Original Article

Evaluation of thermo-mechanical, dielectric and corrosion resistant properties of cardanol benzoxazine-epoxy based hybrid composites: A very low temperature curing pre-polymer for high performance paint related applications

V Selvaraj[1] ⓘ, TR Raghavarshini[1] and M Alagar[2] ⓘ

Abstract

In the present work, the hybrid siloxane-based cardanol-benzoxazine-epoxy (1:1 ratio) matrix (SBCBz-EP) capable of curing at substantially low temperature when compared with that of conventional benzoxazines was prepared and characterized. The matrix SBCBz-EP was reinforced with varying weight percentages (1, 3 and 5 wt%) of hydroxyl-terminated cyclotriphosphazene (HTCP) and the resulting hybrid composites were characterized by modern analytical methods, which can be used for paint-related applications due to their low-temperature curing behaviour. Data obtained from differential scanning calorimeter analysis infer that the glass transition temperature of the hybrid matrix (SBCBz-EP) and HTCP reinforced with 1, 3 and 5 wt% composites was 73°C, 75°C, 82°C, and 88°C, respectively. The polymerization temperature obtained for SBCBz-EP matrix and HTCP-reinforced hybrid composites was considerably lower than that of conventional benzoxazines. The present hybridization approach of benzoxazine and epoxy paves an avenue to alleviate the deficient characteristics of both industrially valuable resins namely high curing temperature and brittle behaviour of benzoxazines and also to improve thermal stability, mechanical strength and flame-retardant behaviour of epoxy resins. Data obtained from mechanical, dielectric, thermal stability and corrosion-resistant studies indicate that the properties of hybrid composites (HTCP/SBCBZ-EP) were enhanced to an appreciable extent according to the wt% of HTCP and it can be suggested that these hybrid composite materials can be used in the form of adhesives, sealants, encapsulants and water-resistant coatings for high performance industrial applications.

Introduction

Polybenzoxazines are modified versatile phenolic resins, which are obtained by Mannich condensation using phenolic compounds, amino derivatives and formaldehyde at appropriate experimental conditions. Benzoxazines are industrially valuable resins, which cure without the release of any volatile on thermal treatment with the formation of hydrogen bonding, which, in turn, exhibit an excellent thermomechanical, dielectric and surface properties useful for different industrial and engineering applications. Although they exhibit outstanding properties, their high-temperature

[1] Department of Chemistry, University College of Engineering Villupuram (A Constituent College of Anna University, Chennai), Villupuram, Tamil Nadu, India
[2] Polymer Engineering Laboratory, PSG Institute of Technology and Applied Research, Neelambur, Coimbatore, Tamil Nadu, India

Corresponding author:
V Selvaraj, Nanotech Research Lab, Department of Chemistry, University College of Engineering Villupuram (A Constituent College of Anna University, Chennai), Kakuppam, Villupuram 605103, Tamil Nadu, India.
Emails: vaithilingamselvaraj@gmail.com; rajselva_77@yahoo.co.in

cure behaviour restricts their utility for high performance applications. Hence, the lowering of curing temperature and improvement of strength properties are inevitable to utilize them for different applications.[1–12]

Diglycidyl ether of bisphenol-A (DGEBA) based epoxy resins are cost competitive, industrially potential materials and are used in the form of coatings, adhesives, sealants, matrices and composites for a wide range of industrial applications. However, their brittle behaviour and inferior flame-retardant properties limit their utility, hence, the improvement of these characteristics is essential to make them suitable for advanced applications.[13,14]

The reinforcements and fillers play a vital role in the improvement of polymer properties, namely, thermal, mechanical, dielectric, flame retardance and surface protection including process ability and cost reduction based on nature and concentration. Further, incorporation of phosphorous, nitrogen, halogen, and so on, containing compounds acts as reinforcements in the polymer matrix that are expected to improve the flame-retardant behaviour, which can be considered better material for fire-resistant coating applications.[15–18] Cyclotriphosphazene (CP) is a compound that has an alternative phosphorous and nitrogen bonded ring structure along with two reactive substituents present in the phosphorous atom has been selected as reinforcement for hybrid matrix in the present investigation, which has good flame-retardant and self-extinguishable properties.[19] The hydroxyl-terminated cyclotriphosphazene (HTCP) is a macromolecule with a flexible structure and expected to provide more flexibility and strength to the resultant hybrid composite materials. In addition, functionalized cyclophosphazene reduces the brittleness to an appreciable extent that has been used as reinforcement in the present study.

In the present work, the attempt has been made to develop hybrid composites from renewable cardanol-benzoxazine blended epoxy resin matrix reinforced with varying weight percentages of HTCP for high-performance coating applications. The developed hybrid composite materials were characterized by different analytical test methods, and the results obtained are discussed and reported.

Experiment

Materials

Cardanol was obtained from Satya Cashew Chemicals Pvt Ltd (Chennai, Tamil Nadu, India). Hexachlorophosphazene was purchased from Merck (Mumbai, India). Tetrahydrofuran (THF) and chloroform were obtained from Fisher Scientific (Mumbai, India). LY 556 epoxy resin and Aradur140 were procured from Hindustan Ciba Giegy Ltd (Mumbai, India). Paraformaldehyde, 4, 4′-sulphonyldiol, sodium hydroxide, sodium sulphate, triethylamine and dichloro dimethyl silane were purchased from Sigma Aldrich

(Bangalore, India). 1,3-Bis (aminopropyl)tetramethyldisiloxane was obtained from Alfa Asear (Mumbai, India).

Preparation of HTCP

The hydroxyl-functionalized CP has been prepared by taking one equivalent weight of hexachlorophosphazene, six equivalent weights of 4, 4′- sulphonyl diol and six equivalent weights of triethylamine in THF solvent.[20] Typically, 1 g of hexachlorophosphazene was taken in a 500-ml round-bottomed flask and dispersed uniformly in 100 ml THF solvent using ultrasonicator for 10 min. Then, 6 g of 4, 4′-sulphonyl diol was added to the above reaction mixture and continued the sonication for half an hour. Triethylamine (8.5 ml) was further added dropwise to the reaction flask under sonication for another 10 min. After sonication, 200 ml of THF solvent was added and vigorous stirring was continued for another 48 h. Finally, the reaction product was filtered and washed with chloroform and THF solvent. As a result, a white HTCP solid was obtained (Figure 1) and its molecular structure was characterized by Fourier transform infrared (FTIR).

Synthesis of siloxane-based cardanol-benzoxazine monomer

A siloxane-based cardanol–benzoxazine (SBCBz) was synthesized by a simple solvent-free chemical reaction method.[21] Seven grams of 1,3-bis(aminopropyl)tetramethyldisiloxane and 2 g of *p*-formaldehyde were stirred at 85°C for 1 h. Ten grams of cardanol was added to the above reaction container and the reaction was allowed for another 10 h at 50°C. Finally, the product obtained was separated by using chloroform and 2 N sodium hydroxide. The separated organic layer was dried over sodium sulphate and the obtained liquid was subjected to vacuum distillation to remove the chloroform and yielded a red coloured SBCBz monomer (Figure 2). The molecular structure of the SBCBz monomer obtained was confirmed using FTIR, NMR and mass spectroscopy studies.

