

Cyclotriphosphazene Fibre Reinforced Poly(benzoxazine-*co*- ϵ -caprolactam) Nanocomposites for Flame Retardant Applications*

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Abstract Cyclophosphazene nanotube (PZT) incorporated poly(benzoxazine-*co*- ϵ -caprolactam) (P(BZ-*co*-CPL)) nanocomposites were developed for improving flame retardant properties. The effects of PZT on the flammability properties of P(BZ-*co*-CPL) matrix were evaluated through UL-94 flammability test and limiting oxygen index (LOI). The UL-94 results of P(BZ-*co*-CPL)/PZT hybrid nanocomposites showed V-1 rating, whereas neat P(BZ-*co*-CPL) showed burning rating. The LOI values are increased from 25.4 to 31.4 for 1.5 wt% PZT incorporated P(BZ-*co*-CPL) nanocomposite systems. SEM was used to study the char morphology of P(BZ-*co*-CPL)/PZT after being exposed to UL-94 flammability test. Data from thermal studies indicate that the PZT incorporated P(BZ-*co*-CPL) systems possess better T_g and thermal degradation behavior when compared to the neat P(BZ-*co*-CPL). The values of dielectric constant are decreased with increasing temperature. From the values, it is ascertained that the P(BZ-*co*-CPL)/PZT systems exhibit stable dielectric behavior with regard to variation in temperature. The TEM images ascertain the uniform dispersion of PZT in the P(BZ-*co*-CPL) matrix.

Keywords: Polybenzoxazine; Phosphazene; Flame retardant; Dielectric properties.

INTRODUCTION

Polymeric materials are commonly used in a day to day life with increasing fire hazards and hence flame retardants are very often incorporated into them to limit their flammability. The mechanism of fire involves the combination of factors including the flammability of the generated volatiles, amount of heat released on burning, rate of heat release, ignitability of the material, *etc.*, therefore, it must be essential to develop flame-retardant materials that are able to withstand both fire risks and hazards^[1].

Polymers are the class of materials often targeted for flammability reduction in product fabrication because of their desirable mechanical, thermal, and electrical properties. Some inherently flame-retardant polymers such as fluoro polymers may be replaced by a lower flame retardant polymer because of cost constraints, recycle requirements, or regulations regarding the elimination of certain compounds (such as halogen or heavy metals)^[2,3]. Usually, halogenated flame retardant was widely incorporated into polymer matrix to improve its flame retardant performance. However, it releases toxic gases and corrosive smoke during combustion^[4–6], so it has given rise to some environmental concerns. Accordingly, to develop non-halogenated flame-retardant system becomes an attractive and emergent subject^[7, 8]. Alternative methods for improving the flammability of polymers without halogenated flame retardants can be considered as three approaches to reduce the flammability of polymers: (i) to use inherently flame resistant polymers^[9, 10], (ii) to structurally modify existing polymers^[11], (iii) to incorporate inherent flame retardant nanofillers into polymers^[12, 13].

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Phosphorus-based flame retardants have generally been used in polymers. Phosphazenes have been investigated as cyclic monomers or as linear polymers over a wide range of molecular weights^[14–18]. Phosphazenes are known to be resistant to hydrolysis, exhibit high thermal stability and flame retardancy, and have been used as halogen-free flame retardants^[19, 20]. Cyclotriphosphazene, with phosphorus and nitrogen atoms in a ring, is known to exhibit good thermal stability and flame retardancy. The incorporation of a substituted cyclotriphosphazene ring into the polymer backbone significantly improved thermal and fire resistance properties. In that study, the sulfone containing cyclophosphazene nanotube (PZT) was synthesized through single step with controllable morphology, simple process route with high yield and low cost^[20]. The synthesized PZT fiber show great heat resistance, radiation resistance and fire retardancy. It is easier for PZTs to disperse in the polymer matrices and form the hybrid organic-inorganic structure. The modification of the PZT is much more convenient and it may help to expand the methods for introducing PZTs into polymer matrices. For example, the PZTs can be introduced to polymeric resin to reinforce the resin matrix as they are expected to have a homogeneous dispersion in the matrix to create a CNT-like effect^[21–25].

Polybenzoxazines are a class of thermosetting phenolic resins that have recently been developed for the electronics, aerospace, matrices for composite materials, high performance adhesives, nanoimprinting technologies and other industries as an attractive alternative to other novolac-type phenolic resins. As thermally stable materials, polybenzoxazines are desired to show good flame retardancy for many of their applications, especially for electronic and aerospace materials. The polymerization of benzoxazine proceeds *via* ring-opening of oxazine rings by thermal cure. On curing, benzoxazine resins create a phenolic-like structure with inherent flame retardant properties. Polybenzoxazines exhibit the characteristics that found in traditional phenolic such as heat resistance, flame retardant, and good electrical insulation property. Besides, they also exhibit lots of unique characteristics including low melt viscosity, dimensional stability, excellent mechanical properties, as well as low water absorption^[26–29]. The objective of the present work is to understand the effect of dispersion of PZT fiber in the matrix with regard to flame retardancy and to improve the flame retardancy of P(BZ-*co*-CPL) using the PZT fiber as flame retardant. The effects of PZT fiber on P(BZ-*co*-CPL) hybrid composites were evaluated through thermal analysis, flammability test, char morphology and dielectric properties and discussed. Although the high rigidity is a unique strength in polybenzoxazines, reduced rigidity may also be desired for certain applications. Copolymerization is considered to be a potentially effective measure to toughen polybenzoxazine, and ϵ -caprolactam is used as a modifier for polybenzoxazine. Hence, the present work is focussed on the preparation of PZT reinforced P(BZ-*co*-CPL) composites.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (HCCP) and 4, 4'-sulfonyldiphenol were purchased from Sigma Aldrich, India. ϵ -Caprolactam was received as complimentary sample from SRF, India. Bisphenol-A, aniline, paraformaldehyde, tetrahydrofuran (THF), triethylamine (TEA) and methanol were received from SRL (India) Ltd. Bisphenol-A/aniline based benzoxazine (Bz) was synthesized as per reported procedure^[30].

