

Maleimido Terminal Triaryl Pyridine Core Skeletal Modified Benzoxazine/Cyanate Ester Co-Cured Polymer (PBZ/CE) Hybrid Blends

S.G. Gunasekaran¹ M. Dharmendirakumar²

¹Department of Chemistry ²Department of Applied Science and Technology

¹Valliammai Engineering College, Kattankulathur-603203, Kancheepuram, India ²Anna University, Chennai-600025, India

Abstract— Three new types of skeletal modified maleimido terminal benzoxazine monomers (MI-BZs) were structurally designed and synthesized using N-(4-hydroxyphenyl) maleimide and formaldehyde solution through Mannich condensation reaction and were characterized by physico-chemical methods. Thermosetting polymer blends composed of benzoxazine-cyanate ester (PBZ/CE) were successfully prepared via co-curing of benzoxazines with cyanate esters such as biscyanate ester (BCE) and methylene diphenyl dicyanate (MDE). The cured new thermosetting blends from benzoxazine and cyanate ester resin exhibited good thermal stability, improved flame retardancy, low dielectric constant and better water uptake resistance. The shift in the luminescence emission has revealed the clear indication of formation of hybrid network via co-curing of benzoxazine matrices with cyanate ester. This was ascribed to the cycloaddition reaction between the two groups followed by the ring-opening of benzoxazine and cyclotrimerization of cyanate ester. The molecular level dispersion of the cyanate ester onto the benzoxazine matrices was evidenced by SEM analysis.

Key words: Benzoxazine; Cyanate Ester; Hybrid Blends; Thermal Stability; Morphology

I. INTRODUCTION

Development of new polymer matrices by co-reactive blending is a viable alternative to derive new matrix system since the co-reaction generally offers a high level of miscibility. Polybenzoxazine is a class of high performance polymer possessing superior mechanical properties and high temperature stability with high T_g [1-3]. However, the dielectric constant of polybenzoxazine (PBa), which is about 3.1-3.5, is insufficient for meeting the requirement of microelectronic applications [4]. In recent years, the preparation of polybenzoxazine with a low k and high performance has become one of the main research focuses [5]. There have been several approaches made to reduce the dielectric constant of polybenzoxazine, which include the incorporation of a fluorinated substituent into polybenzoxazine [6], nanoporous material of poly (caprolactone-co-benzoxazine) [7], epoxy-benzoxazine [8], benzoxazine with bismaleimides [9], POSS-polybenzoxazine nanocomposites [10-11], and introduction of an air gap into the interconnected structures by blending with nanoporous materials [12-14].

Cyanate ester resin has drawn a great deal of attention as one of the high performance thermosets, comparable to epoxy resins and polyimide due to their excellent mechanical properties, high thermal stability, radiation and flame resistance, low out-gassing, low dielectric loss and minimal water absorption [15-16]. They have been regarded as candidates with the greatest competition to fabricate advanced functional, structural materials for many

cutting edge fields including microelectronics, aerospace, transportation, and adhesive industries as replacements for epoxies [17-19]. The cyanate ester monomer undergoes thermal self cyclotrimerization to form a three-dimensional network structure of polycyanurate containing triazine groups [20]. The introduction of cyanate ester resin with high T_g and toughness into a polybenzoxazine matrix could result in a new matrix with some salient features of the epoxy resins and polyimide [21-22]. Kimura et al [23] investigated the curing reaction of bisphenol-A based benzoxazine with cyanate ester resin and the properties of the cured thermosetting resin. Therefore it is also expected that the cured thermosetting resin from benzoxazine resin and cyanate ester resin has high heat resistance, lower dielectric constant, and low moisture absorption.

Introducing heteroaromatic rings containing pyridine into the main chain of a synthetic polymer would impart certain properties such as the rigidity and polarizability to the prepared heteroaromatic polymers [24-25]. In addition, the incorporation of pyridine moiety into the polyimides might improve their electron affinity and electron-transporting properties [26]. Novel diamines containing pyridine were prepared using Chichibabin reaction and used to synthesize new PIs [27]. Liaw and his co-workers designed and fabricated a pyrene pendant core pyridine based diamine to prepare the organo soluble polyimides with fluorescence properties [28]. The introduction of flexible linkages, heteroaromatic rings and bulky pendant pyrene group in between the reactive sites reduced the crosslink density and cause a lowering of the glass transition temperature of the cured products [29].

In this perceptive, we reported the preparation of a series of thermosetting polymer blends composed of polybenzoxazine and cyanate ester and studied their thermal and dielectric properties. The main objective of the work is to develop the highly cross-linked networks of the blend matrix. The co-cured blends are addressed by FT-IR, TGA, Impedance analyzer, UV-Vis, PL and SEM techniques.

II. EXPERIMENTAL METHODS

A. Materials

Benzaldehyde (>98%), pyrene-1-carboxaldehyde (99%), 4-nitroacetophenone (≥96%) were purchased from Acros Organics India Ltd and used as received. Maleic anhydride (98%) and 10 wt % Pd/C were purchased from Alfa Aesar India. Thiophene-2-carboxaldehyde (98%), N,N-dimethyl formamide (99%), ammonium acetate (≥98%), glacial acetic acid (99.5%), paraformaldehyde (98%), celite, anhydrous magnesium sulphate (99%), phosphorus pentoxide (98%), tetrahydrofuran (99.5%), ethanol (99.9%) and diethyl ether (99.5%) were procured from SRL India. Hydrazine hydrate (80%) and 4-aminophenol (98%) was purchased from Loba Chemie, India. Bis (4-hydroxyphenyl) methane (Bisphenol F

98%) was bought from Aldrich chemical company, USA were used as received. Methylene diphenyl dicyanate (MDE) and 1, 4-bis (2-(4-cyanatophenyl)-2-propyl) benzene (BCE) were synthesized as per the reported procedure [30] and used for the present work. The N-(4-hydroxyphenyl) maleimide was also synthesized according to method [31].

B. Synthesis of Triaryl Pyridine Core Aromatic Diamine Derivatives

Triaryl pyridine core aromatic dinitro and diamine derivatives were synthesized by adopting a procedure reported elsewhere [33]. The products were then confirmed by ¹H NMR, ¹³C NMR and FT-IR techniques and matched with earlier reported data [34].