Preparation of HTCP-reinforced SBCBz-EP composites

Initially, HTCP mixed with SBCBz- epoxy hybrid (EP) matrix was prepared using chloroform. In this regard, cardanol–benzoxazine monomer and epoxy resin (DGEBA, LY556) has been taken in different ratios of 1.5:0.5, 0.5:1.5 and 1:1 to optimize the minimum possible low curing temperature and better strength properties of the benzoxazine-epoxy matrix films. From the experimental results, it was concluded that 1:1 ratio of cardanol-benzoxazine:epoxy prepolymer blend forms a flexible film with the cure temperature of 70°C. Hence, varying weight percentages (1, 3 and 5 wt%) of HTCP were reinforced
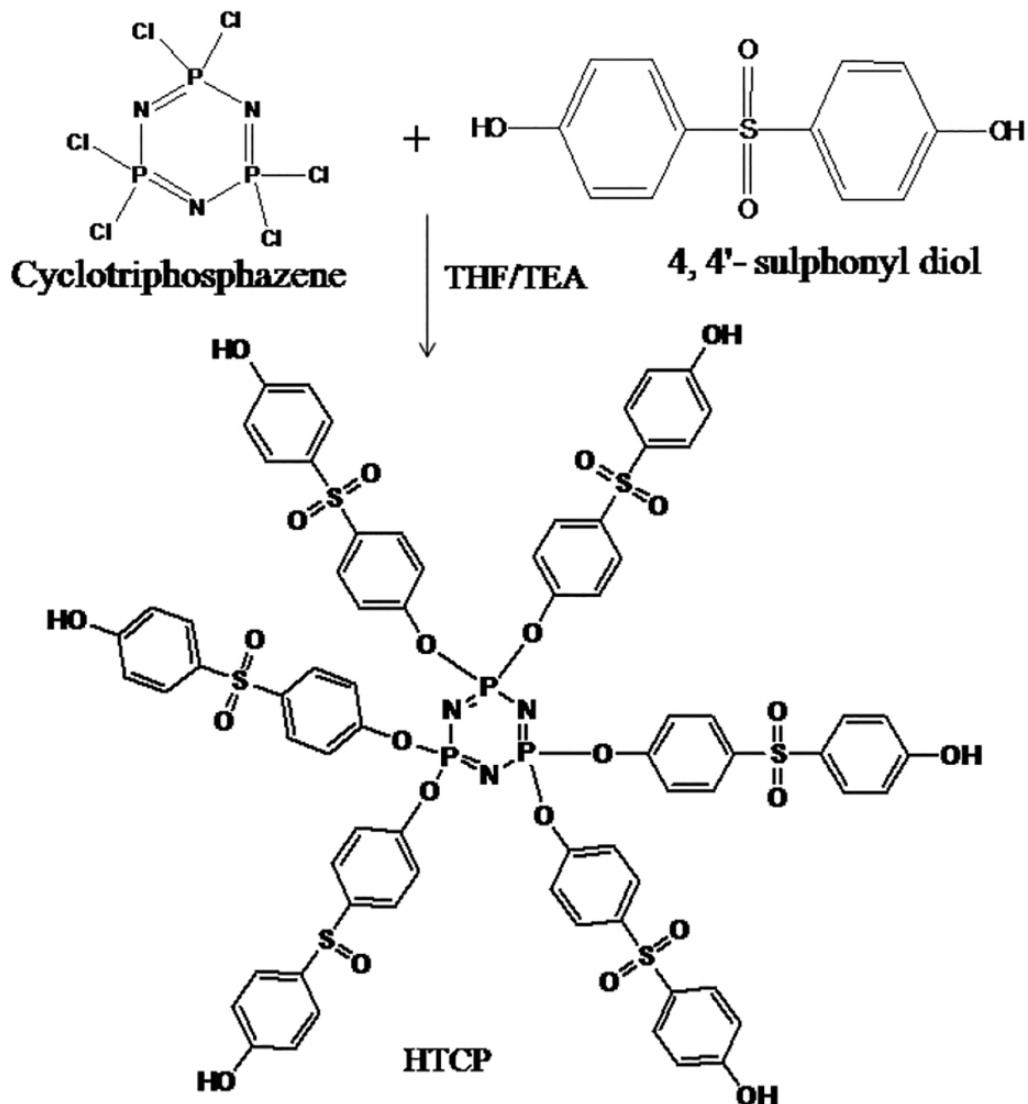
Figure 1. Preparation of HTCP. HTCP: hydroxyl-terminated cyclotriphosphazene.

separately into 1:1 ratio of cardanol–benzoxazine–epoxy matrix. Typically, 2 g of SBCBz monomer and 2 g of epoxy resin were dispersed in 10 ml of chloroform followed by the addition of 0.5 g of Aradur 140. The varying weight percentages (1 wt, 3 wt and 5 wt%) of HTCP as reinforcement in 5 ml chloroform were also added separately in the above reaction blend under continuous stirring. Then, the resulted homogeneous blend solution was poured into a silane-coated glass plate and cured at 30°C for 1 h, 50°C for 1 h and 70°C for 2–5 h to get a flexible thin film of HTCP-reinforced HTCP/SBCBz-EP composites (Figure 2).

Preparation of the mild steel (MS) plate-coated polymer matrix and composites for corrosion studies

The MS plates were cut into 5×1 cm^2, which was washed with distilled water followed by acetone and dried. The cleaned and dried MS plates were dipped in the homogeneous blend prepolymer solution of the matrix resin/composites with 1×1 cm^2 surface area and then dried at ambient temperature and the process was repeated until the formation of homogeneous coating on the MS plate and then cured in a hot air oven as such by following the same procedure adopted in the preparation of benzoxazine-epoxy matrix and HTCP/benzoxazine epoxy composites.

Characterization

FTIR spectra have been taken by PerkinElmer Spectrometer (Waltham, MA, USA) with potassium bromide (KBr) disc for CP and HTCP while without KBr disc for SBCBz-EP polymer matrix and 1, 3 and 5 wt% of HTCP reinforced SBCBz-EP hybrid composites. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker
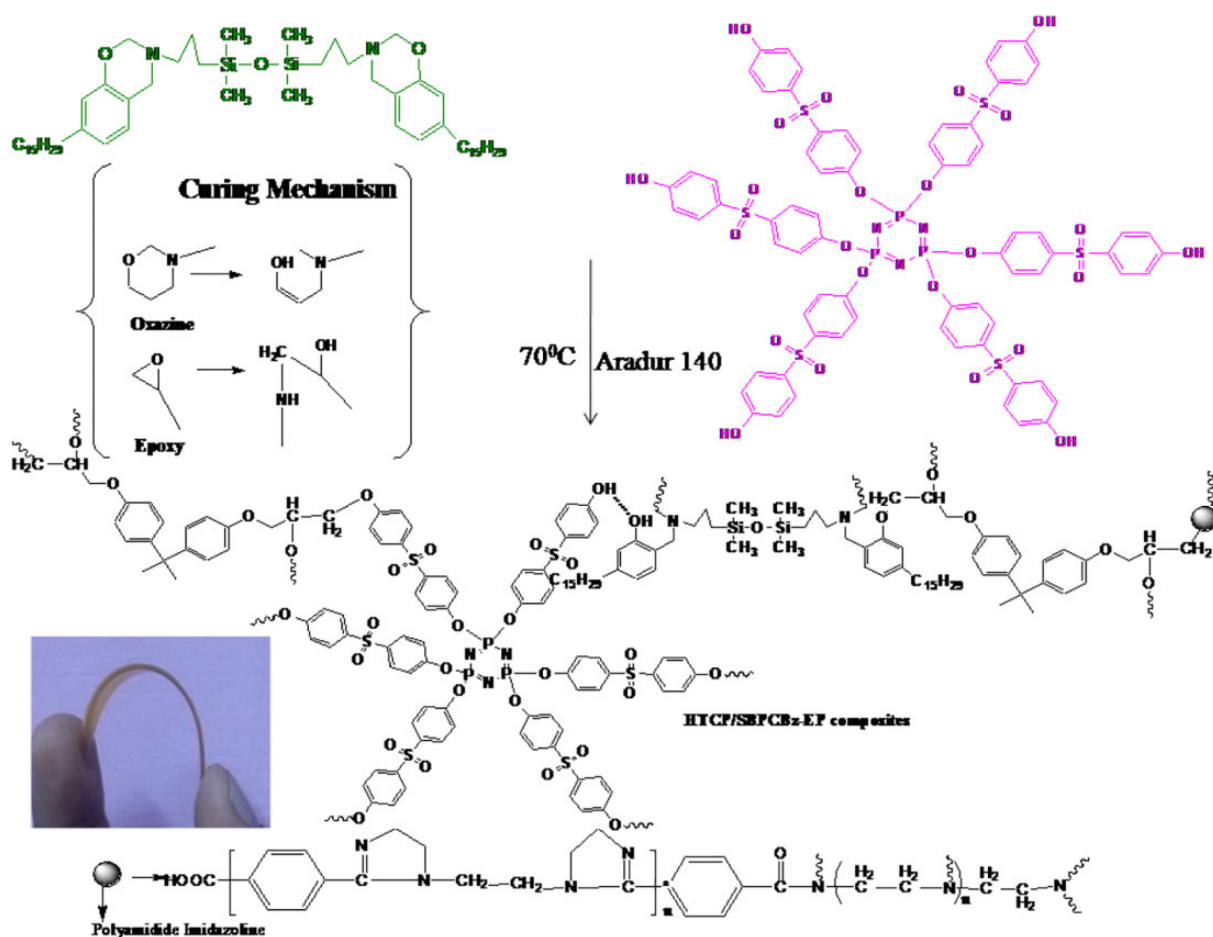
Figure 2. Preparation of HTCP-reinforced SBCBz-EP hybrid composites. HTCP: hydroxyl-terminated cyclotriphosphazene; SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy.