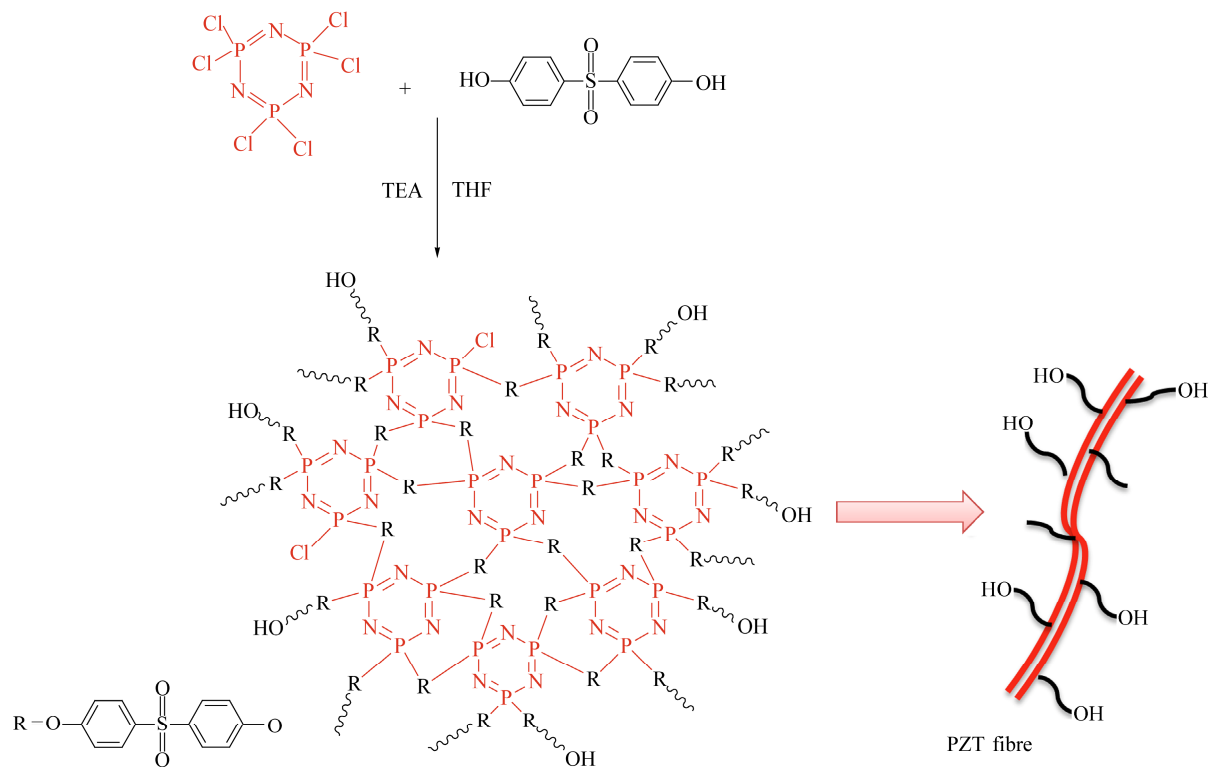
Synthesis of the Sulfone Containing Phosphazene Nanotubes (PZT)

The stoichiometric ratio of HCCP and BPS was reacted to obtain PZT with active hydroxyl groups as described in the literature^[23]. 0.87 g of triethylamine (8.64 mmol) was added to a solution of HCCP (0.50 g, 1.44 mmol) and BPS (1.44 g, 5.76 mmol) in THF (100 mL). The reaction mixture was kept in an ultrasonic bath (100 W, 80 kHz) at 30 °C for 3 h. The product was filtrated and then washed three times with THF and deionized water. The filtered solid was dried in vacuum oven and the PZTs were obtained as white powder (Scheme 1).

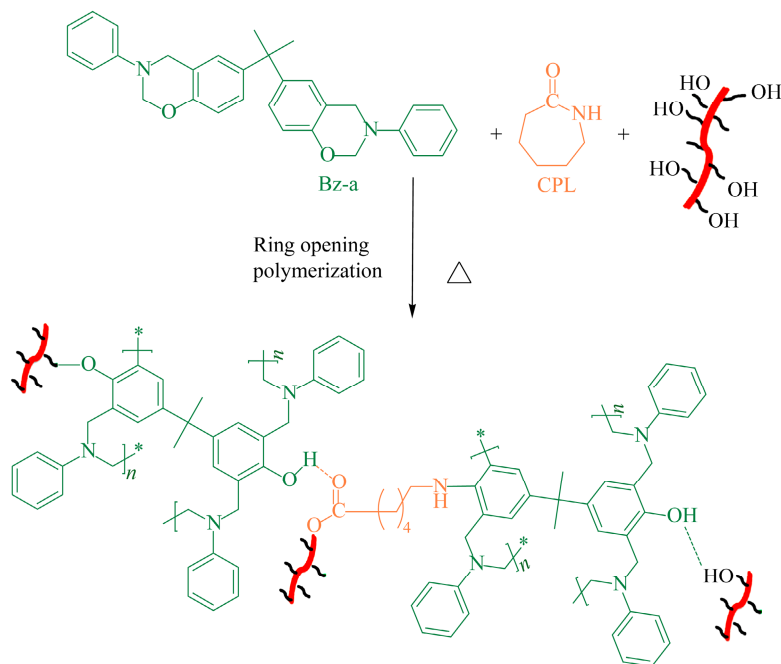
Synthesis of P(BZ-*co*-CPL)/PZT Nanocomposites

The synthesis of PZT reinforced P(BZ-*co*-CPL) nanocomposites, PZT fibre (0 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt%) was added to the freshly prepared P(BZ-*co*-CPL) solution and stirred for 12 h at 30 °C. After 12 h, the P(BZ-*co*-CPL)/PZT solution was cast on a smooth glass substrate and thermally treated at 50 °C for 1 day, and at

80, 100, 120, 140, 160, 180, 200 °C for 1 h each and 220 °C for 2 h. The mole ratio of the benzoxazine monomer and ϵ -caprolactam was 1:1. The thin and light brown colored films were formed and stripped from the glass substrates and then utilized for further characterization (Scheme 2).



