extracted from various renewable sources such as, clove, cinnamon, tulsi, turmeric, pepper and thyme. The chemical structures of eugenol are very exciting as an allyl group on side chain allows further cross-linking with many functional groups with organic and inorganic materials [3]. In addition, the reactive phenol group offers many chemical reactions including esterification, cyanogenation, alkylation, and novalac, epoxy and BZs, etc., [18].

However, eugenol-based PBZs, their wider applications is somehow restricted because of their relatively low crosslink density as the ring opening polymerization is hindered due to less availability of active sites in eugenol [3, 25, 26]. These drawbacks can be resolved by enhancing the crosslinking density by choosing multifunctional BZs, or introducing appropriate organic matrices like cyanate ester, bismaleimides, etc. [1–3, 27] or by introducing hybrid approach using inorganic reinforcements. In recent years, a significant quantity of research works has been fixated for the design and the preparation of organic–inorganic hybrids for numerous applications due to the combined advantages of both materials and polymer composites. Among the inorganic components which can be incorporated into a polymer matrix, silica is highly promising as it can be prepared easily in various forms/process routes including nano-silica (porous and nonporous, polyhedral oligomeric silsesquioxane), and micro-sized silica particles, etc. [6, 10, 11]. Among many process, the sol–gel process is mostly chosen for the preparation of inorganic silica due to its easy process, reaction carried out at low temperature, and a short duration of reaction time [11]. Generally, inorganic phases are chosen with reactive terminal groups that can covalently interact

with organic polymer to enhance the compatibility of both inorganic and organic phase to avoid the aggregation [28–30]. For example, 3-mercaptopropyltrimethoxysilane (MPTMS) as an inorganic silane which contains –SH group covalently reacts with the unsaturated group of eugenol through thiol-ene approach. This simple and easy addition reaction yields the product with high yields without formation of any by-products (atom-economical) and has recently attracted substantial consideration for probable applications [31, 32]. In case of subsequent synthesis of polymers, the acidic behaviour of mercapto groups (–SH) of MPTMS is believed to act as catalyst as well as cross-linker to reduce the curing temperature of the BZ monomers and enhance the thermal and mechanical properties [14, 33]. In our previous report, polybenzoxazine silica hybrid materials were developed using cardanol-based benzoxazine with nominal improvement in the thermal and flame-resistant properties [12]. Still, polybenzoxazine with high thermal stability (T_g , T_d and char residue) and high flame resistant are warranted for high-performance applications.

In this aspect, in this work, eco-friendly fully bio-based polybenzoxazines were developed using eugenol, and furfurylamine as renewable starting materials by Mannich reaction. MPTMS (organosilicone coupling agent) was introduced covalently reacted into BZ–E–F by thiol-ene click reaction and followed by PBZ-silica network prepared with the used tetraethyl orthosilicate (TEOS). The materials were characterized using routine characterization techniques and the curing behaviour of benzoxazine monomer was analysed with the help of differential scanning calorimetry (DSC). The final PBZ–E–F silica hybrid materials were studied for their thermal and flame-retardant behaviour.

Experimental

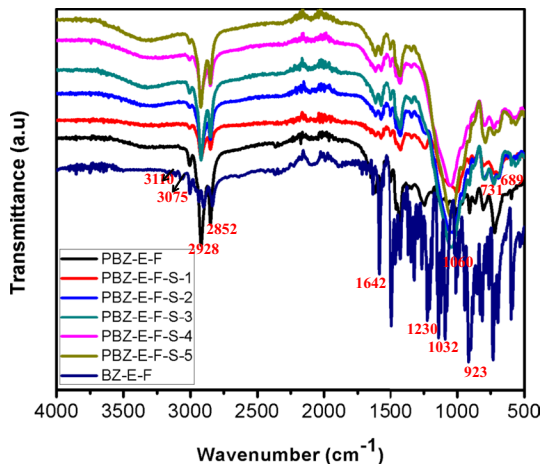
Development of renewable eugenol polybenzoxazine-silica hybrids

BZ–E–F (0.1 mol) and MPTMS (0.1 mol) and 2 ml of 1,4-dioxane were taken in a glass vial and stirred for an hour. In another vial, varying weight concentrations of TEOS (0, 0.25, 0.5, 0.75 and 1.0 with respect to BZ–E–F) were dissolved in THF and added exact equivalents of dilute hydrochloric acid and stirred for an hour. Later, both solutions were mixed well and stirred for another 120 min. The curing of benzoxazine monomer was executed at 100, 120, 140, 160, 180 °C for 60 min each and finally post-curing at 200 °C for 120 min. and the resulting PBZ–E–F–S hybrids were taken for further studies.