EXT41116 Spectrometer (Bruker, Germany) using dimethyl sulfoxide as the solvent. The morphological descriptions were scrutinized using scanning electron microscope (SEM) of JEOL JSM-5610LV (MA, USA). In transmission electron microscopy (TEM), electrons were passing through an ultrathin HTCP/SBCBz-EP film, and images were developed from the contact of the electrons passing through the film by JEOL/JEM 2100 with the source of LaB6. Dielectric constant and dielectric loss values were determined in a frequency range of 10 Hz–1 MHz using HIOKI 3532 50LCR HITESTER (Nagano, Japan). Thermogravimetric analysis (TGA) results were obtained using METTLER TOLEDO (Schwerzenbach, Switzerland) micro and ultramicro balances with submicrogram resolution at a temperature range up to 800°C. Differential scanning calorimeter (DSC) analysis was carried out using DSC Q200 V23.10 Build 79 model and DSC data were measured in the temperature range from 0°C to 300°C. Mechanical properties have been studied as per ASTM D 695 using universal testing machine (maximum capacity: 100 kN). Temperature of the specimen can be controlled up to 300°C. Impact strength was analysed using Charpy impact strength as per ASTM D 6110 and ISO 179 (at room temperature). Primary camera (13 MP) was used to determine the photo images of flame-retardant behaviour of SBCBz-EP cured matrix and its composite films. To ascertain the corrosion-resistant behaviour, the electrochemical, Nyquist and Tafel plots were attained using Biologic VSP2 multichannel (France) workstation analyzer and silver electrode as a reference electrode.

Results and discussion

Structural characterization

The HTCP has been prepared in accordance with the previous report[22] and characterized with proton nuclear magnetic resonance imaging (^{1}H NMR), carbon (^{13}C) NMR and phosphorus (^{31}P) NMR spectroscopy to confirm the formation of HTCP. The ^{1}H NMR spectrum of hydroxyl-functionalized CP is shown in Figure 3. In this spectrum, the hydroxyl (–OH) group proton peak was appeared at 9.8 ppm, which confirms the sulphonyl diol group was incorporated in the CP compound. The peaks obtained between 6.8 ppm and
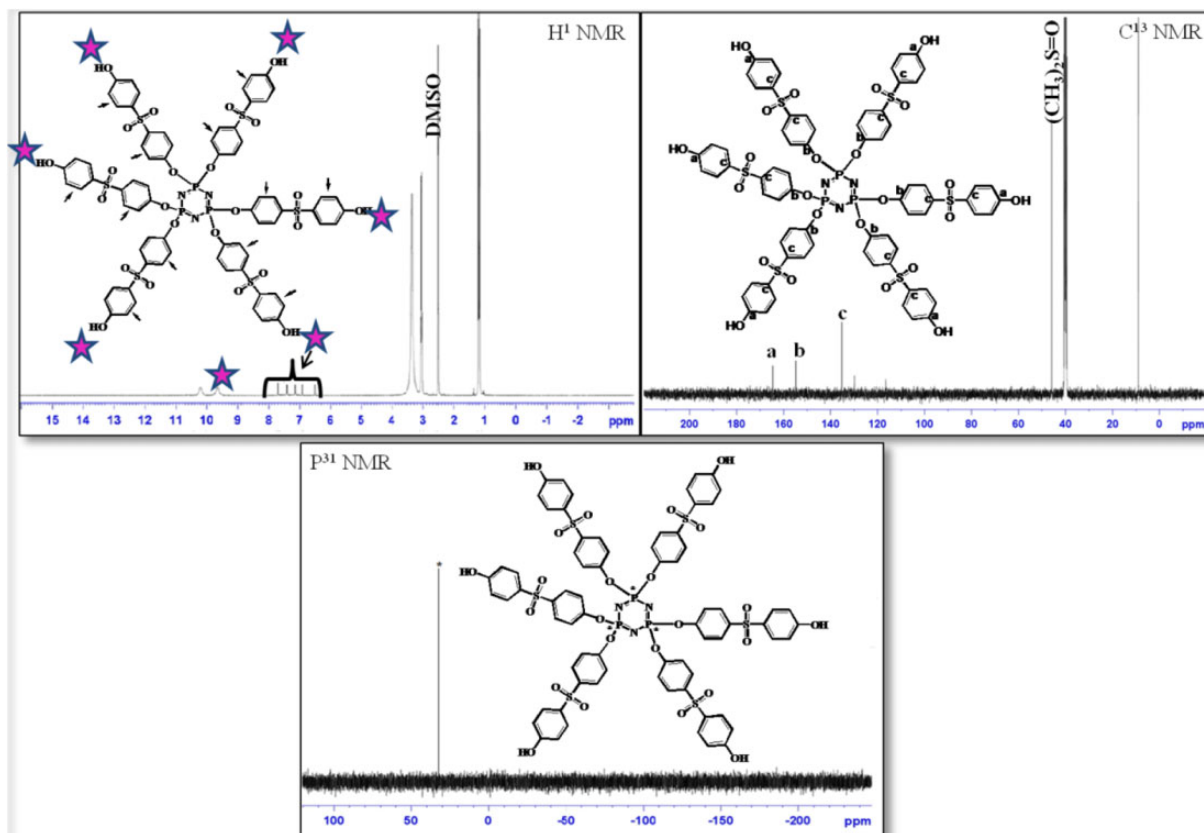
Figure 3. NMR studies of HTCP. HTCP: hydroxyl-terminated cyclotriphosphazene.

7.4 ppm ascertain the presence of aromatic ring protons in the sulphonyl diol group. Hence, the ^{1}H NMR confirms that 4,4′-sulphonyl diol has been chemically bonded and structurally modified with CP compound.

The ^{13}C NMR spectrum of HTCP sample was shown in Figure 3. The peak obtained at 155.3 ppm indicates the C–O–P linkage, which confirms the formation of chemical bonding between sulphonyl diol and CP compounds. The peaks observed at 163.5 and 134 ppm represents the terminal C–O (C–OH) and C–S linkages present in the hydroxyl-functionalized CP. The ^{13}C NMR spectroscopy results confirm the formation of HTCP.

The ^{31}P NMR spectrum (Figure 3) shows a single peak at 32 ppm, which indicates the presence of alternative phosphorous atoms arrangement in the ring structure of the CP covalently bonded with sulphonyl diol.[23] The NMR studies are used to further confirm the incorporation of sulphonyl diol hydroxyl group through chemical linkages into the CP without any change in the position of the phosphorous.

Infrared spectra of hydroxyl-functionalized CP were compared with that of the CP compound (Figure 4). The characteristic absorption peaks appeared between 1293 cm^{-1} and 863 cm^{-1} are corresponding to P=N and P–N stretching bands in CP.[24] The stretching vibration absorption of P–O–Ph bond was obtained at 940 cm^{-1} for only
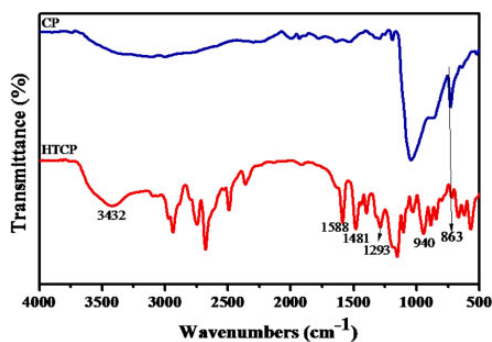

Figure 4. FTIR spectra of CP and HTCP. HTCP: hydroxyl-terminated cyclotriphosphazene; CP: cyclotriphosphazene; FTIR: Fourier transform infrared.

