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Design and Development of Allyl Terminal Triaryl Pyridine Core Skeletal Modified Benzoxazines Based Polybenzoxazine-Silica (PBZ-SiO₂) Hybrid Nanocomposites

R. Padhma Priya, S. G. Gunasekaran, and M. Dharmendirakumar*

Department of Applied Science and Technology, Anna University, Chennai 600025, India

A series of skeletal modified novel allyl terminal benzoxazines (BZ-als) have been successfully designed and developed using triaryl pyridine core diamines via conventional onepot Mannich reaction. The polybenzoxazine-silica (PBZ-SiO₂) nanocomposites were prepared by thermal ring-opening polymerization of benzoxazines with different weight percentages of 3-methacryloxypropyltrimethoxysilane through *in-situ* sol–gel method. The formation of hybrid nanocomposites was confirmed by FT-IR. The substantial enhancement in the glass transition temperature was remarked for PBZ-SiO₂ hybrids than their respective neat PBZ systems. The dielectric constant of the nanocomposites was found decreased with an increment in the silica content. The shift in the characteristic absorption/emissions corresponding to the neat PBZs toward lower wavelength ascertains the successful formation of PBZ-SiO₂ nanocomposites. The discernible phase behaviour observed morphological studies reveals the molecular-level dispersion of silica particles over the organic networks.

Keywords: Allyl Benzoxazine, Polybenzoxazine-SiO₂ Nanocomposites, Glass Transition Temperature, Thermal Stability, Dielectric Constant, Absorbance, Fluorescence, Morphology.

1. INTRODUCTION

Over the past decades, organic–inorganic hybrid nanocomposites have been attracted considerable research interest for various applications in mechanical, optical and electronic fields.¹⁻⁴ Organic–inorganic hybrids comprising inorganic segments and organic polymers on a molecular scale possess the advantages of both organic and inorganic components. Organic–inorganic hybrids comprising inorganic segments and organic polymers on a molecular scale possess the advantages of both organic and inorganic components. The properties of organic–inorganic hybrid materials obtained from the polymeric and inorganic components provide an easy processability, better toughness and good thermal and oxidative stability.^{5, 6}

Polybenzoxazines (PBZ) are a new class of novel phenolic resins which exhibit more useful properties for different industrial applications. But their brittle behavior and also the need of high temperature for the ring opening reaction restrict their utility for high performance applications.^{7–15} Polybenzoxazine based organic–inorganic hybrid nanocomposites can be synthesized via a number of routes and one that has been particularly successful is the *in-situ* polymerization of metal alkoxide precursors in the presence of polymer matrices via the sol–gel method. The sol–gel technique is a convenient method for the synthesis of nanocomposite materials consisting of organic polymers and inorganic compounds.^{16–21} A variety of valuable organic–inorganic hybrid polymers have been synthesized through the sol–gel process.^{22–25}

New types of polybenzoxazine-silica hybrids were developed by incorporating silica nanoparticles into allyl terminated benzoxazines through sol–gel process.²⁶ Santhosh Kumar et al. prepared a blend of bisphenol-A based benzoxazine and 2,2'-bis(8-allyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane (Bz-allyl) with bismaleimide (2,2-bis[4(4-maleimido phenoxy)

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^{*}Author to whom correspondence should be addressed.

phenyl]propane.²⁷ Ishida and Low²⁸ prepared an allyl containing benzoxazine monomer from allyl phenol, aniline and paraformaldehyde.²⁸ The synthesis of a bi-functional vinyl terminated benzoxazine based graphene nanocomposites was reported and their thermal properties were also studied.²⁹ Different types of novel benzoxazines containing allyl groups with improved thermal stability were developed and characterized.^{30,31} Vengatesan et al. prepared a series of polybenzoxazine (PBZ) hybrid nanocomposites from new type of allyl terminated benzoxazine monomer and POSS.³² Agag and Takeichi³³ investigated the preparation and properties of nanocomposites of OMM and allyl functionalized benzoxazine/OMM. The thermal stability was significantly improved with increasing clay content and was evidenced by the higher char yield of these hybrid materials.³³ Dual-cure hybrid polymer networks were prepared by sequential thiol-ene photo polymerization followed by thermal ring-opening polymerization of benzoxazines with increased glass transition temperature and improved processibility.³⁴