1) Structure of Phenyl Pendant Pyridine Core Aromatic Diamine (BBAPP)

FT-IR (KBr, cm⁻¹): 3352 (NH₂), 2952 (symmetric stretching), 2862 (asymmetric stretching), 1597 (Ar stretching), 1227 (Ar-O-CH₂).

¹H NMR (400MHz, CDCl₃, δ): 8.01 (s, 4H), 7.56 (s, 2H), 7.41 (s, 2H), 7.40 (s, 2H), 6.78 (s, 1H), 3.85 (d, 4H).

¹³C NMR (400MHz, CDCl₃, δ): 158, 150, 145, 138, 139, 127, 116, 115 (aromatic carbon).

2) Structure of Thiophenyl Pendant Pyridine Core Aromatic Diamine (TBAPP)

FT-IR (KBr, cm⁻¹): 3353 (NH₂), 2952 (symmetric stretching), 2861 (asymmetric stretching), 1596 (Ar stretching), 1226 (Ar-O-CH₂).

¹H NMR (400MHz, CDCl₃, δ): 7.91 (s, 4H), 7.56 (s, 2H), 7.44 (s, 2H), 7.34 (s, 2H), 6.68 (s, 4H), 4.1 (s, 4H).

¹³C NMR (400MHz, CDCl₃, δ): 158, 147, 144, 142, 117, 114 (aromatic carbon).

3) Structure of Pyrenyl Pendant Pyridine Core Aromatic Diamine (PBAPP)

FT-IR (KBr, cm⁻¹): 3351 (NH₂), 2953 (symmetric stretching), 2864 (asymmetric stretching), 1595 (Ar stretching), 1224 (Ar-O-CH₂).

¹H NMR (400MHz, CDCl₃, δ): 8.77 (d, 1H), 8.55 (d, 1H), 8.36 (s, 2H), 8.27 (d, 1H).

¹³C NMR (400MHz, CDCl₃, δ): 160, 158, 150, 143, 137, 135, 129, 128, 126, 125, 122, 121, 117, 114, 91, 54 (aromatic carbon).

C. Synthesis of 1,4-Bis (2-(4-Cyanatophenyl)-2-Propyl) Benzene (BCE)

FT-IR (KBr, cm⁻¹): 2968 (symmetric stretching), 2862 (asymmetric stretching), 2237 (-OCN), 1505, 1227.

¹H NMR (400MHz, CDCl₃, δ): 7.1 (s, 4H), 7.2 (d, 4H), 7.3 (d, 4H) and 1.6 (s, 12H, aliphatic proton).

¹³C NMR (400MHz, CDCl₃, δ): 149, 148, 147, 127, 125, 113, 108 (aromatic carbon), 41, 25 (aliphatic carbon).

D. Synthesis Of N-(4-Hydroxyphenyl) Maleimide (HPM)

FT-IR (KBr, cm⁻¹): 3482 (Ph-OH), 1706 (C=O symmetrical), 1384 (C-N) and 715 (C=O bending).

¹H NMR (400MHz, DMSO-d₆, δ): δ 6.82 (d, 2H), 7.09 (d, 2H), 7.15 (d, 2H) and 9.71 (s, 1H).

¹³C NMR (400MHz, DMSO-d₆, δ): 170.5, 157.6, 134.7, 128.5, 122.7 and 115.7.

E. Synthesis of Methylene Diphenyl Dicyanate (MDE)

FT-IR (KBr, cm⁻¹): 2961 (symmetric stretching), 2865 (asymmetric stretching), 2234 (-OCN), 1507, 1225.

¹H NMR (400MHz, CDCl₃, δ): 7.0 (d, 4H), 7.1 (d, 4H) and 4.1 (s, 2H, aliphatic proton).

¹³C NMR (400MHz, CDCl₃, δ): 153, 148, 135, 118 (aromatic carbon), 41 (aliphatic carbon).

F. Synthesis of Maleimido Terminal Triaryl Pyridine Core Aromatic Diamine Based Benzoxazine Monomers (MI-Bzs)

Three different types of benzoxazine monomers were synthesized according to the reported route [35]. Here, benzoxazines are denoted as MI-BZ_a = BBAPP-HPM; MI-BZ_b = TBAPP-HPM; MI-BZ_c = PBAPP-HPM.

G. Preparation of PBZ/CE Hybrid Blends

The benzoxazines (BZs) and cyanate ester (CE) monomers such as BCE or MDE were co-dissolved in 10 mL of 1, 4-dioxane and the molar ratio of the mixture was 1/1 [36]. The synthesis of cyanate ester modified polybenzoxazine (PBZ/CE) hybrid blends was represented by Scheme 1. The blends were then cast on the corresponding glass plates and pretreated with dichlorodimethylsilane. The benzoxazines (MI-PBZs) and cyanate ester monomers BCE or MDE were subjected to a cure schedule as follows: 120°C/1 h, 140°C/1 h, 180°C/1 h, 220°C/1 h and 250°C/1 h to obtain PBZ/CE blended systems.

H. Characterization

FT-IR spectra were recorded on a Perkin Elmer 6X FT-IR spectrometer. About 100 mg of optical-grade KBr was ground with sufficient quantity of the solid sample to make 1.0 wt % mixture for making KBr pellets. After the sample was loaded, a minimum of 16 scans were collected for each sample at a resolution of ±4 cm⁻¹. All ¹H NMR and ¹³C NMR analyses were done in d-CHCl₃ and DMSO-d₆ recorded on a Bruker 300 spectrometer.