Scheme 1 Synthesis of sulfone containing phosphazene fibre



Scheme 2 Schematic representation of P(BZ-co-CPL)/PZT nanocomposites

Characterization

FTIR spectrum was recorded on a Perkin Elmer 6X FTIR 60 spectrometer, India. About 100 mg of optical grade KBr was ground with sufficient quantity of solid sample to make 1 wt% mixture to prepare KBr pellets. After the sample was loaded, a minimum of 16 scans were collected for each sample at a resolution of $\pm 4 \text{ cm}^{-1}$.

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 Thermogravimetric Analyzer, USA. The samples (about $\sim 10 \text{ mg}$) were heated from ambient temperature to 800°C under a continuous flow of nitrogen (20 mL/min), at 10 K/min . The differential scanning calorimetric analysis (DSC) was performed on a Netzsch DSC-200, USA. Measurements were performed under a continuous flow of nitrogen (20 mL/min). All the samples (about $\sim 10 \text{ mg}$) were heated from ambient temperature to 300°C and the thermograms were recorded at a heating rate of 5 K/min .

Dielectric constant was determined by impedance analyzer (Solartron impedance/gain phase analyzer 1260) using a platinum 40 (Pt) electrode at 30°C at a frequency range of 100 Hz to 1 MHz . This experiment was repeated four times under the same conditions.

Wide-angle X-ray spectra were obtained using a Rich Seifert (Model 3000) diffractometer (with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) for the ground powder of cured composites. The spectral window ranged from $2\theta = 0^\circ$ to 70° .

The scanning electron microscopy of the char samples was performed using a JEOL JSM Model 6360 microscope. The specimens were coated with gold and were exposed to an accelerating voltage of 20 kV . A JEOL JEM-3010 analytical transmission electron microscope, operating at 300 kV with a measured point-to-point resolution of 0.23 nm was used, and the samples were prepared by dissolving the composites in DMF, mounted on carbon-coated Cu TEM grids and dried for 24 h at room temperature (RT) to form a film and characterized.

The XPS was measured using an Omicron nanotechnology instrument at a pressure below $1.322 \times 10^{-7} \text{ Pa}$. The sample was mounted on sample stubs. The wide scan, C1s, O1s and N1s core level spectra were recorded with a monochromatic $\text{Al-K}\alpha$ radiation (photon energy = 1486.6 eV) at a pass energy of 15 eV and electron take-off angle of 608° .

RESULTS AND DISCUSSION

Hexachlorocyclotriphosphazene (HCCP) is a cyclic inorganic compound formed by three —P=N— units and six chlorine substitutes. The high reactivity of these substitutes offers the possibility to build up polymers with interesting properties. In this work, we have synthesized a cyclo-triphosphazene-containing nanofiber by polycondensation of HCCP and 4, 4'-sulfonyldiphenol in the presence of triethylamine. The FTIR spectra of neat and P(BZ-co-CPL)/PZT are shown in Fig. 1. The stretching bands at 1257 , 1187 and 881 cm^{-1} correspond to the P=N and P—N characteristic absorption; the characteristic peaks at 1355 , and 1115 cm^{-1} are assigned to O=S=O ; the intense absorption at 955 cm^{-1} corresponds to the P—O—(Ph) band^[23]. From the figure the disappearance of peaks at 1520 cm^{-1} for trisubstituted benzene ring and 947 cm^{-1} for oxazine ring, and appearance of new peaks at 1496 cm^{-1} for the tetra-substituted benzene ring, peaks at 2926 cm^{-1} and 2860 cm^{-1} for symmetric and asymmetric aliphatic CH_2 groups (oxazine ring and ϵ -caprolactam) and the peak at 1667 cm^{-1} for the carbonyl stretching of the ester group indicated the presence of ϵ -caprolactam in the resulting nanocomposites.

Thermal Properties

The thermal properties of neat P(BZ-co-CPL) and PZT reinforced P(BZ-co-CPL) nanocomposites were characterized using DSC and TGA. From an industrial application point of view, the T_g value of a material is considered to be a crucial thermal parameter. Both chain rigidity and polarity are predominant factors in the glass transitions of polymers, and cross-linking degree also affects the T_g values of polymers. Thus, taking an advantage of these direct correspondences is a feasible approach for the enhancement of T_g in molecular design. The glass transition temperatures (T_g) of the neat P(BZ-co-CPL) and $0.5 \text{ wt\%}$, $1.0 \text{ wt\%}$ and $1.5 \text{ wt\%}$ PZT

incorporated P(BZ-*co*-CPL) systems were studied, using the DSC analysis with the temperature ranging from ambient temperature to 300 °C at a heating rate of 5 K/min, and the values of T_g are presented in Table 1 and Fig. 2. It has already been known that glass transition is generally attributed to the segmental motion of the polymeric networks, and T_g is determined by the degree of freedom for the segmental motion, cross-linking and entanglement constraints, and the packing density of the segments. The data from the DSC analysis show that the values of T_g for neat P(BZ-*co*-CPL) and 0.5 wt%, 1.0 wt%, and 1.5 wt% PZT incorporated P(BZ-*co*-CPL) are 162, 170, 181 and 192 °C respectively. The PZT incorporated P(BZ-*co*-CPL) system possesses higher values of T_g than that of neat P(BZ-*co*-CPL). This is because the incorporation of cyclophosphazene fiber increases the steric hindrance, and restricts the movement of polymer chain segments. It is reasonable to believe that the rotational hindrance restricts the segmental motion and consequently results in an improvement in the T_g of the thermoset.