The inclusion of heteroaromatic rings into the main chain of a synthetic polymer would impart certain properties such as the rigidity and polarizability to the resultant polymers.^{35, 36} In addition, the incorporation of pyridine moiety into the polyimides (PI) might improve their electron affinity and electron-transporting properties.³⁷ Tamami prepared novel diamines containing pyridine using Chichibabin reaction and synthesized new PIs.³⁸ Liaw and his co-workers designed and fabricated a pyrene pendant core pyridine based diamine for the preparation of organo soluble polyimides with fluorescence properties.³⁹ The introduction of flexible linkages, heteroaromatic rings and bulky pendant pyrene group in between the reactive sites reduced the crosslink density and caused the glass transition temperature of the cured products lowered.⁴⁰

In this context, the present work deals the synthesis of polybenzoxazine-silica (PBZ-SiO₂) hybrids via *in-situ* sol–gel method using allyl terminal benzoxazines (BZ-al) monomers and TEOS in the presence of MPTMS as a coupling agent. The thermal, dielectric and morphological properties of PBZ-SiO₂ hybrid nanocomposites were studied by DSC, TGA, UV-vis spectroscopy, PL, impedance and SEM techniques and the results indicated that the PBZ-SiO₂ hybrids possess better properties for high performance applications.

2. EXPERIMENTAL METHODS

2.1. Materials

Benzaldehyde, pyrene-1-carboxaldehyde, 4-nitroacetopheneone were purchased and used as received from Acros Organics India Ltd. Maleic anhydride and 10 wt% Pd/C were bought from the Lancaster Chemicals UK. Thiophene-2-carboxaldehyde, N,N-dimethyl formamide (DMF), ammonium acetate, potassium carbonate, paraformaldehyde, calcium hydride, celite, anhydrous magnesium sulphate, pyridine and diethyl ether were procured from SRL India. 4-aminophenol was purchased from Loba, India. 2-allyl phenol and 3-methacryloxypropyl trimethoxysilane (MPTMS) were obtained from Sigma Aldrich and used as received.

2.2. Synthesis of Triaryl Pyridine Core Aromatic Diamine Derivatives

Triaryl pyridine core aromatic dinitro and diamine derivatives were synthesized by adopting a procedure reported elsewhere^{41,42} as shown in Scheme 1. The structural formation of the products were then confirmed by ¹H-NMR, ¹³C-NMR and FT-IR techniques and matched with earlier reported data.⁴³

2.2.1. Structure of Phenyl Pendant Pyridine Core Aromatic Diamine (BBAPP)

IUPAC name: 4-(1-Benzene)-2,6-bis(4-aminophenyl)pyridine (BBAPP)

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

¹*H* NMR (400 MHz, $CDCl_3$, δ): 8.01 (*s*, 4 H), 7.56 (*s*, 2 H), 7.41 (*s*, 2 H), 7.40 (*s*, 2 H), 6.78 (*s*, 1 H), 3.84 (*s*, 4 H).

¹³*C NMR* (400 MHz, CDCl₃, δ): 158, 150, 145, 138, 139, 130, 127, 116,115 (aromatic carbon)

2.2.2. Structure of Thiophenyl Pendant Pyridine Core Aromatic Diamine (TBAPP)

IUPAC name: 4-(1-*Thiophene*)-2,6-*bis*(4-*aminophenyl*)*pyridine* (*TBAPP*)

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

¹*H* NMR (400 MHz, $CDCl_3$, δ): 7.91 (*s*, 4 H), 7.56 (*s*, 2 H), 7.44 (*s*, 2 H), 7.34 (*s*, 2 H), 6.68 (*s*, 4 H), 4.1 (*s*, 4 H).