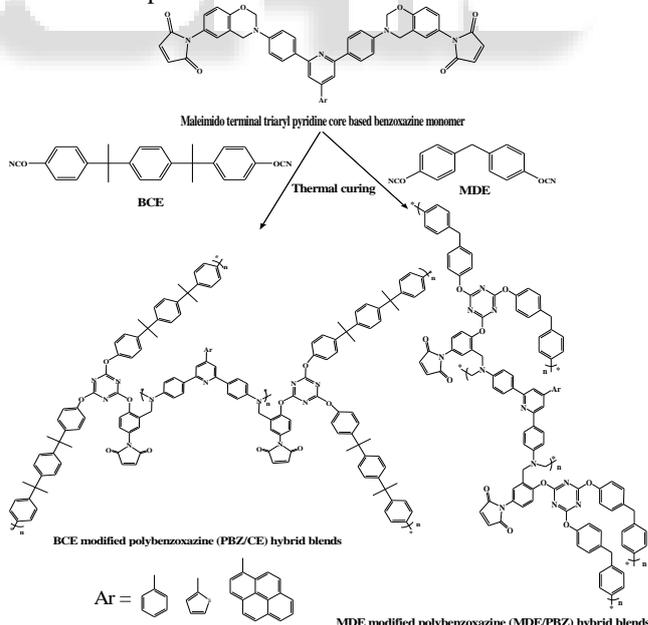


Fig. 1: Schematic representation of synthesis of cyanate ester co-cured polybenzoxazine (PBZ/CE) hybrid blends

A Netzsch DSC-200 differential scanning calorimeter was used for the calorimetric analysis. The instrument was calibrated with Indium supplied by Netzsch. Measurements were performed under a continuous flow of nitrogen (60 mL/min). All the samples (about 10 mg in weight) were heated from ambient to 400°C and the

thermograms were recorded at a heating rate of 10°C/min. Thermo gravimetric analysis (TGA) was performed in a DSC-2920 from TA Instruments coupled with a TA-2000 control system. The samples were heated at a scanning rate of 10°C/min under nitrogen atmosphere in order to diminish oxidation. The dielectric constants of the neat PBZs and the PBZ/CE hybrid blends were determined with the help of an impedance analyzer (Solartron impedance/gain phase analyzer 1260) using a platinum (Pt) electrode at 30°C in a frequency range of 1 MHz.

The neat PBZs and PBZ/CE hybrid blends were characterized by UV-Vis-NIR spectrophotometer (UV-Vis-NIR) (U-4100, Hitachi, Japan). The absorbance of the solution was measured with a wavelength range of 200 to 500 nm. The emission properties of the neat PBZs and the PBZ/CE hybrid blends were studied using Fluorescence spectrophotometer (Cary Eclipse, FL1201M002, Japan) with wavelength range from 300 to 600 nm. Scanning electron microscope (SEM) (Hitachi S-3400N) was used to observe the surface morphology of the neat PBZs and the PBZ/CE hybrid blends.

III. RESULTS AND DISCUSSION

A. Structure of Benzoxazine Monomers

Three different types of maleimido terminal benzoxazine monomers were synthesized and characterized by ¹H-NMR, ¹³C-NMR, FT-IR, UV-Vis and PL techniques and matched with earlier reported data [35].

B. Structure of MI-BZ_a monomer

FT-IR (KBr, cm⁻¹): 2935 (symmetric stretching), 1734 (C=O), 1458 (substituted benzene), 1384 (C-N), 1247 (C-O), 942 (N-CH₂-O).

¹H NMR (400 MHz, DMSO-d₆, δ): 8.43 (s, 4H), 7.97 (s, 2H), 7.71 (s, 2H), 7.35 (s, 2H), 7.30 (s, 2H), 6.99 (s, 4H), 6.70 (s, 2H, ArH), 6.06 (s, 4H) 4.72 (s, 4H).

¹³C NMR (400 MHz, DMSO-d₆, δ): 162, 158, 151, 143, 139, 137, 131, 129, 128, 127, 121, 117, 114, 113, 90, 57 (aromatic carbon).

1) Structure of MI-BZ_b monomer

FT-IR (KBr, cm⁻¹): 2935 (symmetric stretching), 1734 (C=O), 1458 (substituted benzene), 1384 (C-N), 1245 (C-O), 942 (N-CH₂-O), 840, 702 (symmetric stretching, C-S).

¹H NMR (400 MHz, DMSO-d₆, δ): 7.72 (s, 3H), 7.68 (s, 3H), 7.61 (s, 3H), 6.06 (s, 4H) 4.82 (s, 4H).

¹³C NMR (400 MHz, DMSO-d₆, δ): 163, 161, 158, 148, 144, 142, 138, 131, 129, 128, 128, 127, 125, 121, 118, 113, 90, 54 (aromatic carbon).

2) Structure of MI-BZ_c monomer

FT-IR (KBr, cm⁻¹): 2938 (symmetric stretching), 1731(C=O), 1457 (substituted benzene), 1387 (C-N), 1244 (C-O), 943 (N-CH₂-O), 840, 702 (symmetric stretching, C-S).

¹H NMR (400 MHz, DMSO-d₆, δ): 8.76 (s, 1H), 8.26 (s, 4H), 7.76 (s, 4H), 7.53 (s, 2H), 6.06 (s, 2H) 4.74 (s, 4H).

¹³C NMR (400 MHz, DMSO-d₆, δ): 161, 159, 150, 143, 138, 131, 113, 112, 90, 54 (aromatic carbon).

3.1.4 UV-Vis absorption properties of MI-BZ monomers

UV-Vis (THF): λ_{max}=308 (MI-BZ_a), 312 (MI-BZ_b), 277, 346 (MI-BZ_c)

3) PL Properties of MI-BZ Monomers

Emission (nm): 450 (MI-BZ_a), 466 (MI-BZ_b), 447 (MI-BZ_c)

C. Characterization of PBZ/CE Polymer Blends

The pyridine core benzoxazine and cyanate ester blended systems were synthesized and represented in Scheme 1. Figure 1 shows the FT-IR spectra of neat PBZs and PBZ/CE blends.