HTCP and not in CP, indicating the chemical bond for matrix between CP and sulphonyl diol compound. The broad peak appeared at 3432 cm^{-1} indicates the presence of the hydroxyl group in HTCP compound. The two peaks observed at 1588 and 1481 cm^{-1} are assigned to aromatic C–C from 4,4′-sulphonyl diol in HTCP spectrum.[25] The peak in HTCP spectrum obtained at 1383 cm^{-1} also confirms the presence of O=S=O group.[20] From FTIR spectra results, it is concluded that there is a presence of terminal hydroxyl group through aromatic derivative in CP compound.
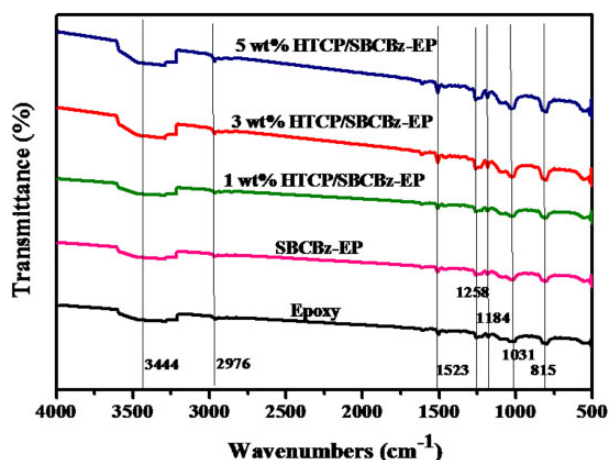
Figure 5. FTIR analysis spectra of epoxy, SBCBz-EP matrix and varying weight percentages of HTCP-incorporated SBCBz-EP composites. FTIR: Fourier transform infrared; SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.

FTIR spectra of epoxy matrix, SBCBz-EP matrix and different weight percentages of HTCP-reinforced SBCBz-EP composites are shown in Figure 5. The absorption peak appeared at 3444 cm^{-1} depicts the –OH . . . O intermolecular hydrogen bonding [26] and the peak obtained at 2976 cm^{-1} indicates –CH$_2$ stretching vibrations. The asymmetric and symmetric stretching peaks appeared at 1258 and 1184 cm^{-1}, respectively, are due to ether linkage obtained from the cleavage of oxirane ring of an epoxy group in DGEBA resin.[27] The intensity of the absorption peak visible at 1031 cm^{-1} is gradually increased from EP matrix to 5 wt% HTCP/SBCBz-EP composites, which is due to an increase in number of ether (C–O–C) linkage formation with the reinforcement of hydroxyl-functionlized CP in the SBCBz-EP polymer matrix. Then, the intensity of the absorption peak becomes perceptible at 815 cm^{-1} illustrates the aromatic –C–H out of plane bending vibration mode.[28] In accordance with the previous report,[29] the peak disappeared at 913 cm^{-1} confirms the cleavage of the oxazine ring structure. Thus, FTIR studies infer that the curing of the polymer matrix and its composites proceeds with the formation of three-dimensional cross-linked network at considerably lower temperature. Further, the structure and morphology of prepared polymer matrix and its composites have also been studied using SEM and TEM analysis.

Morphological studies

The SEM images of HTCP at different magnifications are shown in Figure 6. The morphological investigation of HTCP shows a needle-like shaped structure[30,31] at the microlevel surface. Therefore, this facilitates to enhanced cross-linked network structured toughened hybrid composites.

SEM images of SBCBz-EP matrix and varying weight percentages of HTCP-reinforced siloxane-based benzoxazine-epoxy composites are shown in Figure 7. The smooth surface was noticed for cardanol-benzoxazine-epoxy matrix, whereas the roughness of the surfaces was increased when benzoxazine-epoxy matrix was reinforced with different weight percentages of HTCP (Figure 7). The intensity of roughness was also increased with increasing the weight percentage of HTCP due to its bundled or rope like structure at microlevel as observed from SEM images. The fluffy images were also noticed due to the epoxy phase, which acts as a binding matrix to the HTCP reinforcement. From SEM results, it was concluded that the benzoxazine matrix has a smooth surface when compared to that of the composites because the reinforcement imparts the structural disorder with flexibility and also contributes to an enhanced strength to the polymer composites.

The TEM images of HTCP-reinforced SBCBz-EP composites with different magnifications are shown in Figure 8. Here, the smooth surface with less porosity was noticed at nanolevel, indicating the occurrence of strong interaction among the components present in the HTCP/SBCBz-EP composites.[32] This may be explained due to the homogeneous distribution of HTCP reinforcement throughout the cardanol–benzoxazine–epoxy matrix with the formation of chemical linkages and hydrogen bonding in the hybrid composites after curing.

Thermal studies

Thermal characteristics of SBCBz-EP matrix and different weight (1, 3 and 5 wt%) percentages of HTCP-reinforced SBCBz-EP hybrid composites were studied using TG analyzer. The values of thermal degradation temperature and percentage char yield obtained from TGA measurements are presented in Table 1. From Figure 9(a), it can be noted that the value of decomposition temperature at 5% weight loss of the sample was increased from 297°C to 330°C for cardanol–benzoxazine–epoxy matrix to 5 wt% HTCP-reinforced hybrid composites. Similarly, the value of percentage char yield was also considerably enhanced from 4.98% to 16.01% for cardanol–benzoxazine–epoxy matrix to 5 wt% HTCP-reinforced hybrid composites. Data obtained from TGA infer that the HTCP reinforcement in cardanol–benzoxazine–epoxy matrix appreciably improved both thermal stability and flame-retardant behaviour, suggesting the utility of these hybrid composites for high performance applications.[33,34]

The glass transition temperature (T_g) for polymers and the composites is one of the most important thermal behaviours, which was determined by DSC thermograms (Figure 9(b)). The T_g demonstrates the mobility behaviour of the polymeric composites from the glassy state to the rubbery behaviour. The value of T_g enhanced when HTCP is reinforced with cardanol–benzoxazine–epoxy matrix
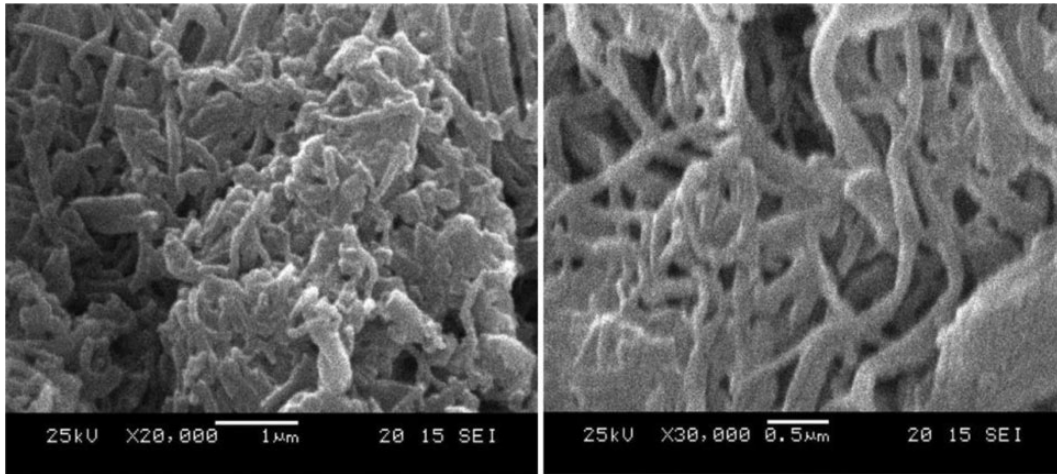
Figure 6. SEM images of hydroxyl terminated cyclotriphosphazene at different magnifications. SEM: scanning electron microscope.
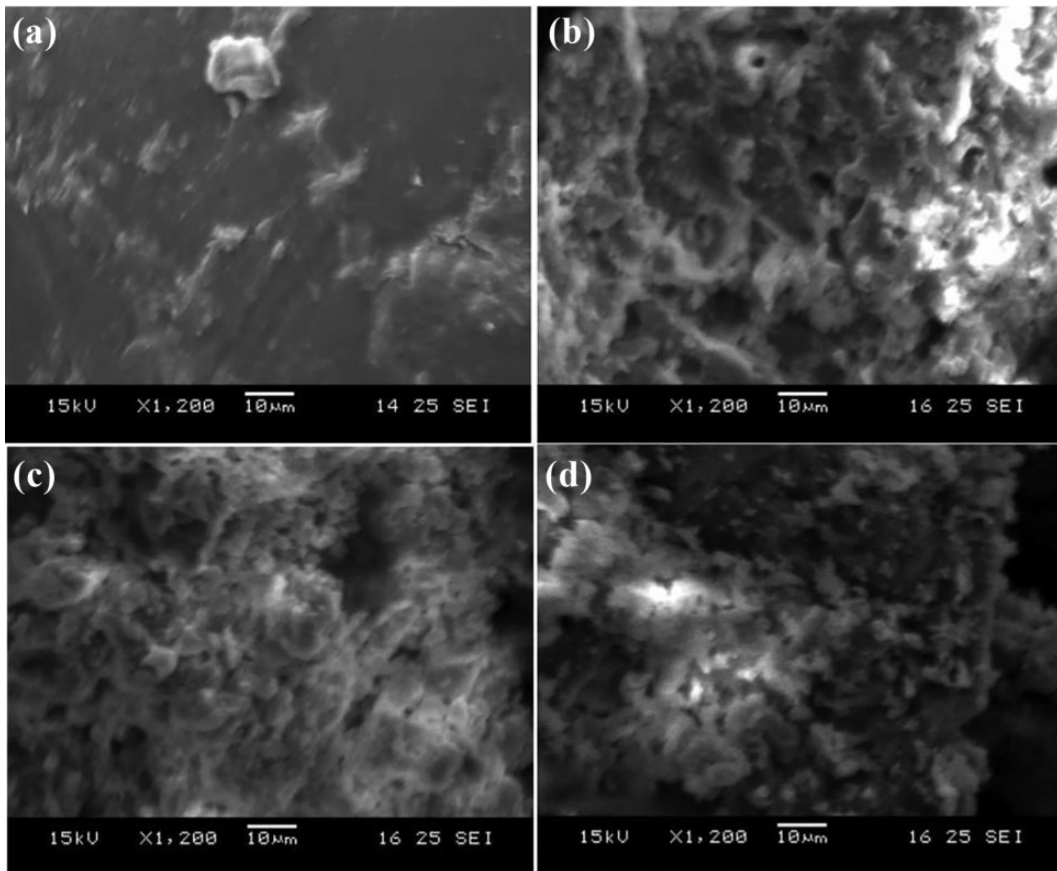