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

2.2.3. Structure of Pyrenyl Pendant Pyridine Core Aromatic Diamine (PBAPP)

IUPAC name: 4-(1-Pyrene)-2,6-bis(4-aminophenyl)pyridine (PBAPP)

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

¹*H NMR* (400 MHz, CDCl₃, δ): 8.77–8.75 (*d*, 1 H, *J* = 9.2 Hz), 8.55 (*d*, 1 H, *J* = 9.6 Hz), 8.36 (*s*, 2 H), 8.27 (*d*, 1 H, *J* = 4.0 Hz).

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



4-(1-aryl)-2,6-bis(4-aminophenyl)pyridine

Scheme 1. Synthesis of triaryl pyridine core aromatic diamine derivatives.

2.3. Synthesis of Bisallyl Terminal Triaryl Pyridine Core Aromatic Diamine Based Benzoxazine Monomers (BZ-als)

To 100 ml of 1,4-dioxane solvent, triaryl pyridine diamine (BBAPP) (0.0148 mol, 5.0 g), 2-allyl phenol (OAP) (0.03 mol, 3.9 ml) and paraformaldehyde (0.065 mol, 1.97 g) were added and refluxed at 110 °C for 6 h. The reaction mixture was then filtered and washed once with 1 M NaHCO₃ aqueous solution (200 ml) and dried with anhydrous sodium sulphate for 12 h. Removal of solvent by evaporation and drying under vacuum yielded benzoxazine as a light brown powder (Scheme 2). The yield was 83%. The other two monomers such as BZ_{h} al and BZ_c-al were also synthesized in a similar way as reported elsewhere^{44,45} and formed the precursors (yellow and light yellow) in the form of powder with yields of 87 and 85% respectively. Here, BZs are denoted as BZ_a -al = BBAPP-OAP; BZ_b -al = TBAPP-OAP; BZ_c -al = PBAPP-OAP.

2.4. Preparation of Polybenzoxazine-Silica (PBZ-SiO₂) Hybrid Nanocomposites

In a flask, 0.2 g TEOS was dissolved in 4 ml of 1,4dioxane and an exact equivalent of dilute acid (0.1 N HCl) was added.²¹ Then, 0.2 g BZ-al and varying molar equivalents (0.5, 1.0, 1.5 and 2.0) of MPTMS with respect to BZ-al were dissolved in 4 ml of 1,4-dioxane separately in another flask as listed in Table I. Both solutions were mixed and agitated for 60 min. The curing process was then performed at 100 °C for 60 min, at 150 °C for 120 min and finally post cured at 200 °C for 120 min (Scheme 3).

2.5. Characterization

FT-IR spectra were recorded on a Perkin Elmer 6X FT-IR spectrometer. About 100 mg of optical-grade KBr was grounded 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 was 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 400 spectrometer. 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 PBZ-SiO₂ nanocomposites 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-SiO₂ nanocomposites were characterized by UV-vis-NIR spectrophotometer (UV-vis-NIR) (U-4100, Hitachi, Japan). The absorbance of the solution was measured with a wavelength ranging from 200 to 1300 mm. The emission properties of the PBZ-SiO₂ nanocomposites were also studied using Fluorescence spectrophotometer (Cary Eclipse, FL1201M002, Japan) with an excitation wavelength. Scanning electron



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Scheme 2. Synthesis of bis allyl terminal benzoxazines (BZ-als).

microscope (SEM) (Hitachi S-3400N) was used to observe the surface morphology of the PBZ-SiO₂ nanocomposites. The transmission electron microscope (TEM) observations were carried on a JEOL JEM-3010, IITM, India, with an accelerating voltage of 300 KV.

Table I. Curing time cycle of PBZ-SiO₂ hybrid nanocomposites.