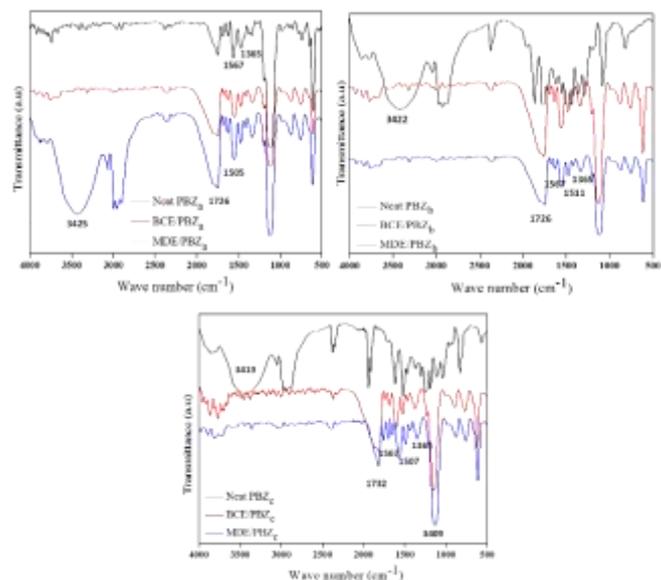


Fig. 2: FT-IR spectra of neat PBZ and PBZ/CE hybrid blends

The absorption band at 3425 cm⁻¹ confirmed the ring opening polymerization of benzoxazines, as indicated in Figure 1. The disappearance of bands at 2237 cm⁻¹ (-OCN-group of the cyanate ester) and 914 cm⁻¹ (oxazine group) and the appearance of a new band at 1565 and 1365 cm⁻¹ corresponding to triazine group of copolymerized cyanate esters onto the benzoxazine matrices. The symmetric and asymmetric stretching frequencies of the -CH₂ group were appeared at 2924 cm⁻¹ and 2868 cm⁻¹ respectively [36].

D. Thermal Properties

1) Differential Scanning Calorimetry

Differential scanning calorimetric analysis was performed to determine the glass transition temperatures of the neat PBZ matrices and PBZ/CE blends and the T_g values are listed in Table 1. The DSC thermograms of the neat PBZ and PBZ/CE blends are presented in Figure 2.

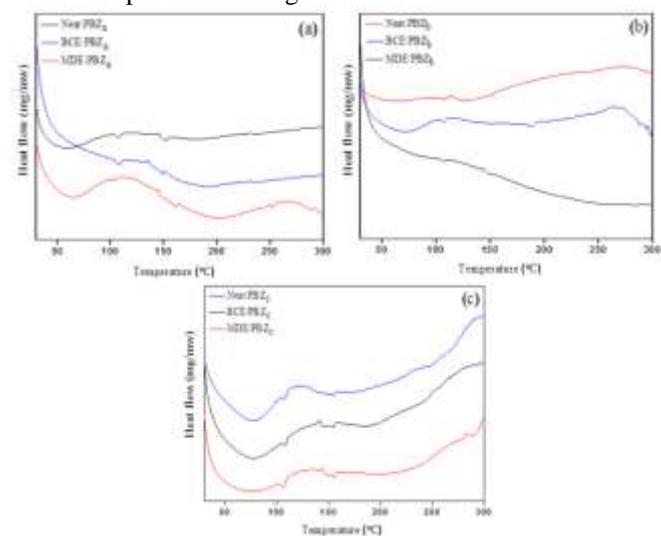


Fig. 3: DSC thermograms of neat PBZ and PBZ/CE hybrid blends

The incorporation of BCE/MDE has the effect of increasing the T_g of the matrix over that of the neat PBZ³⁷. However, the BCE blended PBZ systems exhibit lower T_g values, compared to that of MDE-PBZ blends. The increase in the values of glass transition temperatures of the PBZ/CE blends may be explained due to the flexible nature of cyanate skeleton molecules. Since the inclusion of BCE into the BZ matrix increases both the internal rotations and thermal motions of the polymer chains of the resulting system, the PBZ-CE blends exhibited lower T_g values than that of MDE-PBZ blends [30,37].

Systems	T_g (°C)	Char Yield (at 700°C) (%)	Dielectric Constant (ϵ)	LOI (at 700°C) (σ)+17.5	Water absorption (%)
Neat PBZ _a	190	41.2	3.73	34.0	0.64
BCE/PBZ _a	193	48.1	2.92	36.7	0.54
MDE/PBZ _a	198	49.8	3.41	37.4	0.45
Neat PBZ _b	194	61.8	4.11	42.2	0.62
BCE/PBZ _b	198	65.5	3.11	43.7	0.59
MDE/PBZ _b	205	68.0	3.74	44.7	0.52
Neat PBZ _c	195	61.7	3.65	42.2	0.63
BCE/PBZ _c	199	62.5	2.70	42.5	0.57
MDE/PBZ _c	203	64.2	3.01	43.2	0.47

Table 1: Thermal and dielectric properties of neat PBZ and PBZ/CE hybrid blends

T_g = Glass transition temperature;

LOI= Limiting oxygen index

Thermo gravimetric Analysis

The thermo gravimetric analysis was used to ascertain the thermal stability of the neat PBZs and PBZ/CE blends, and the data obtained from the TG analysis are presented in Figure 3 and Table 1. The PBZ/CE blends exhibited higher thermal stability and higher char yield than those of the neat PBZ matrices. The T_d values are increased with blending of CE in the matrices.

It was observed that the rates of mass loss from segmental decompositions were significantly decreased due to the formation of blends. The thermal decomposition of the PBZ/CE blends shift towards the higher temperature range, which confirms the enhancement of thermal stability of the PBZ matrices. In this case, cyanate esters were involved in the formation of cross-linked triazine network because of the copolymerization of CE and these CE were tethered onto the benzoxazine matrices. The ether linkage present in the cyanate ester (BCE) system which induces free rotational movement and reduces the thermal stability of the resulting BCE/PBZ systems than those of the MDE/PBZ systems [36].

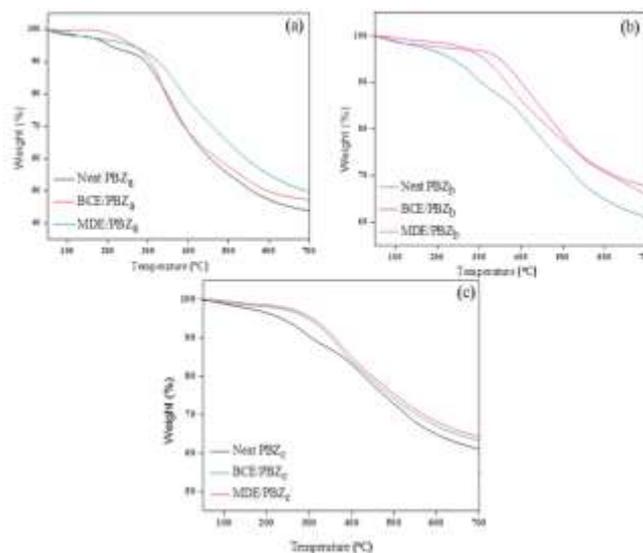


Fig. 4: TGA thermograms of neat PBZ and PBZ/CE hybrid blends

2) Limiting Oxygen Index (LOI)

The present study describes the flame retardant behaviour of the neat PBZs and PBZ/CE blends for their char yield at 700°C. The LOI values are presented in Table 1 and Figure 4.