Figure 7. SEM images of (a) SBCBz-EP, (b) 1 wt% HTCP/SBCBz-EP, (c) 3 wt% HTCP/SBCBz-EP and (d) 5 wt% HTCP/SBCBz-EP hybrid composites. SEM: scanning electron microscope; SBCBz-EP: siloxane-based cardanol benzoxazine-epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.

according to the weight percentage due to the formation of three-dimensional complex network structure.[35] The value of T_g observed for cardanol-based benzoxazine–epoxy matrix is 73°C, whereas that of 1, 3 and 5 wt% HTCP-reinforced composites are increased to 75°C, 81°C and 88°C, respectively (Table 1). From the values of T_g, it can be tentatively predicted the continuous service temperature of the specimens and processing methods.

The DSC analysis was carried out to ascertain the curing temperature of the composite material and a very low
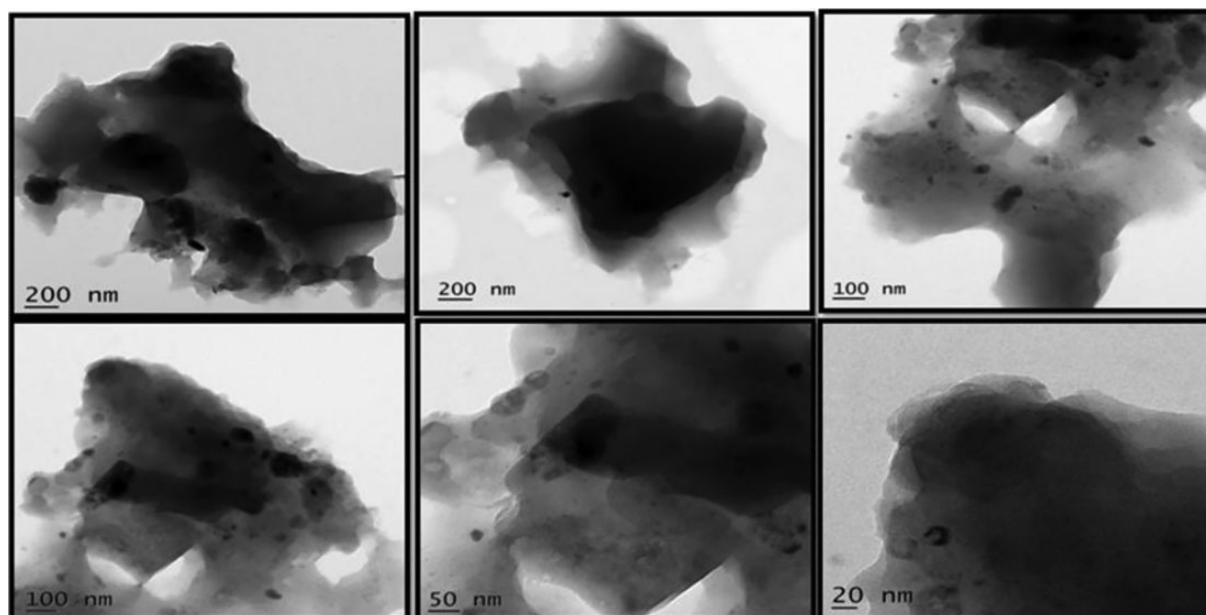
Figure 8. TEM images of HTCP/SBCBz-EP hybrid composites at different magnifications. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene; TEM: transmission electron microscope.

Table 1. Thermal and dielectric data of siloxane based cardanol benzoxazine–epoxy polymer matrix and HTCP/SBPCBz-EP hybrid composites.

S. no.	Samples	T_g (°C)	5% Weight loss (°C)	10% Weight loss (°C)	T_{max} (°C)[a]	Char yield (800 C)	Dielectric constant (k)	Dielectric loss
1	Epoxy matrix	71	297	333	404	4.98	3.08	−0.13
2	SBCBz-EP matrix	73	307	341	409	11.44	2.42	−0.17
3	1 wt% HTCP/SBCBz-EP	75	316	344	416	12.66	2.12	−0.22
4	3 wt% HTCP/SBCBz-EP	82	323	353	421	14.12	2.03	−0.33
	5 wt% HTCP/SBCBz-EP	88	330	356	425	16.01	1.82	−0.48

SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.
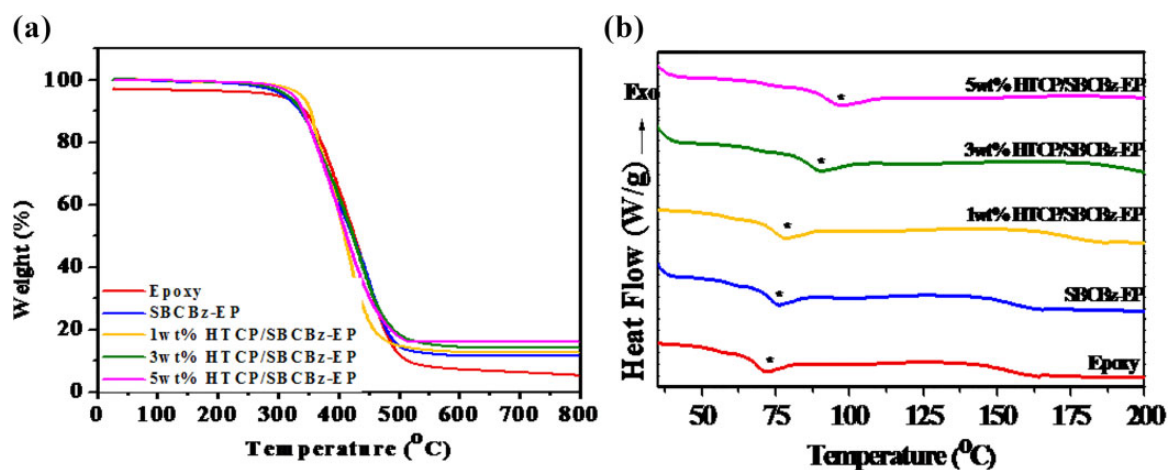[a]The temperature at which the maximum weight loss occurs at 50%, respectively.