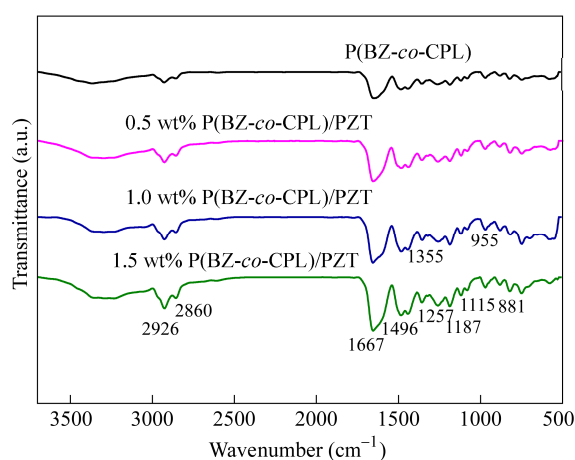


Fig. 1 FTIR spectra for P(BZ-*co*-CPL)/PZT nanocomposites

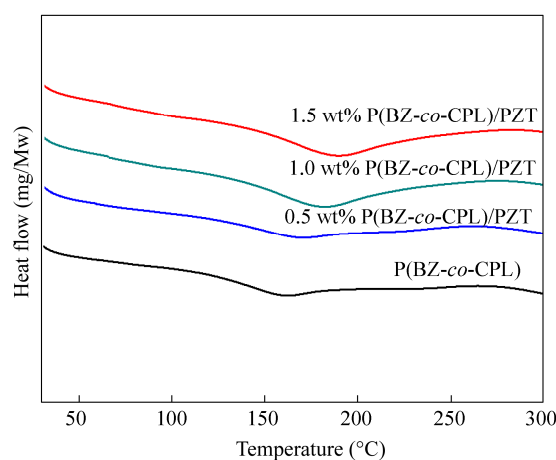


Fig. 2 DSC thermo grams for P(BZ-*co*-CPL)/PZT nanocomposites

Table 1. Thermal, flame resistant and dielectric properties of neat P(BZ-*co*-CPL) and P(BZ-*co*-CPL)/PZT nanocomposites

Sample code	T_g (°C)	T_d 5 % weight loss (°C)	Char yield at 800 °C (%)	LOI	UL-94	Dielectric constant at 1 MHz		Dielectric loss at 1 MHz	
						30 °C	200 °C	30 °C	200 °C
PBZ ^[30]	180	254	36.0	31.8	—	3.48	—	—	—
P(BZ- <i>co</i> -CPL)	162	218	19.8	25.4	—	3.39	2.56	0.059	0.111
0.5 wt% P(BZ- <i>co</i> -CPL)/PZT	170	230	27.2	28.3	V-1	3.08	2.04	0.048	0.041
1.0 wt% P(BZ- <i>co</i> -CPL)/PZT	181	236	31.0	29.9	V-1	2.82	1.78	0.040	0.031
1.5 wt% P(BZ- <i>co</i> -CPL)/PZT	192	243	34.8	31.4	V-1	2.47	1.63	0.033	0.019

The thermal stability of neat P(BZ-*co*-CPL) and cyclotriphosphazene fiber reinforced P(BZ-*co*-CPL) was investigated by TGA under nitrogen atmospheres. The TGA thermograms of these thermosets are illustrated in Fig. 3 and the data are summarized in Table 1. From the TGA thermograms it is observed clearly that the P(BZ-*co*-CPL)/PZT nanocomposites exhibit a two-stage thermal degradation. The first stage of thermal degradation is caused by the hydrocarbon segments of the thermoset, and the second one is attributed to the decomposition of the major backbones of polymeric networks due to their higher thermal stability. From the TGA results it was inferred that the initial decomposition (5 wt% loss) temperatures of neat P(BZ-*co*-CPL) and 0.5 wt%, 1.0 wt%, 1.5 wt% PZT reinforced P(BZ-*co*-CPL) are 218, 230, 236 and 243 °C respectively. The increase in initial degradation is due to the cyclophosphazene fiber present in the composite system which increases the steric

hindrance also high crosslinking network formation between polymer and PZT fiber. These results imply that the the phosphorus-rich residues may inhibit further decomposition of the P(BZ-*co*-CPL) matrix.

Figure 4 shows the DTA patterns of the neat P(BZ-*co*-CPL) and PZT reinforced P(BZ-*co*-CPL) hybrid nanocomposites systems. There are double degradation curves for neat P(BZ-*co*-CPL) and three degradation curves for PZT fibre reinforced P(BZ-*co*-CPL). In the case of neat P(BZ-*co*-CPL), the first decomposition below 250 °C is attributed to the CPL evaporation and second degradation occurs at around 400 °C due to the phenolic groups. In the case of PZT fibre reinforced P(BZ-*co*-CPL) the first degradation is aliphatic segment in the CPL (~250 °C), the second degradation is the phenolic groups in the PBZ (~400 °C) and finally the third degradation occurs at ~510 °C for cyclic phosphazene segments in the system.