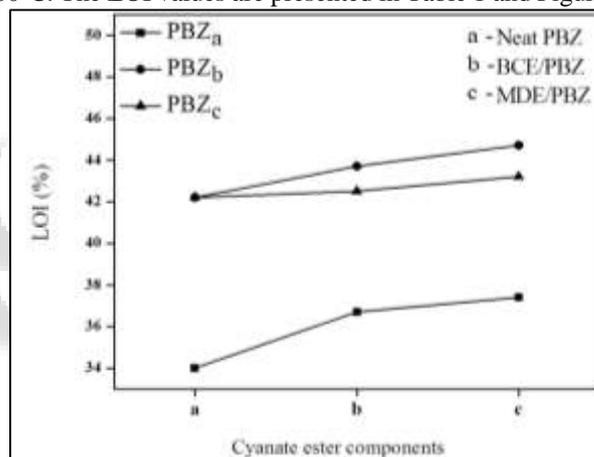


Fig. 4: LOI values of neat PBZ and PBZ/CE hybrid blends

The LOI values were found to be in the range of 19.5-28.4. Furthermore, the flame retardancy increased after the blending of cyanate esters with the benzoxazine matrices. The burning behaviour was correlated to the crosslink density of the organic matrix, i.e., with increasing crosslink density; the flammability resistance increases due to the formation of higher char yield. Thus, the formation of triazine skeleton attained from the copolymerization of cyanate ester systems with benzoxazines would lead to better flame retardancy.

E. Water Absorption Behavior

Water absorption characteristics of the PBZ/CE systems are presented in Figure 5 and Table 1. The water absorption test was carried out by immersing the specimen of appropriate dimension in deionized water at RT for 48 h. The percentage water uptake of the neat PBZ is 0.64 (PBZ_a), 0.63 (PBZ_b) and 0.62 (PBZ_c). The blending of cyanate esters (BCE/MDE) into the PBZ hybrids decreased the percentage water uptake than that of the neat PBZs. During the course of polymerization, it is likely that the phenolic hydroxyl groups resulting from the ring opening of oxazine moiety may react with cyanate moiety via iminocarbonate intermediate that ultimately forms

the triazine network. Hence, this unavailability of free OH is the cause for uptake of water molecules leading to the decreased water absorption properties [38-39].

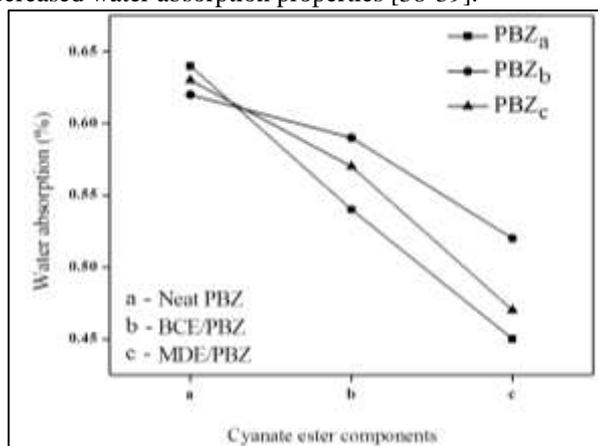


Fig. 5: Water absorption behaviour of neat PBZ and PBZ/CE hybrid blends

F. Dielectric Constant

Table 1 gives the values of the dielectric constant of the neat PBZ and PBZ/CE blends. The dielectric constant of the PBZ/CE systems decreases after the blending cyanate ester (BCE/MDE) into the PBZ matrix. Among the PBZ/CE systems studied, the BCE/PBZ based system possesses the lowest dielectric constant, and the neat PBZ systems exhibit the highest dielectric constant (Figure 6). The dielectric constant can be reduced by an increase in the free volume of the molecule or by a reduction in the polarization [40]. The iminocarbonate, via co-curing of benzoxazine with dicyanates, led to more spacing between the polymer molecules, resulting in less efficient chain packing and an increase in the free volume of the cyanate esters, which reduced the dielectric constant of the cyanate esters. In addition, less polar diphenyl ether, resulted from co-curing may also reduce the dielectric constant of the hybrid blends than that of the neat PBZ systems [38]. Furthermore, the presence of a low-polar, fully cured cyanate ester (triazine structure) might have increased the hydrophobicity and therefore, reduced the dielectric constant. The lower dielectric constant could also be interpreted as the reduction of unreacted OCN groups, which resulted from increased mobility when the iminocarbonate cyanate ester took part in the curing process [38-40].

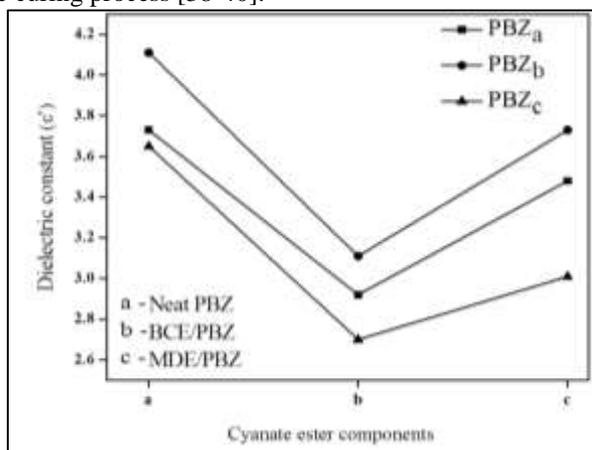


Fig. 6: Dielectric behaviour of neat PBZ and PBZ/CE hybrid blends

G. Optical Properties

1) UV-Vis Absorption Spectra

The UV-vis absorption studies of the neat PBZ and PBZ/CE blends were illustrated in Figure 7.