Figure 9. (a) Thermogravimetric and (b) differential scanning calorimetric analysis of SBCBz-EP blended matrix and varying weight percentages of HTCP-reinforced SBCBz-EP hybrid composites. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.
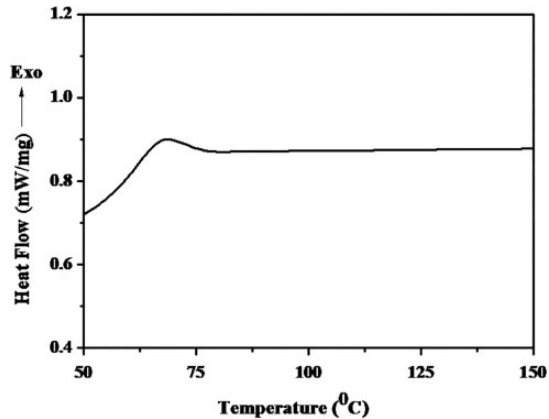
Figure 10. Curing behaviour of HTCP-reinforced SBCBz-EP hybrid composites studied by DSC method. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene; DSC: differential scanning calorimeter.

curing temperature was noticed for HTCP-reinforced SBCBz-EP composites (Figure 10). Generally, if any functional monomers, polymers (like epoxies, cyanate esters, urethanes, bismaleimides, etc.), amines, acids, oxazoline, pyridine, thiol, imidazloe, and so on are incorporated with benzoxazine, it precedes curing or cross-linking comparatively at lower temperature. So, the low temperature curing observed may be due to the addition of curing agent (Aradur 140)/aliphatic amine, which acts as a catalyst and influence the ring-opening polymerization of benzoxazine and retrieves the phenolic moiety during ring-opening polymerization, which, in turn, expected to act as catalyst/promoter for curing of the epoxy resin.[36,37] The combination of both benzoxazine and epoxy resin contributes to a synergistic effect, which, in turn, lowers the curing temperature of benzoxazine-epoxy blends significantly to a lower temperature.[38] Such a synergic effect of one of the reaction chemical such as curing agent used for epoxy may lower the curing temperature of benzoxazine (base catalyzed curing) and the product resulted from curing of benzoxazine causes the lowering of epoxy curing temperature for blended matrix and its composites. Hence, the curing temperature of the benzoxazine blended epoxy hybrid matrix and its composites were significantly reduced, which can be considered as most useful for high-performance surface coating-related applications.

Dielectric studies

The drop-off dielectric constant values of the SBCBz-EP matrix and its composites are shown in Figure 11(a) and Table 1. From this, it is observed that the values of dielectric constant are gradually decreased with respect to increase in the quantity of hydroxyl-functionalized CP reinforced with cardanol–benzoxazine–epoxy matrix. This may be explained due to the free space generated in the hybrid composites and constrained polarization behaviour

occurred between epoxy and benzoxazine, which, in turn, leads to the reduction of dipole–dipole interaction in the composite systems and contributes to lowered values of dielectric constant.[39,40]

The value of dielectric loss of epoxy matrix, SBCBz-EP matrix and different weight percentages of HTCP/ SBCBz-EP hybrid composites are shown in Figure 11(b) and Table 1. The dielectric loss values were symbolized by tan δ sequence and are decreased from -0.272 to -4.275 for moving from epoxy to 5 wt% HTCP/ SBCBz-EP composites. The reinforcement of HTCP restricts the polarization behaviour and, in turn, leads to lower the values of tan δ. Further, HTCP is considered to be a cyclic bulky compound and its reinforcement to cardanol-benzoxazine-epoxy matrix also restricts the movement of the polymer segment in the composite systems and thus decreased the values of dielectric loss.[6,41] From dielectric studies, it was concluded that the lower values of dielectric constant and dielectric loss indicate the enhanced insulation capacity of hybrid composites and can be used in the form of adhesives, sealants and potting compounds for microelectronics applications.

Mechanical studies

The variation of tensile behaviour with respect to the reinforcement of varying weight percentages of HTCP in the SBCBz-EP hybrid matrix was studied (Figure 12) and the results obtained are presented in Table 2. The determination of tensile strength was carried out by using material specimens of 60 mm length, 10 mm width and 1 mm thickness. From tensile strength results, it was noticed that the value of tensile strength was increased with respect to increasing weight percentage of HTCP to cardanol–benzoxazine–epoxy matrix. The improvement in the values of tensile strength and modulus may be explained due to the fibrous nature; efficient interaction occurred between HTCP and SBCBz-EP matrix and the formation of hydrogen bonding and cross-linked network structure of cured hybrid composite systems.[42,43] Similarly, the value of tensile modulus was also enhanced, when HTCP reinforced with SBCBz-EP matrix according to the weight percentage and this may be due to the toughness behaviour imparted by HTCP reinforcement. The SBCBz matrix shows lower values of stress/strain curve because of the presence of aliphatic chain in the molecule, which contributes to the formation of flexible segments and, in turn, leads to loosely packed when compared with the structural arrangement of 5 wt% HTCP/SBCBz-EP composites. Thus, the lower value of tensile modulus indicates that the polymeric material is flexible in nature and minimum stress is sufficient to produce a maximum amount of strain. Generally, the tensile modulus is the ratio of stress to elastic strain in tension. The value of low tensile modulus observed infers that the material possesses flexible and resilient behaviour and
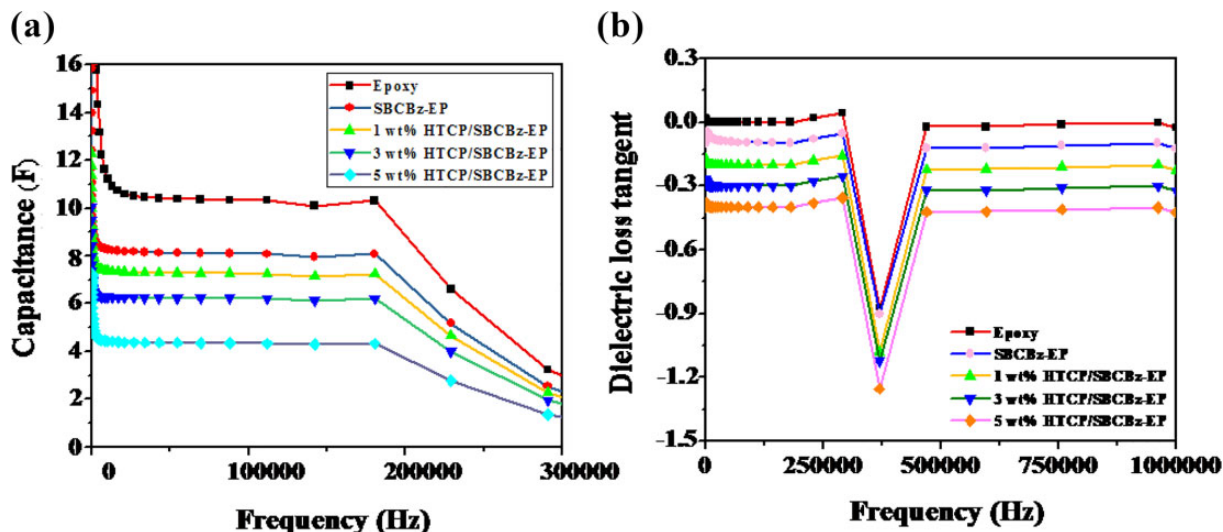
Figure 11. (a) Dielectric constant and (b) dielectric loss behaviour of epoxy matrix, SBCBz-EP matrix and HTCP/SBCBz-EP hybrid composites. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.
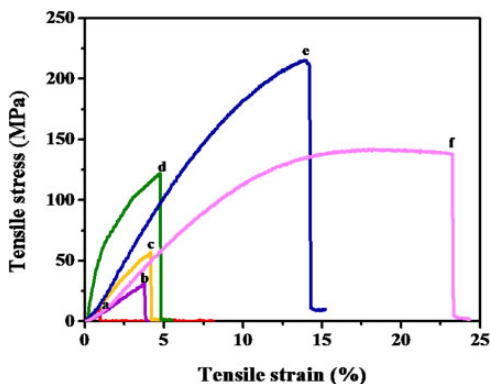