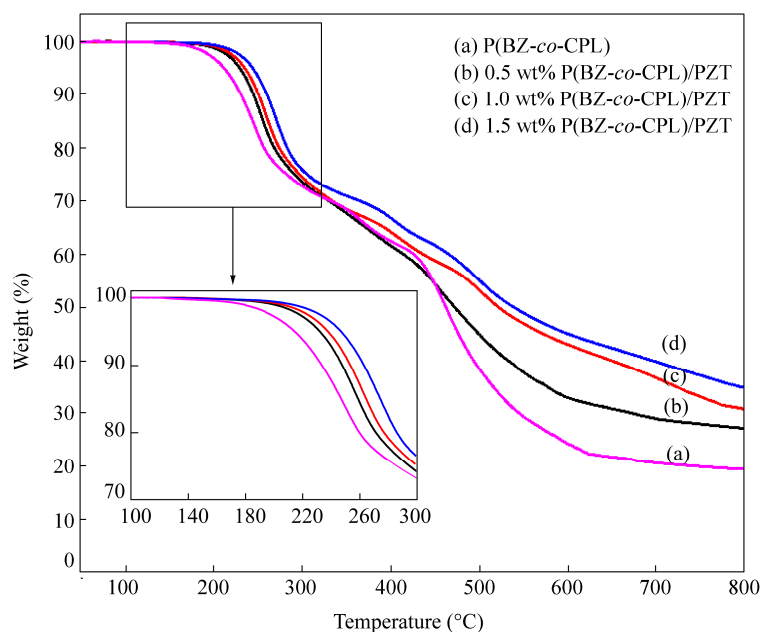


Fig. 3 TGA curves for P(BZ-*co*-CPL)/PZT nanocomposites

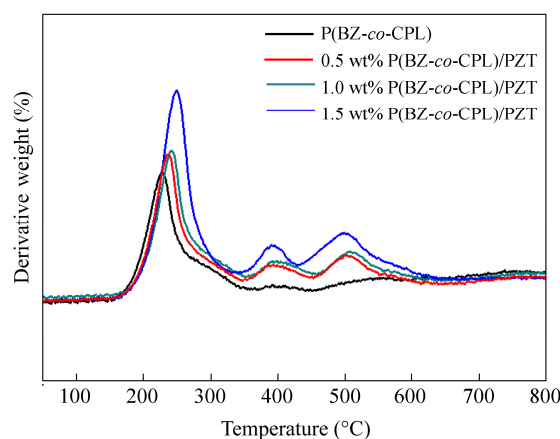


Fig. 4 Derivatives of TGA curves for P(BZ-*co*-CPL)/PZT nanocomposites

The char yield of neat and PZT incorporated P(BZ-*co*-CPL) is shown in Table 1, the char yields are 19.8%, 27.2%, 31.0% and 34.8% respectively. The achievement of such high char yields may be explained by the highly thermal stable phosphazene rings in the P(BZ-*co*-CPL) matrix, which promote char formation during pyrolysis.

In addition, the PZT incorporated P(BZ-*co*-CPL) exhibits char yield higher than that of neat P(BZ-*co*-CPL), which indicates that the high cross-linking density imparted by incorporating PZT into P(BZ-*co*-CPL) matrix dominates the formation of char. The formation of phosphorus-rich char in the decomposition of PZT incorporated P(BZ-*co*-CPL) systems not only increased the degradation temperature and also resulted in a high char yield. An increase in char formation can usually limit the production of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, and decrease the thermal conductivity of the surface of a burning material.

The XPS analysis of the 1.5 wt% PZT reinforced P(BZ-*co*-CPL) nanocomposites before and after TGA analysis was investigated, and the results are shown in Fig. 5. From the XPS survey figure, C1s, N1s, O1s and P2p peaks can be seen. As shown in Fig. 5, the binding energy values of C1s, N1s, O1s and P2p are 285.7, 399.9, 533.3 and 136.5 eV respectively for both before and after char formation of 1.5 wt% P(BZ-*co*-CPL)/PZT hybrid. The weak peak at around 136.5 eV in P2p spectra can be assigned to the pyrophosphate and polyphosphate^[31] which confirms the presence of phosphorus in the P(BZ-*co*-CPL) composite. From these results, the presence of pyrophosphate and polyphosphate structures plays the major role for improving their thermal properties. Further the concentrations of C, O, N, and P before and after char formation of the 1.5 wt% P(BZ-*co*-CPL)/PZT are listed in Fig. 5. The increasing concentration of phosphorus content may be due to the formation of pyrophosphate and polyphosphate structures after charring, which is helpful for improving the thermal stability of the resulting composites.

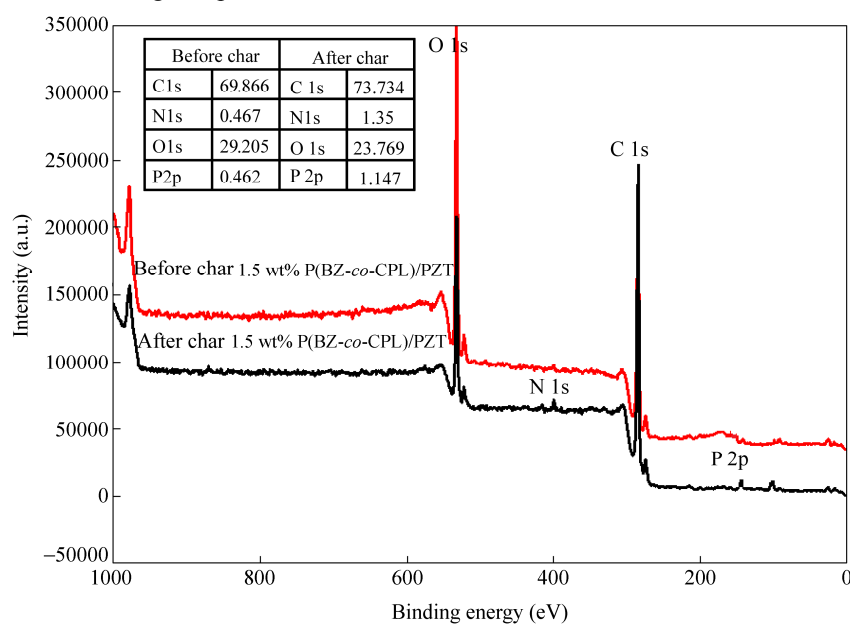


Fig. 5 XPS for P(BZ-*co*-CPL)/PZT nanocomposites

The flame-retardant properties of P(BZ-*co*-CPL)/PZT systems were further examined through measurements of the values of LOI (100 mm length, 10 mm width and 3 mm thickness). The LOI values of the neat P(BZ-*co*-CPL) and PZT incorporated P(BZ-*co*-CPL) systems are shown in Table 1. The LOI values are increased with increase in weight concentration of PZT. The LOI value increases to 31.4 (1.5 wt% P(BZ-*co*-CPL)/PZT) from 25.4 (neat P(BZ-*co*-CPL)), which indicates the improvement of flame retardant behaviour of all the PZT incorporated P(BZ-*co*-CPL) systems. This was ascribed to the presence of high content of nitrogen and phosphorus in the polymers, which are believed to have a synergistic effect during burning. The photo images of all the composites after LOI tests are shown in Fig. 6. From the figure the neat polymer shows irregular shape and more shrinkage is observed whereas PZT reinforced composites do not show any shrinkage, and this may be due to the crosslinking of PZT fiber with P(BZ-*co*-CPL) matrix.