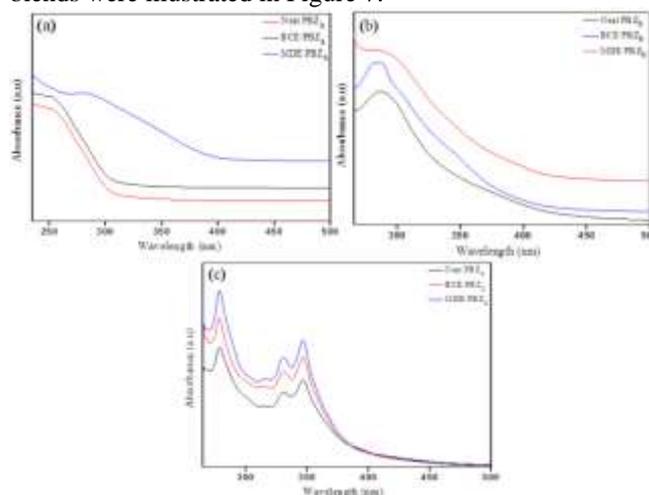


Fig. 7: UV-Vis absorption spectra of neat PBZ and PBZ/CE hybrid blends

The UV-Vis absorption behaviour was investigated in THF using UV-Vis radiation as shown in Figure 7. It was found that the neat PBZs display one prominent band with an unsymmetrical shape, which corresponds to benzoxazine matrix. The absorption of neat PBZs is shifted by about 10 nm from that of diamine after polycondensation ($n-\pi^*$ transition). As seen in Figure 7, the PBZ/CE blends (BCE/PBZ and MDE/PBZ) showed a band at 288 nm, which thus reveals the successful uniform dispersion of CE into the PBZ matrix.

2) Photoluminescence Spectra

Figure 8 shows the PL spectra of the neat PBZ and PBZ/CE blends. It is clear that the emission peak was originated from the pyridine core present in the benzoxazine structure. The emission peak is resulted from the overlapping of the absorption of the polymer exhibited as weak bands.

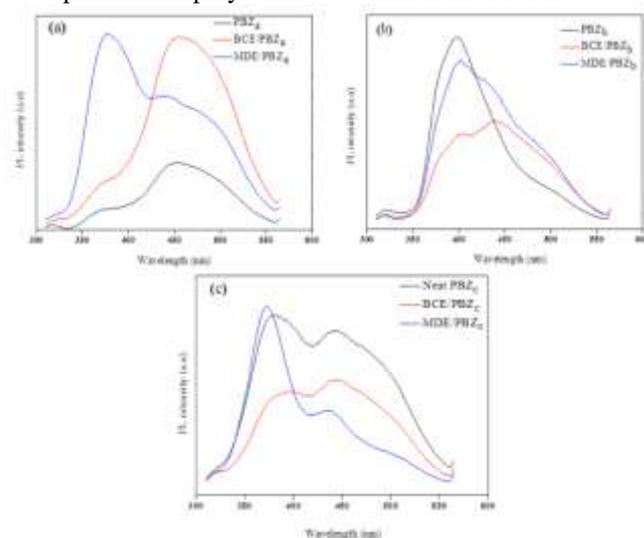


Fig. 8: Photoluminescence spectra of neat PBZ and PBZ/CE hybrid blends

No apparent changes were observed for the emission of the PBZ/CE systems. This study further confirms the homogeneous dispersion of CE in the PBZ matrix. The strong fluorescent peaks were observed at the wavelength of 453 nm

for PBZ_a, 398 nm for PBZ_b and 381 & 444 nm for PBZ_c. The cyanate ester modified polybenzoxazine blended systems also showed the strong fluorescent bands at 458 nm for BCE/PBZ_a, 378 nm for MDE/PBZ_a, 441 nm for BCE/MI-PBZ_b, 402 nm for MDE/PBZ_b, 396 & 444 nm for BCE/PBZ_c, 372 & 437 nm for MDE/PBZ_c. Hence, these emission peaks corresponding to the polybenzoxazine-cyanate ester blends show their photoluminescence properties.

H. Morphology of The PBZ/CE Polymer Blends

The morphology of the neat PBZs and cyanate ester blended polybenzoxazine systems was examined by using SEM analysis. Figure 9 shows the SEM micrograph of the neat PBZs and PBZ/CE blends. The SEM images indicated the smooth and homogeneous morphology of the neat PBZs and PBZ/CE systems. No discernible phase separation was observed for the neat PBZ system. The cyanate ester molecules can be seen as spherical nodules, which can be ascribed to the polycyanurate dispersed in the co-reacted PBZ/CE network. This indicates the good miscibility (compatibility) of CE with the BZ systems, and ascribes the formation of interlinked network between BZ and cyanate ester [36].

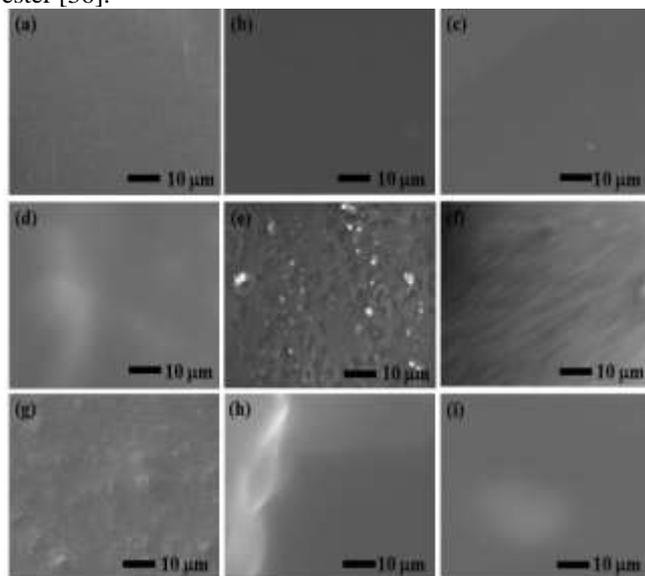


Fig. 9: SEM micrographs of (a) neat PBZ_a, (b) neat PBZ_b, (c) neat PBZ_c, (d) BCE/PBZ_a (e) BCE/PBZ_b, (f) BCE/PBZ_c, (g) MDE/PBZ_a, (h) MDE/PBZ_b and (i) MDE/PBZ_c hybrid blends