Results and discussion

Renewable, sustainable and environmentally friendly fully bio-based benzoxazines were synthesized by green synthetic approach in one pot method using eugenol and furfurylamine as raw materials through Mannich reaction (Scheme S-1). The synthesized BZ–E–F benzoxazine monomer was confirmed by ^1H NMR (Figure S-1)

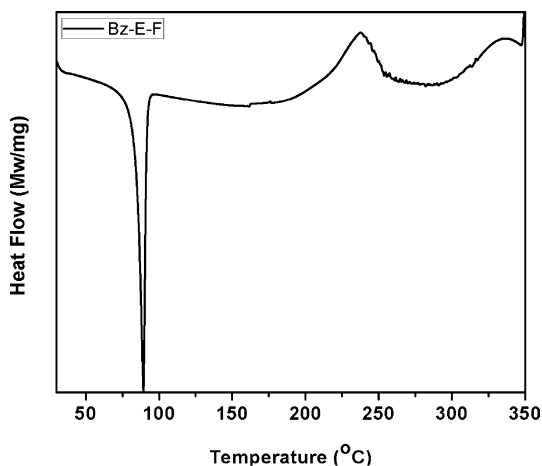
Fig. 1 FT-IR spectra for renewable eugenol-based BZ–E–F, pristine PBZ–E–F and PBZ–E–F–S hybrids



and FT-IR (Fig. 1). From NMR data, the proton peaks at 3.9 (s, 2H) and 4.8 ppm (s, 2H) represent the oxazine ring of BZ–E–F ($-\text{O}-\text{CH}_2-\text{N}-$ and $\text{Ph}-\text{CH}_2-\text{N}-$). The singlet peak observed at 3.8 ppm corresponds to the methoxy ($-\text{OCH}_3$) and peaks appeared at 3.2, 5.0 and 5.8 ppm are assigned to allyl [$-\text{CH}_2-\text{CH}=\text{CH}_2$] protons of eugenol. The peaks appeared at 6.2, 6.8, and 7.3 ppm are identified as aromatic protons of furan and also proton peak at 3.9 ppm denotes the methylene ($-\text{CH}_2-$) linking the furan and oxazine ring. From the infra-red (IR) spectra, the typical vibration peaks at 1230 and 1032 cm^{-1} correspond to $-\text{C}-\text{O}-\text{C}-$ asymmetric and symmetric stretching, respectively. The vibration peak at 923 cm^{-1} confirms the existence of oxazine ring attached with benzene ring in the BZ–E–F [12]. The peaks at 2928 and 2852 cm^{-1} indicate the asymmetric and symmetric vibration of aliphatic $-\text{CH}_2-$ group of benzoxazine.