Figure 12. Tensile stress versus strain behaviour of (a) SBCBz, (b) epoxy matrix, (c) SBCBz-EP, (d) 1 wt% HTCP/SBCBz-EP, (e) 3 wt% HTCP/SBCBz-EP and (f) 5 wt% HTCP/SBCBz-EP hybrid composites. SBCBz-EP: siloxane-based cardanol benzoxazine-epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.

minimum stress is sufficient to produce a reasonable amount of strain. Further, it was noticed that the value of tensile modulus increased with increasing the percentage weight of reinforcement in the hybrid composites due to the formation of network molecular structure. The low values of modulus observed for all the samples may be explained due to the presence of flexible biophenolic structure arises from cardanol moiety in the composites. In addition, the low modulus may be also due to low-temperature curing process, which may be useful for paint-related applications when compared with high temperature curing polymers.[44] In addition, the flexible film can also be expected to accommodate other ingredients during the formulation of coatings using these hybrid matrix systems developed in the present work and makes them useful for high performance coating applications.

The toughness of SBCBz-EP has been increased with the reinforcement of HTCP.[45,46] The 5 wt% HTCP/SBCBz-EP hybrid composites possess higher toughness behaviour than that of other composite specimens. The hybrid composite specimens prepared in the present work possess better strength properties when compared with those of neat benzoxazine and epoxy matrices. Further, the hybridization of epoxy and benzoxazine followed by the reinforcement improves the toughness behaviour and removes brittle behaviour of epoxy and benzoxazine matrices and, in turn, contributes to high performance strength characteristics useful for different industrial applications. Furthermore, the value of tensile modulus is increased with increasing the quantity of the reinforcement in the composites, which is due to increased cross-linked network structure and the balanced flexibility of the hybrid composites. The balanced flexibility means that the brittleness of the epoxy matrix was balanced by the flexibility of cardanol-based benzoxazine and flexible behaviour of polybenzoxazine was also balanced by cross-linking behaviours of the reinforcements. Hence, improved mechanical properties were noticed in the case of hybrid composites developed in the present work.

The impact strength of SBCBz-EP hybrid matrix with varying weight percentages of HTCP-reinforced composites is shown in Figure 13. The cured matrix and composites were cut into 2 mm thickness with 10 mm cross section and 54 mm length, which was analyzed for the impact strength, which shows perfect upward trend with the increase of the HTCP ratio and contributes to the maximum impact strength to the SBCBz-EP matrix and (1, 3 and 5 wt%) of HTCP/SBCBz-EP composites compared with that of SBCBz and neat epoxy matrix respectively. According to the data presented in Table 2, the increase

Table 2. Mechanical properties of SBCBz, epoxy, and HTCP/SBCBz-EP hybrid composites.

Samples	Tensile strength (MPa)	Ultimate strain (%)	Tensile modulus (MPa)	Degree of endcapping (%)	Impact strength (J m^{-1})
SBCBz matrix	0.94	0.65	1.44	56.68	1.23 $\pm$ 0.06
Epoxy matrix	3.16	0.60	5.25	79.34	30.96 $\pm$ 0.92
SBCBz-EP matrix	5.50	0.59	9.38	79.68	35.72 $\pm$ 0.64
1 wt% HTCP/SBCBz-EP	12.29	0.57	21.39	80.48	56.24 $\pm$ 0.83
3 wt% HTCP/SBCBz-EP	21.53	0.41	51.99	89.99	75.39 $\pm$ 0.64
5 wt% HTCP/SBCBz-EP	24.96	0.26	95.32	95.75	116.25 $\pm$ 0.71

SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.
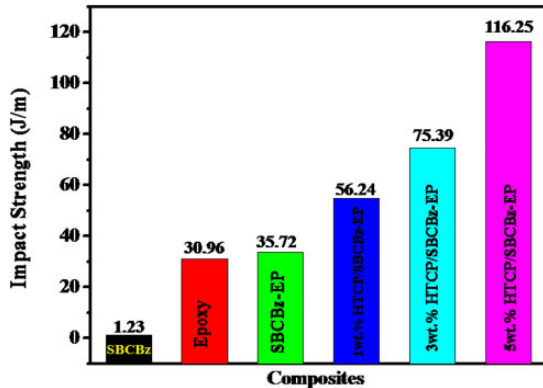

Figure 13. The impact strength of SBCBz matrix, epoxy matrix, SBCBz-EP matrix and (1, 3 and 5 wt%) of HTCP/SBCBz-EP hybrid composites. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.

of HTCP weight percentages in SBCBz-EP increases the toughness due to the copolymerization rather than SBCBz and neat epoxy matrix, which are likely to be self-polymerized. Hence, the value of impact strength of hybrid HTCP-reinforced SBCBz-EP composites is higher than that of SBCBz matrix and neat epoxy matrix. This result further confirms the formation of covalent bond between HTCP unit and SBCBz-EP hybrid matrix, which influence the development of network structure and the flexible ether bonds.[47,48]

Flame-retardant properties

The flame-resistant properties were carried out for thin films in accordance with the previous report.[49,50] This is a simple technique and easy methodology to confirm the fire-resistant properties of the thin films. So, the flame-resistant behaviour studies were manually carried out for all the samples and their optical images obtained are shown in Figure 14. The samples have been taken in the dimensions of 120 mm length × 12 mm width × 2 mm thickness. These samples were introduced in the Bunsen burner and the times taken for burning to charring were recorded. The epoxy matrix catches fire immediately and burned with a sooty flame up to 120 s and produced a char, which is

presented in Figure 14(a), whereas the SBCBz-EP matrix burned with smoky flame up to 72 s (Figure 14(b)). However, 1, 3 and 5 wt% HTCP-reinforced SBCBz-EP hybrid composites burned up to 60, 30 and 9 s, respectively, and are shown in Figure 14(c) to (e). The HTCP reinforcement in SBCBz-EP matrix enhances the flame-retardant behaviour according to the weight percentage when compared with that of neat benzoxazine and epoxy matrices. This may be explained due to the presence of inert nitrogen and flame-retardant phosphorous.[51] The introduction of HTCP in the form of reinforcement imparts flame retardancy to benzoxazine and epoxy matrices and makes them suitable for high performance flame-resistant applications.

Corrosion resistance studies

The protection recitals of coatings were determined based on the property of blockade capability against the salty water, moisture and electrolytes. The electrochemical charge transfer resistance is related to transmission of oxidization of the reactants and interfacial reaction of the materials. The higher charge transfer resistance indicates the higher corrosion-resistant behaviour. The corrosion studies were carried out for biobased benzoxazine–epoxy blended matrix and its composites coated on MS plates (Figure 15) by electrochemical spectroscopy.

Tafel plots of the coated and uncoated MS materials were engrossed in 3.5% sodium chloride solution for 2 h. Then, the corrosion analysis was carried out in two electrodes system in which Ag/AgCl electrode was used as a reference and coated as well as bare MS plates were taken as working electrodes. The electrochemical corrosion studies were carried out at their open circuit potential and the resulted parameters indicate that the hybrid benzoxzine–epoxy composites possess an excellent corrosion-resistant behaviour. The corrosion-resistant behaviour was also carried out using Tafel and Nyquist plots obtained from electrochemical impedance spectroscopy (EIS) (Figure 16) and EIS parameters were presented in Table 3.