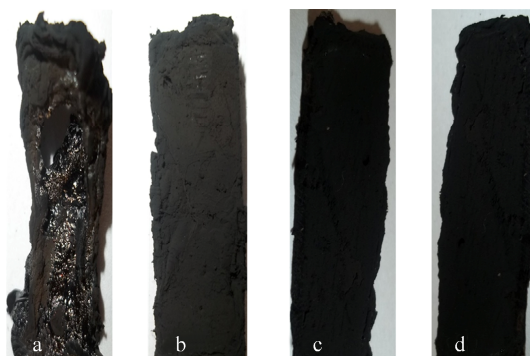


Fig. 6 Photo images of (a) neat, (b) 0.5 wt% (c) 1.0 wt% and (d) 1.5 wt% of P(BZ-co-CPL)/PZT nanocomposites

The three vertical ratings, V-2, V-1 and V-0 indicate that the material was tested in a vertical position and self-extinguished within a specified time after the ignition source was removed. To comply with the 20 mm UL 94 (150 mm length, 25 mm width and 3 mm thickness) V-0 vertical burn test, specimen must extinguish in less than 10 s. A second flame is then applied, the total flaming and glowing time of the sample must be less than 30 s. The total flaming time for all five samples must be less than 50 s. In addition, to attain the UL 94 V-0 rating, specimens cannot burn through their entire link and cannot drip flaming particles onto a cotton indicator located below the sample.

To further assess the material flammability, especially the ability of a polymer to drip and spread flame in a fire, vertical open flame testing was performed on samples. The composites are exposed to methane-fuelled flame for 5 s and in a flame testing hood free of passing air currents. After the 5 s of ignition period, the flame is removed and the time for the sample to self-extinguish is recorded. The behaviour of sample dripping and cotton ignition are also noted. The P(BZ-co-CPL) shows a burning rate, while P(BZ-co-CPL)/PZT shows a V-1 rating. It is noted that the PZT fibre reinforced nanocomposites did not exhibit an aggressive combustion during the tests, and the emission of few smoke and no flaming drips were observed as well. UL94 photo images of P(BZ-co-CPL) and P(BZ-co-CPL)/PZT are shown in Fig. 7.

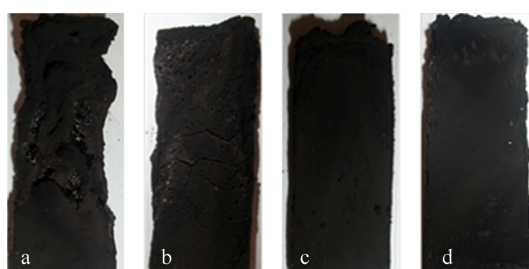


Fig. 7 UL 94 Photo images of (a) neat, (b) 0.5 wt%, (c) 1.0 wt% and (d) 1.5 wt% of P(BZ-co-CPL)/PZT nanocomposites

The morphologies of the chars obtained after UL 94 testing was examined by SEM and the results are shown in Fig. 8. The residual char was divided into two portions. The upper portion corresponded to the burnt portion, which was combustible and the other portion corresponded to the unburned portion, which was noncombustible. During combustion, a compact char layer was formed and gave the upper portion a very smooth surface. In the lower portion, only a relatively rough layer was formed and dispersed homogeneously in the complex. Obviously, the compact char layer was a very excellent thermal insulating layer acting as a barrier to inhibit gaseous products from diffusing to the flame and to shield the inside polymer from heat and oxygen. The loose and continuous carbonaceous structure is observed in the outer surface of the P(BZ-co-CPL) char (Fig. 8). However, the outer surface of the P(BZ-co-CPL)/PZT char shows a more compact and dense char layer compared with the P(BZ-co-CPL), which provides a good barrier to inhibit the transmission of heat and heat

diffusion when the sample is exposed to flame. The inner surface of the P(BZ-*co*-CPL)/PZT char has a swollen charred layer with a lot of small bubbles; in contrast, there are no bubbles on the inner surface of the P(BZ-*co*-CPL) char. This indicates that the phosphorus-nitrogen containing PZT in the P(BZ-*co*-CPL) promotes the formation of a compact and swollen char in condensed phase during combustion in a polymer matrix, which effectively prevents the inside thermal decomposition products from entering into the flame zone and also the oxygen from entering into the underlying polymer matrix. It is concluded that the thermo-oxidative stability of cyclotriphosphazene moieties enhances the char formation during combustion, which results in a protective char layer formed on the surface of thermosets serving as a barrier against heat and oxygen diffusion, and consequently the flame retardancy of the thermosets is improved significantly.

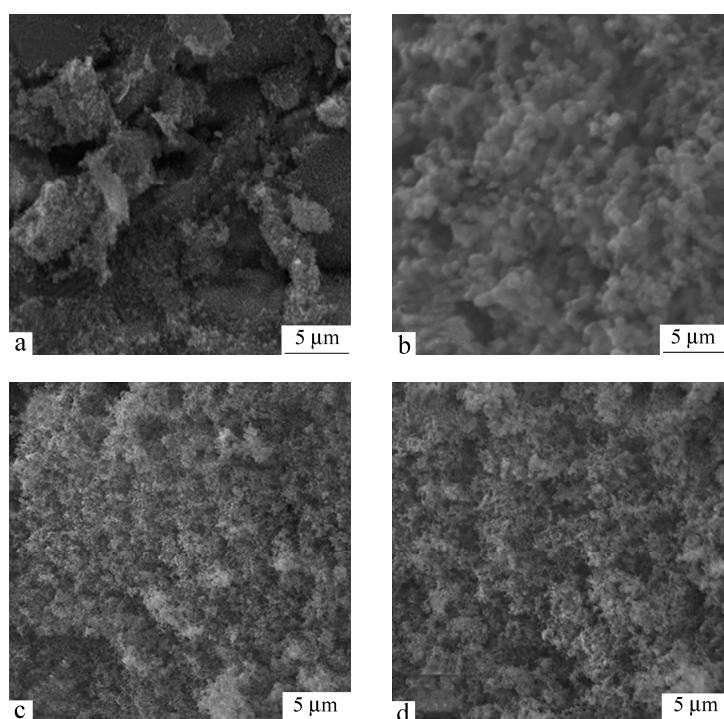


Fig. 8 SEM images of (a) neat, (b) 0.5 wt%, (c) 1.0 wt% and (d) 1.5 wt% of P(BZ-*co*-CPL)/PZT nanocomposites after UL94 testing