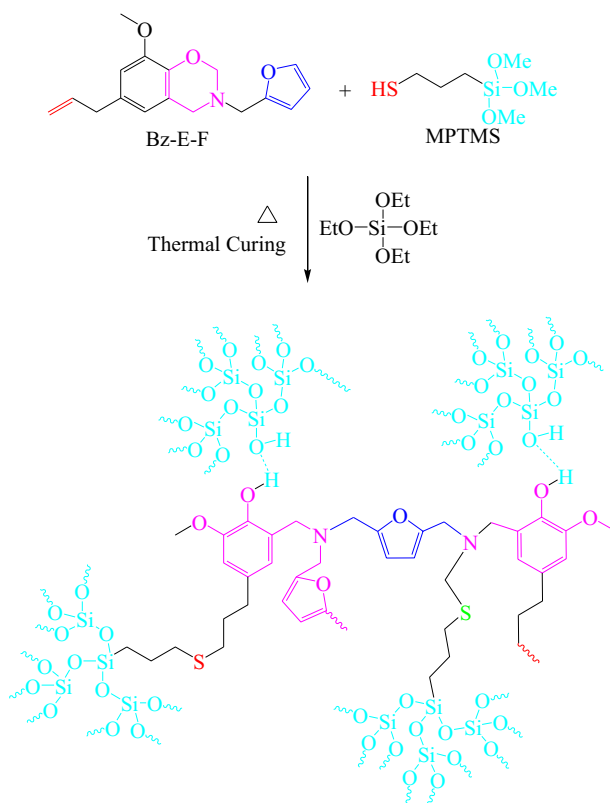
DSC techniques were used to characterize the curing nature of synthesized BZ–E–F and are shown in Fig. 2. From DSC, the melting temperature (T_m) of

Fig. 2 DSC curing behaviour of renewable BZ–E–F monomer



BZ–E–F observed at 86 °C. The ring-opening polymerization exothermic peak starts at (T_i) 180 °C and reaches to a peak maximum (T_p) of about 231 °C for BZ–E–F, respectively. After 300 °C, a new exothermic peak was observed, presumably due to the degradation of traces of oligomeric moieties from PBZ matrices.

PBZ–E–F silica hybrids were prepared by sol–gel approach with the use of BZ–E–F, MPTMS and TEOS (Table S1 and Scheme 1). Further, to explain the presence of possible reacting sites and occurrence of cross-linking reactions during curing of benzoxazine has been shown in Scheme S-2 (Supporting information). The successful preparation of pristine PBZ–E–F and silica hybrid materials was confirmed with FT-IR analysis (Fig. 1). From FT-IR, the disappearance of bending vibrations peaks at 923, 1032, and 1230 cm^{-1} corresponds to the ring opening polymerization oxazine ring. The complete vanishing of peaks at 3075, 3110 cm^{-1} along with diminishing the intensity of peak at 1642 cm^{-1} and the appearance of new vibration peaks observed at 689 and 731 cm^{-1} ascertain the C–S–C linkage due to the thiol-ene reaction between MPTMS (mercapto group) and eugenol benzoxazine (allyl group) (Scheme 1). The wide vibration peak appeared at 1060 cm^{-1} indicates the presence of silica groups (Si–O–Si) within the polybenzoxazine matrix.



Scheme 1 Schematic representation for the preparation of renewable PBZ–E–F–silica hybrids