The maximum diametric curves (Figure 16(a)) were observed for coated MS specimens designated as SBCBz-EP/MS, HTCP/SBCBz-EP/MS, and this behaviour

Figure 14. Digital photo images of flame-retardant behaviour of (a) epoxy matrix, (b) SBCBz-EP matrix, (c) 1 wt% HTCP/SBCBz-EP, (d) 3 wt% HTCP/SBCBz-EP and (e) 5 wt% HTCP/SBCBz-EP hybrid composites. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.
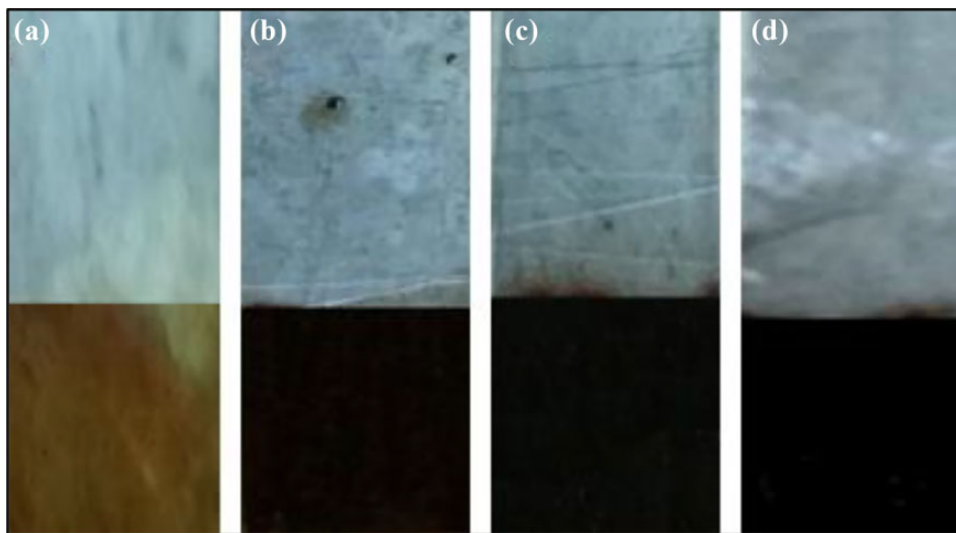

Figure 15. Photo images of (a) SBCBz-EP, (b) 1 wt% HTCP/SBCBz-EP, (c) 3 wt% HTCP/SBCBz-EP and (d) 5 wt% HTCP/SBCBz-EP coated on mild steel plates. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene.

confirms the improved corrosion-resistant properties than that of the bare MS plate. The charge transfer resistance (R_{ct}) is directly proportional to anticorrosion activity[52,53] and R_{ct} value of 5 wt% HTCP/SBCBz-EP is 8.327 kW cm^{-2},

which is significantly higher value when compared to that of uncoated MS plate (-12.860 kW cm^{-2}).

The Tafel plot values obtained for uncoated MS to coated MS substrate in 3.5% NaCl solution are presented
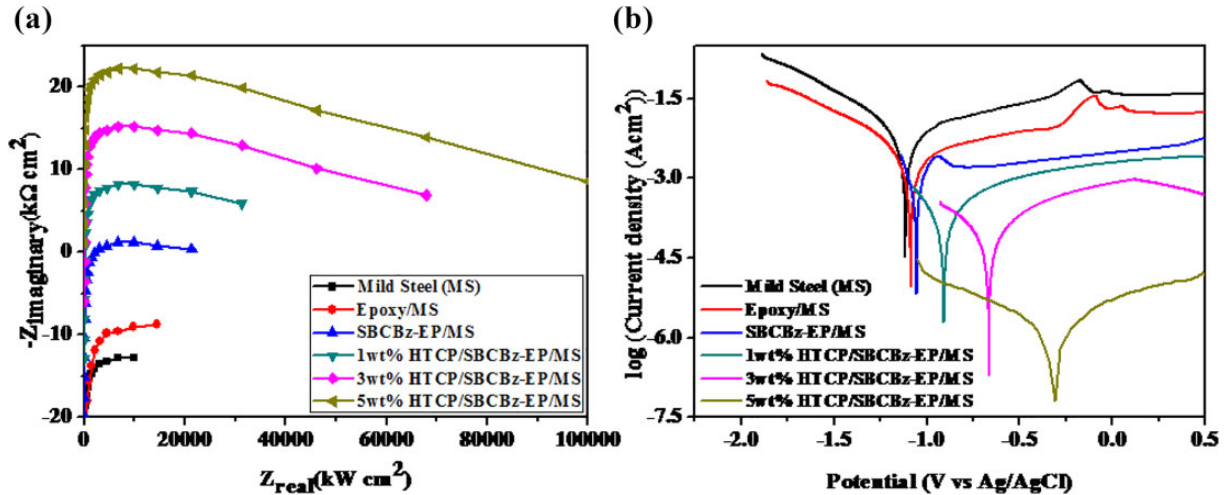
Figure 16. (a) Nyquist plot and (b) Tafel graph of MS, EP-MS, SBCBz-EP/MS, and various weight percentages of HTCP/SBCBz-EP/MS in 3.5% sodium chloride solution. SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene; MS: mild steel.

Table 3. The electrochemical measurement of bare MS specimen and MS specimens coated with hybrid composites in 3.5% NaCl solution.

Samples	R_{ct}	I_{corr} (A cm^{-2})	E_{corr} (V)	Corrosion rate (mm year^{-1})	η (%)
MS	−12.86	−2.06	−1.12	146.41	–
EP/MS	−8.82	−2.45	−1.06	98.38	95.89
SBCBz-EP/MS	0.23	−2.95	−1.05	60.58	97.47
1 wt% HTCP/SBCBz-EP/MS	6.02	−3.74	−0.91	27.44	98.85
3 wt% HTCP/SBCBz-EP/MS	7.12	−4.15	−0.67	18.25	99.23
5 wt% HTCP/SBCBz-EP/MS	8.33	−5.97	−0.33	02.90	99.87

SBCBz-EP: siloxane-based cardanol benzoxazine–epoxy; HTCP: hydroxyl-terminated cyclotriphosphazene; MS: mild steel.

in Figure 16(b) and Table 3. The corrosion potential (E_{corr}) and corrosion current densities (I_{corr}) of SBCBz-EP matrix and varying weight percentages of HTCP-reinforced composites are calculated by using equation (1) and the results obtained are presented in Table 3[54]:

$$CR = \frac{I_{corr} \times K \times EW}{\rho A} \quad (1)$$

where CR is corrosion rate, K is corrosion rate constant (3272 mm year^{-1}), EW is equivalent weight for MS (27.9 g), ρ is material density for MS (7.85 g cm^{-3}) and A is sample area (1 cm^2) and also the percentage protection efficiency (E %) are calculated using equation (2)[55]:

$$E(\%) = \frac{I_{corr} - I_{corr(c)}}{I_{corr}} \times 100 \quad (2)$$

where I_{corr} is corrosion current obtained for MS and $I_{corr(c)}$ is corrosion current for coated MS.

Data obtained from corrosion studies infer that the HTCP-reinforced SBCBz-EP hybrid composites coated on MS plates have retarded the corrosion rate due to the hydrophobic nature with improved cross-linking density,

efficient compatibility with benzoxazine–epoxy matrix and formation of hydrogen bonding networks.[56] Hence, the developed cardanol–benzoxazine–epoxy hybrid composites can be used as an effective coating material to protect the MS surfaces from corrosion.

Conclusion

The renewable low temperature curing SBCBz-EP hybrid matrix reinforced with HTCP composites was prepared and characterized by different analytical techniques and test methods. Data obtained from different studies inferred that the hybridization of benzoxazine and epoxy resin followed by the reinforcement of hydroxyl-terminated cyclophosphazene is an effective and novel method to alleviate deficient behaviour as well as to improve the vital properties of both benzoxazine and epoxy resin to an appreciable extent and utilize them as high performance material for different industrial and engineering applications in the form of adhesives, sealants, encapsulants, matrices and coatings. Further, the reinforcement of HTCP to benzoxazine–epoxy hybrid matrix enhances the thermal behaviour and

mechanical properties and reduces the values of dielectric constant and dielectric loss. The reinforcement of HTCP in the hybrid benzoxazine–epoxy matrix significantly improved both flame-resistant and corrosion-resistant properties due to the presence of nitrogen, phosphorous and aromatic structure. Further, the results obtained from different studies suggested that the low cure temperature (70°C) of cardanol–benzoxazine–epoxy hybrid matrix and composites can be used for multifunctional applications like polymeric coatings and microelectronics insulation uses, etc.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

ORCID iD

V Selvaraj 🄳 https://orcid.org/0000-0001-6557-4986
M Alagar 🄳 https://orcid.org/0000-0002-6073-4693

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