The overall result suggests that with phosphate and phosphazene moieties in the P(BZ-*co*-CPL)/PZT system, the formation of a vapor phase to dilute the oxygen concentration above the sample together with the formation of a phosphorus rich condensed phase to inhibit further decomposition of the sample during the thermal degradation results in the high char yield and the enhanced flame-retardancy effect as indicated by the high LOI value. This demonstrates that the phosphate and cyclotriphosphazene containing P(BZ-*co*-CPL)/PZT prepared in the present work has potential for wide versatility in applications. The P(BZ-*co*-CPL)/PZT composites after LOI were analyzed by Raman spectra, and the results are shown in Fig. 9. From the figure, the I_D/I_G values of all the composites (0.5 wt%, 1.0 wt% and 1.5 wt%) are 0.8379, 0.8533 and 0.8653 respectively, and the intensity of the composites also increases with increase in weight percentage of PZT. This may be due to the enhancement of phosphorus content in the composites.

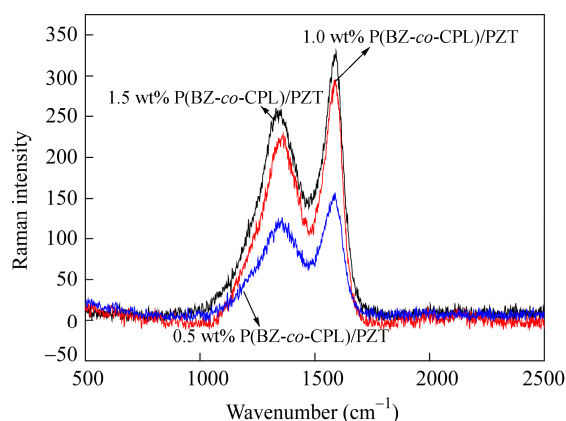


Fig. 9 Raman spectra for P(BZ-co-CPL)/PZT nanocomposites

Dielectric Properties

The rapid developments of high-speed rail transportation, wind-power generation and hydroelectric power generation put forward the increasingly newer and higher requirements to high-performance electrical insulation materials with much better thermal resistance, lower dielectric constant and dielectric loss. Low-dielectric (k) films are one of the performance drivers for continued scaling of integrated circuit devices. These films are required in microelectronic device interconnects to lower power consumption and minimize cross talk between metal lines that “interconnect” transistors. Lowering the dielectric constant reduces the propagation delays, RC constant (R = the resistance of the metal lines; C = the line capacitance) and metal cross-talk between wires. Hence, these materials should have a low dielectric constant and at the same time high thermal stability^[32, 33].

The development of new low- k materials can be carried out by two main approaches. The first method is to decrease the dipole strength by using materials with non-polar bonds. The other approach is to decrease the dipole density of the material itself, by introducing porosity or increasing of the free volume. An enhanced crosslinking tends to restrict the mobility of polymer chains, and thus decreases the dielectric constant; while a larger free volume plays an opposite effect on the dielectric properties. The value of dielectric constant of neat P(BZ-co-CPL) and P(BZ-co-CPL)/PZT is analyzed at 1MHz with varying temperature range (30 °C to 200 °C) and the values are shown in Fig. 10 and Table 1. The values of dielectric constant are decreased with increasing the temperature. From the values, it is ascertained that the P(BZ-co-CPL)/PZT systems exhibit stable dielectric behavior with regard to variation in temperature. The dielectric constant of P(BZ-co-CPL)/PZT systems is determined by the free volume, charge distribution and also by statistical thermal motion of polar groups. The values of dielectric constant of neat P(BZ-co-CPL) and 1.5 wt% P(BZ-co-CPL)/PZT nanocomposite are 3.39 and 2.47 at 30 °C, when the temperature was raised to 200 °C the values of dielectric constant are further reduced to 2.56 and 1.63 respectively. The reduction in the value of dielectric constant may be explained by an enhanced free volume imparted by PZT fiber and also the increase in temperature, as a result, the molecules have acquired more thermal energy and increased random thermal motion. Thus the molecules are less closely aligned with each other; hence the polarization of the molecules lowers the values of dielectric constant.

The values of dielectric loss of neat P(BZ-co-CPL) are marginal between the temperatures 30 °C and 120 °C and above 120 °C the values of dielectric loss are significant and this behavior supports the concept of free volume theory^[32] according to which the molecular mobility near T_g depends mainly on free volume. In the glassy state below T_g , the free volume will be frozen in and remain fixed. As the temperature increases, the glassy state will expand due to expansion and mobility of molecules, which results from the changing irrational amplitude of bound distances^[32]. This leads to the maximum dielectric loss at T_g for neat P(BZ-co-CPL) (Fig. 11). In the case of PZT fibre reinforced P(BZ-co-CPL) nanocomposites the value of dielectric loss was reduced significantly with increasing temperature and the reverse trend in the case of dielectric loss was observed above 150 °C, due to an increase in the value of T_g . This is interpreted on the basis of the nano

reinforcement of PZT fibres, which could restrict the motions of macromolecular chains. Further, an enhancement in the value of T_g is not only ascribed to the nano reinforcement of PZT fibre but also attributed to the additional crosslinking of the nano-composites due to the inter component reaction between PZT and P(BZ-co-CPL).