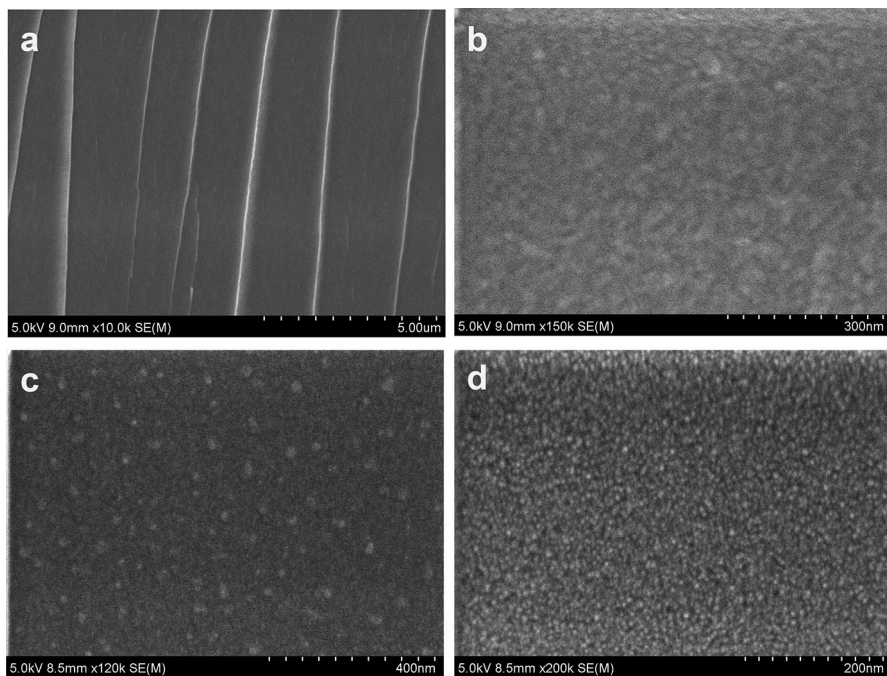


Fig. 3 SEM images of (a) neat PBZ–E–F, (b) PBZ–E–F–S-1, (c) PBZ–E–F–S-2 and (d) PBZ–E–F–S-5

The surface morphology of the pristine PBZ–E–F and PBZ–E–F silica hybrids was characterized using SEM techniques (Fig. 3). The SEM images show a smooth, uniform morphology with no substantial aggregation, localized domains and phase separation in the PBZ hybrid systems, indicating that the silica materials are uniformly dispersed in the PBZ–E–F system without no considerable cracks or flaws.

The thermal stability of pristine PBZ–E–F and PBZ–E–F–S was checked with the help of DSC and TGA. Glass transition temperature (T_g) is one of the important key parameters to assess the working/processing temperature of polymeric materials for utilizing in various applications. DSC results of pristine PBZ–E–F and PBZ–E–F–S are displayed in Fig. 4 and Table 1. The DSC data reveal that the T_g values are enhanced with increase in the weight content of TEOS into PBZ. This might be due to the covalent interaction between the nano-sized silica and the benzoxazine matrix through the thiol-ene reaction, which decreases the molecular rotation of polymer chains and in-turn increases the T_g [11, 28].

The TGA thermogram of the bio-based PBZ–E–F and silica hybrid materials is exposed in Fig. 5 and Table 1. The TGA results indicate that the neat PBZ–E–F hybrid begins to decompose at ~ 275 °C. 10% weight loss degradation temperature (T_d^1) occurred between 285 and 345 °C and 20% weight loss degradation temperature (T_d^2) happened between 332 and 443 °C. Further, the derivative thermogram is shown in Fig. 6. From the figure, silica hybrid showed double degradation behaviour. The first degradation may be due to the aliphatic allyl group and second degradation may be the benzoxazine main chain degradation. The degradation

Fig. 4 DSC thermogram for renewable pristine PBZ–E–F and PBZ–E–F-silica hybrids

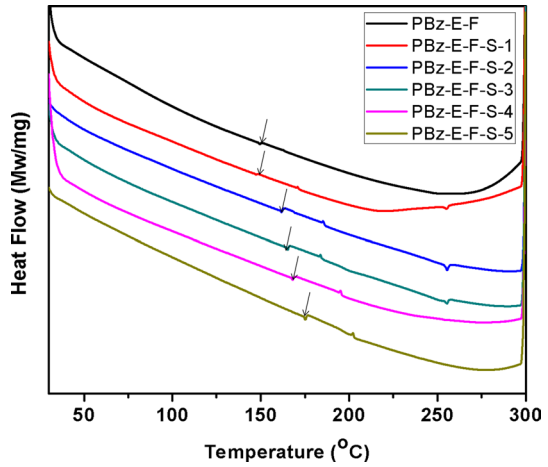


Table 1 Thermal and flame-retardant properties of pristine PBZ–E–F and PBZ–E–F silica hybrids

Sample	T_g	TGA (%)		Char yield (%)	LOI 0.40 (σ) + 17.5
		T_d^1	T_d^2		
PBZ–E–F	150	284	332	41.32	34.03
PBZ–E–F–S-1	161	285	335	53.64	38.96
PBZ–E–F–S-2	165	290	363	55.43	39.67
PBZ–E–F–S-3	168	302	393	62.78	42.61
PBZ–E–F–S-4	171	318	415	65.16	43.56
PBZ–E–F–S-5	175	345	447	67.54	44.52