IV. CONCLUSION

In the present work, a new series of novel polybenzoxazine-cyanate ester (PBZ/CE) hybrid blends have been successfully developed via co-curing of benzoxazine with cyanate ester. The formation of polymer blends was confirmed by various spectral analyses. The hybrid PBZ/CE systems showed higher glass transition temperature when compared to that of the neat PBZ matrices. Among the PBZ/CE hybrids, the hybrid obtained using MDE possesses a higher T_g 198 (PBZ_a), 205 (PBZ_b) and 203 (PBZ_c) than that of blend prepared using BCE as cyanate ester. The data from the TG analysis indicate that the PBZ/CE blends exhibit excellent thermal stability and higher char yield compared to polybenzoxazine matrix. The value of the dielectric constant

(ϵ') of PBZ incorporated CE is lower compared to that of the neat PBZs. It was observed that the values of the dielectric constant obtained for the PBZ/CE hybrid systems are lower ($k=2.92$ for BCE/PBZ_a, 3.41 for MDE/PBZ_a, 3.11 for BCE/PBZ_b, 3.74 for MDE/PBZ_b, 2.70 for BCE/PBZ_c and 3.01 for MDE/PBZ_c) than those of neat PBZ systems ($k=3.73$ for neat PBZ_a, 4.11 for neat PBZ_b and 3.65 for neat PBZ_c). The water uptake percentage was reduced to 30 % for polybenzoxazine-cyanate ester blends due the unavailability of hydroxyl groups after the formation of cross-linked triazine network. The polybenzoxazine-cyanate ester hybrid blends showed strong fluorescent emission peaks, as evidenced by photoluminescence analyses. The molecular level distinct phase morphology of the PBZ/CE systems was confirmed from homogeneous dispersion of cyanate ester in the co-reacted network by the SEM analysis.

ACKNOWLEDGEMENTS

The authors acknowledge the Dr. R. Jayavel, Director, Centre for Research, Anna University, Chennai, India for providing the Scanning electron microscope analysis facility. The authors also thank K. Srinivasan, Department of Chemistry, Anna University, Chennai, for providing PL studies.

REFERENCES

- [1] X. Ning and H. Ishida, "Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers," *J. Polym. Sci. A: Polym. Chem*, vol. 32, pp. 1121-1129, 1994.
- [2] C. P. Reghunadhan Nair, "Advances in addition-cure phenolic resins," *Prog. Polym. Sci*, vol. 29, pp. 401-498, 2004.
- [3] Y. Yagci, B. Kiskan and N. N. Ghosh, "Recent advancement on polybenzoxazine-A newly developed high performance thermoset," *J. Polym. Sci. A: Polym. Chem*, vol. 47, pp. 5565-5576, 2009.
- [4] G. Liang and M. Zhang, "Enhancement of processability of cyanate ester resin via copolymerization with epoxy resin," *J. Appl. Polym. Sci*, vol. 85, pp. 2377-2381, 2002.
- [5] M. R. Vengatesan, S. Devaraju, K. Dinakaran and M. Alagar, "SBA-15 filled polybenzoxazine nanocomposites for low-k dielectric applications," *J. Mater. Chem*, vol. 22, pp. 7559-7566, 2012.
- [6] Y. C. Su and F. C. Chang, "Synthesis and characterization of fluorinated polybenzoxazine material with low dielectric constant," *Polymer*, vol. 44, pp. 7989-7996, 2003.
- [7] Y. C. Su, W. C. Chen, K. L. Ou and F. C. Chang, "Study of the morphologies and dielectric constants of nanoporous materials derived from benzoxazine-terminated poly (3-caprolactone)/ polybenzoxazine copolymers," *Polymer*, vol. 46, pp. 3758-3766, 2005.
- [8] H. Ishida and D. J. Allen, "Physical and mechanical characterization of near-zero shrinkage polybenzoxazines," *J. Polym. Sci. B: Polym. Phys*, vol. 34, pp. 1019-1030, 1996.
- [9] K. S. Santhosh Kumar, C. P. R. Nair and K. N. Ninan, "Benzoxazine-bismaleimide blends: Curing and