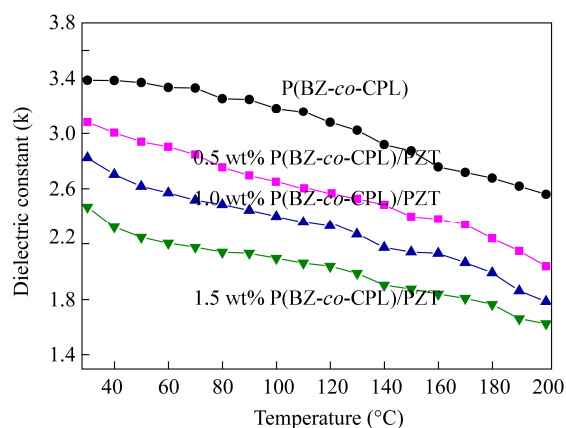


Fig. 10 Temperature variation of dielectric constant for P(BZ-co-CPL)/PZT

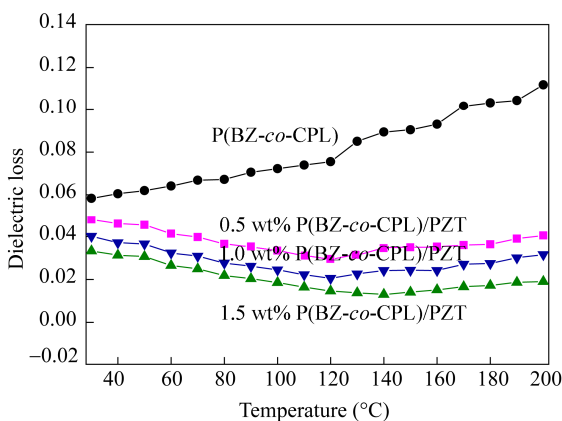


Fig. 11 Temperature variation of dielectric loss for P(BZ-co-CPL)/PZT nanocomposites

Morphology

XRD (Rich Seifert (Model 3000, Germany) diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm) is used to characterize the neat P(BZ-co-CPL), PZT reinforced P(BZ-co-CPL)/PZT nanocomposites. The X-ray diffraction patterns for the neat P(BZ-co-CPL) and PZT reinforced P(BZ-co-CPL) systems are shown in Fig. 12. The diffraction patterns of neat P(BZ-co-CPL) and 0.5 wt%, 1.0 wt% and 1.5 wt% PZT reinforced P(BZ-co-CPL)/PZT nanocomposites show a broad amorphous peak at $2\theta = 18.95^\circ$, 18.62° , 18.53° and 18.46° respectively, which suggests that the nanosized PZT fibres are uniformly dispersed in the P(BZ-co-CPL) matrix system. This dispersion was further confirmed by TEM.

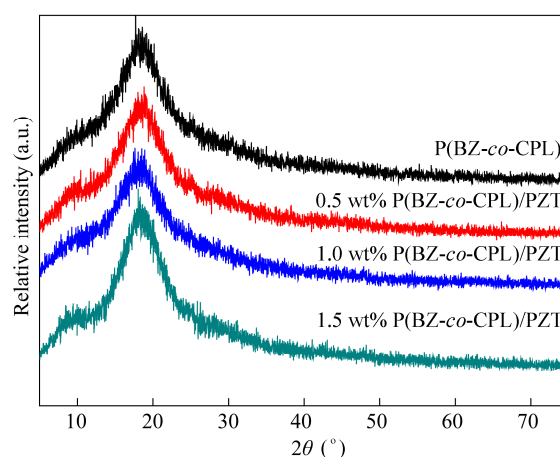


Fig. 12 XRD patterns for P(BZ-co-CPL)/PZT nanocomposites

The morphology behavior of P(BZ-co-CPL)/PZT was analyzed using HRTEM, and the images are shown in Fig. 13. The TEM images indicate the products were almost in the form of nanofibre and showed a narrow length distribution. It was ascertained that most of the nano fibres are about 2–6 μ m in length, with inner diameter of about 30–50 nm. Further, it can be seen that PZT nanofibres are homogeneously dispersed in the

P(BZ-*co*-CPL) composites, which suggests their good compatibility. The interpenetrating network formed between PZT nanofibres and P(BZ-*co*-CPL) polymer matrix imparts enhanced thermal and dielectric characteristics to the resulting nanocomposites.

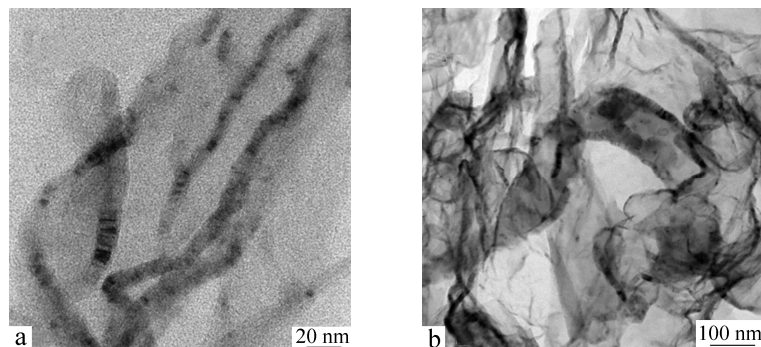


Fig. 13 HRTEM images of (a) 0.5 wt% and (b) 1.0 wt% of P(BZ-*co*-CPL)/PZT nanocomposites

CONCLUSIONS

In the present work, phosphorus and sulfur containing organic-inorganic hybrid cyclophosphazene nanofibres are used as flame retardant for P(BZ-*co*-CPL) matrix. Varying weight percentages (0.5 wt%, 1.0 wt% and 1.5 wt%) of PZT were incorporated into P(BZ-*co*-CPL) by solution polymerization *via* thermal cure. The resulting P(BZ-*co*-CPL)/PZT composite systems possess enhanced thermal properties and significant flame retardant behavior than those of neat P(BZ-*co*-CPL) matrix. The UL-94 results showed that P(BZ-*co*-CPL)/PZT hybrid nanocomposites are in the category of V-1 rating and in the case of neat P(BZ-*co*-CPL) system showed burning rating. The values of LOI are increased with increase in weight percentage of PZT in P(BZ-*co*-CPL). Data from TGA and DSC analyses indicate that the introduction of PZT can contribute an improved values of T_g and thermal stability, as well as higher percentage of char yield. SEM images showed that an increased PZT loading in P(BZ-*co*-CPL) matrix resulted in more compact and continuous char morphologies indicating an improved flame retardant behavior of the hybrid composites. The values of dielectric constant are decreased with increasing temperature, it is ascertained that the P(BZ-*co*-CPL)/PZT systems exhibit stable dielectric behavior with regard to variation in temperature. The uniform dispersion of PZT in P(BZ-*co*-CPL) composites was confirmed by TEM. Data from different studies indicate that the nanocomposites developed in the present study can be used as potential candidate as fire and heat resistant material for high performance aerospace, electrical and electronic applications.

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