T_d^1 —10% weight loss degradation temperature

T_d^2 —20% weight loss degradation temperature

Fig. 5 TGA thermogram for renewable pristine PBZ–E–F and PBZ–E–F-silica hybrids

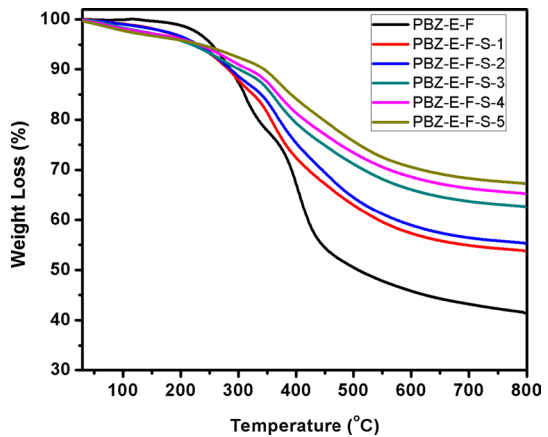
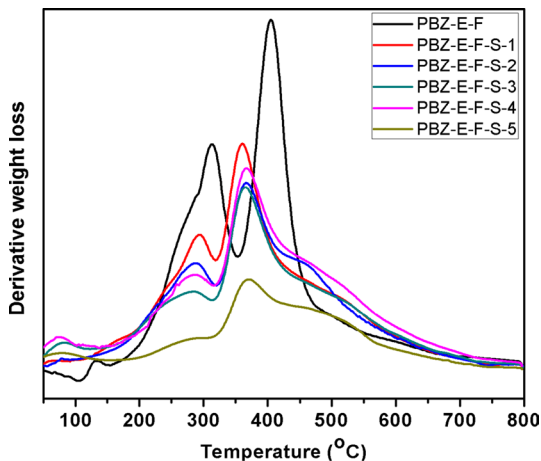


Fig. 6 TGA derivative thermogram for renewable pristine PBZ–E–F and PBZ–E–F-silica hybrids



temperature increased with increasing the content of silica since the increasing silica content can be attributed to restrict the further degradation of PBz hybrid. Also, the silica network enhanced the char residue values to a substantial range. The char residue at 800 °C of pristine PBZ–E–F is 41.32%, while the same for PBZ–E–F–S silica hybrids is in the range of 53.64–67.54%. Accordingly, thermal properties of silica hybrids are greater than that of pristine PBZ–E–F as well as traditional bisphenol-A/aniline-based poly-benzoxazine (PBA-a) [12], owing to our hybrid approach of integrating silica component with the organic matrix via covalent interaction. The silica material can act as a protective passive layer on the surface of the PBZ material, which protects and prevents further oxidation of the inner part of the PBZ, thereby increasing the char residues of the material.

Limiting oxygen index (LOI) is the best method to calculate flame-retardant behaviour of polymers. The LOI values are calculated using Van Krevelen's equation and are shown in Table 1. The polymeric material with $\text{LOI} > 21$ may show the flame-retardant behaviour, since oxygen content in the air is about 21% [34–37]. Flame retardation properties of polymers directly correlate with their char residue at high-temperature region. The LOI values are obtained in the range of 34.03 and 44.52. Moreover, the flame-retardant behaviour enhanced with the higher weight content of silica introduced into PBZ. The inorganic silica into PBz acts as barrier layer which subsequently hinders the burning of PBz moieties, resulting in enhanced flame-resistant property. Hence, the prepared bio-based PBZ–E–F silica hybrids materials can be deliberated as efficient materials for fire-retardant applications.

Conclusion

Eco-friendly PBZ–E–F–S hybrid materials were successfully prepared with the use of renewable starting materials via thiol-ene approach. Silica materials were introduced by an in-situ sol-gel technique. The surface morphology and the structure of the prepared PBZ–E–F–S hybrids were checked with SEM and FT-IR analysis. Data

attained from different studies, it was inferred that PBZ–E–F–S hybrids revealed better thermal stability and good flame-resistant properties than those of pristine PBZ and commercial PBA-a. These hybrid materials, prepared via greener and environmentally benign approach can be used for varying aerospace and engineering applications for better performance in near future.

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