- thermal properties,” *Eur. Polym. J.*, vol. 43, pp. 2504-2514, 2007.
- [10] M. C. Tseng and Y. Liu, “Preparation, morphology and ultra-low dielectric constants of benzoxazine-based polymers/ polyhedral oligomeric silsesquioxane (POSS) nanocomposites,” *Polymer*, vol. 51, pp. 5567-5575, 2010.
- [11] M. R. Vengatesan, S. Devaraju, A. Ashok Kumar and M. Alagar, “Studies on thermal and dielectric properties of octa (maleimido phenyl) silsesquioxane (OMPS)-polybenzoxazine (PBZ) hybrid nanocomposites,” *High Perform. Polym.*, vol. 23, pp. 441-456, 2011.
- [12] Y. W. Chen and E. T. Kang, “New approach to nanocomposites of polyimides containing polyhedral oligomeric silsesquioxane for dielectric applications,” *Mater. Lett.*, vol. 58, pp. 3716-3799, 2004.
- [13] C. M. Leu, Y. T. Chang and K. H. Wei, “Polyimide-side-chain tethered polyhedral oligomeric silsesquioxane nanocomposites for low-dielectric film applications,” *Chem. Mater.*, vol. 15, pp. 3721-3727, 2003.
- [14] L. Yang, C. Zhang, S. Pilla and S. Gong, “Polybenzoxazine-core shell rubber-carbon nanotube nanocomposites,” *Compos. A: Appl. Sci. Manufactur.*, vol. 39, pp. 1653-1659, 2008.
- [15] I. Hamerton and J. N. Hay, “Recent developments in the chemistry of cyanate esters,” *Polym. Inter.*, vol. 47, pp. 465-473, 1998.
- [16] M. Suguna Lakshmi and B. S. R. Reddy, “Synthesis and characterization of new epoxy and cyanate ester resins,” *Eur. Polym. J.*, vol. 38, pp. 795-801, 2002.
- [17] T. Fang and D. A. Shimp, “Polycyanate esters: science and applications,” *Prog. Polym. Sci.*, vol. 20, pp. 61-118, 1995.
- [18] A. Chaplin, I. Hamerton, B. J. Howlin and J. M. Barton, “Development of Novel Functionalized Aryl Cyanate Ester Oligomers. 1. Synthesis and Thermal Characterization of the Monomers,” *Macromolecules*, vol. 27, pp. 4927-4935, 1994.
- [19] C. P. R. Nair, M. Dona and K. N. Ninan, “Imido-phenolic-triazine network polymers derived from maleimide-functional novolac,” *Eur. Polym. J.*, vol. 37, pp. 315-321, 2001.
- [20] C. P. R. Nair, D. Mathew and K. N. Ninan, Cyanate ester resins, recent developments, *Adv. Polym. Sci.*, vol. 155, pp. 1-99, 2001.
- [21] H. Kimura, K. Ohtsuka and A. Matsumoto, “New type of phenolic resin: Curing reaction of phenol-novolac based benzoxazine with bisoxazoline or epoxy resin using latent curing agent and the properties of the cured resin,” *J. Appl. Polym. Sci.*, vol. 112, pp. 1762-1770, 2009.
- [22] X. Li, Y. Xia, W. Xu, Q. Ran and Y. Gu, “The curing procedure for a benzoxazine-cyanate-epoxy system and the properties of the terpolymer,” *Polym. Chem.*, vol. 3, pp. 1629-1633, 2012.
- [23] H. Kimura, K. Ohtsuka and A. Matsumoto, “Curing reaction of bisphenol-A based benzoxazine with cyanate ester resin and the properties of the cured thermosetting resin,” *express Polym. Lett.*, vol. 5, pp. 1113-1122, 2011.
- [24] M. A. Shahram, M. M. Rezvaneh and N. Majid, “Synthesis and characterization of heat resistant, pyridine-based polyimides with preformed ether and ester groups,” *Eur. Polym. J.*, vol. 41, pp. 1024-1029, 2005.
- [25] T. Kanbara, N. Saito, T. Yamamoto and K. Kubota, “Preparation and properties of poly (quinolinediyl)s and poly(isoquinoline-1,4-diyl) with new π -conjugation systems,” *Macromolecules*, vol. 24, pp. 5883-5885, 1991.
- [26] S. Dailey, M. Halim, E. Rebourt, L. E. Horsburgh, I. D. W. Samuel and A. P. Monkman, “An efficient electron-transporting polymer for light-emitting diodes,” *J. Phys. Condens. Matter*, vol. 10, pp. 5171-5188, 1998.
- [27] B. Tamami and H. Yeganeh, “Preparation and properties of novel polyimides derived from 4-aryl-2,6 bis(4-amino phenyl)pyridine,” *J. Polym. Sci. A: Polym. Chem.*, vol. 39, pp. 3826-3831, 2001.
- [28] D. J. Liaw, K. L. Wang and F. C. Chang, “Novel organosoluble poly (pyridine-imide) with pendent pyrene group: synthesis, thermal, optical, electrochemical, electrochromic, and protonation characterization,” *Macromolecules*, vol. 40, pp. 3568-3754, 2007.
- [29] Y. C. Kung and S. H. Hsiao, “Solution-processable, high-Tg, ambipolar polyimide electrochromics bearing pyrenylamine units,” *J. Mater. Chem.*, vol. 21, pp. 1746-1754, 2011.
- [30] S. Devaraju, M. R. Vengatesan, M. Selvi, A. Ashok Kumar, I. Hamerton, J. S. Go and M. Alagar, “Low surface free energy cyanate ester-silica hybrid (CE-SiO₂) nanomaterials for low k dielectric applications,” *RSC Adv.*, vol. 3, pp. 12915-12921, 2013.
- [31] D. H. Choi, S. Song, W. S. Jahng and N. Kim, “Optimal Synthetic Design of Second-Order Nonlinear Optical Material with Good Temporal Stability,” *Mol. Cryst. Liq. Cryst.*, vol. 280, pp. 17-26, 1996.
- [32] N. Amutha and M. Sarojadevi, “Synthesis and characterization of pyridine and anthracene containing bismaleimides, bisnadimides and polyaspartimides,” *J. Polym. Res.*, vol. 15, pp. 487-499, 2008.
- [33] R. Hariharan, S. Bhuvana, M. Anitha Malbi and M. Sarojadevi, “Synthesis and characterization of polyimides containing pyridine moiety,” *J. Appl. Polym. Sci.*, vol. 93 pp. 1846-1853, 2004.
- [34] S. Yan, W. Chen, X. Yang, C. Chen, M. Huang, Z. Xu, K. W. K. Yeung and C. F. Yi, “Soluble polyimides based on a novel pyridine-containing diamine m,p-PAPP and various aromatic dianhydrides,” *Polym. Bull.*, vol. 66, pp. 1191-1206, 2011.
- [35] S. Devaraju, M. R. Vengatesan, A. Ashok Kumar and M. Alagar, “Polybenzoxazine-silica (PBZ-SiO₂) hybrid nanocomposites through insitu sol-gel method,” *J. Sol-Gel Sci. Technol.*, vol. 60, pp. 33-40, 2011.
- [36] K. S. Santhosh Kumar, C. P. Reghunadhan Nair and K. N. Ninan, “Investigations on the cure chemistry and polymer properties of benzoxazine-cyanate ester blends,” *Eur. Polym. J.*, vol. 45, pp. 494-502, 2009.
- [37] C. P. R. Nair, T. Francis, T. M. Vijayan and K. Krishnan, “Sequential interpenetrating polymer networks from bisphenol A based cyanate ester and bismaleimide: Properties of the neat resin and composites,” *J. Appl. Polym. Sci.*, vol. 74, pp. 2737-2746, 1999.

- [38] C. H. Lin, S. J. Huang, P. J. Wang, H. T. Lin and S. A. Dai, "Miscibility, Microstructure, and Thermal and Dielectric Properties of Reactive Blends of Dicyanate Ester and Diamine-Based Benzoxazine," *Macromolecules*, vol. 45, pp. 7461-7466, 2012.
- [39] J. Y. Shieh, Y. S. Yang, M. F. Wu and C. S. Wang, "Synthesis and characterization of novel low-dielectric cyanate esters," *J. Polym. Sci. A: Polym. Chem*, vol. 42, pp. 2589-2600, 2004.
- [40] C. H. Lin, Z. R. Jiang, and C. S. Wang, "Low dielectric thermoset. II. Synthesis and properties of novel 2,6-dimethyl phenol-dipentene epoxy," *J. Polym. Sci. A: Polym. Chem*, vol. 40, pp. 4084-4097, 2002.