Systems	BZ-al (g)	TEOS (g)	MPTMS (g)	1,4-dioxane (ml)	Colour
Neat PBZ _a	1	0	0	4	Brown
0.5 wt% PBZ _a -SiO ₂	1	1	0.17	4	Brown
1.0 wt% PBZ _a -SiO ₂	1	1	0.34	4	Light brown
1.5 wt% PBZ _a -SiO ₂	1	1	0.68	4	Brown
2.0 wt% PBZ_a -SiO ₂	1	1	1.36	4	Brown
Neat PBZ_{h}	1	0	0	4	Brown
0.5 wt% PBZ _b -SiO ₂	1	1	0.17	4	Light brown
1.0 wt% PBZ _b -SiO ₂	1	1	0.34	4	Brown
1.5 wt% PBZ _b -SiO ₂	1	1	0.68	4	Dark brown
2.0 wt% PBZ_b -SiO ₂	1	1	1.36	4	Dark brown
Neat PBZ _c	1	0	0	4	Brown
0.5 wt% PBZSiO_	1	1	0.17	4	Brown
1.0 wt% PBZ _c -SiO ₂	1	1	0.34	4	Light brown
1.5 wt% PBZSiO_	1	1	0.68	4	Brown
2.0 wt% PBZ_c^2 -SiO ₂	1	1	1.36	4	Dark brown

3. RESULTS AND DISCUSSION

3.1. Structure of Bis Allyl Benzoxazine Monomers

Three different types of bis allyl terminal benzoxazine monomers were synthesized by and characterized by ¹H-NMR, ¹³C-NMR, FT-IR, UV-Vis and PL techniques and matched with earlier reported data.^{12, 21, 27–30}

3.1.1. Structure of BZ_a-al (BZ-Ph-al)

FT-IR (KBr, cm⁻¹): 2956 (symmetric stretching), 2880 (asymmetric stretching), 1505 (substituted benzene), 1387 (C–N), 1245 (C–O), 1122 (allyl), 948 (N–CH₂–O).

¹*H NMR* (400 MHz, CDCl_3 , δ): 8.07 (*s*, 4 H), 7.63 (*s*, 2 H), 7.60 (*s*, 2 H), 7.45 (*s*, 3 H), 7.10 (*s*, 2 H), 6.91 (*s*, 2 H), 6.80 (*s*, 4 H), 6.09 (*s*, 4 H), 5.38 (*s*, 4 H), 5.37 (*s*, 4 H), 4.68 (*s*, 4 H).

¹³*C NMR* (400 MHz, CDCl₃, δ): 159, 158, 150, 143, 132, 129, 128, 126, 124, 122120, 117, 113, 112, 90, 54 (aromatic carbon).

3.1.2. Structure of BZ_b-al (BZ-Th-al)

FT-IR (KBr, cm⁻¹): 2955 (symmetric stretching), 2881 (asymmetric stretching), 1506 (substituted benzene), 1384



Allyl terminal benzoxazine based Polybenzoxazine-Silica (PBZ-SiO₂) hybrid nanocomposites

Scheme 3. Schematic representation of synthesis of polybenzoxazine-silica (PBZ-SiO₂) hybrid nanocomposites.

(C–N), 1242 (C–O), 1121 (allyl), 948 (N–CH₂–O), 832, 670 (symmetric stretching, C–S).

¹*H* NMR (400 MHz, CDCl_3 , δ): 8.18 (*s*, 2 H), 7.68 (*s*, 2 H), 7.59 (*s*, 2 H), 7.47 (*s*, 2 H), 7.15 (*s*, 2 H), 6.99 (*s*, 2 H), 6.88 (*s*, 4 H), 6.03 (*s*, 3 H), 5.59 (*s*, 2 H), 5.48 (*s*, 2 H), 4.80 (*s*, 4 H).

¹³*C NMR* (400 MHz, CDCl₃, δ): 159, 158, 150, 143, 133, 132, 129, 128, 126, 124, 122, 120, 117, 113, 112, 90, 56 (aromatic carbon).

3.1.3. Structure of BZ_c-al (BZ-Py-al)

FT-IR (KBr, cm⁻¹): 2955 (symmetric stretching), 2883 (asymmetric stretching), 1502 (substituted benzene), 1384 (C–N), 1244 (C–O), 1125 (allyl), 948 (N–CH₂–O).

¹*H NMR* (400 MHz, DMSO-d₆, δ): 8.56 (*s*, 1 H), 8.35 (*s*, 1 H), 7.88 (*s*, 1 H), 7.48 (*s*, 2 H), 7.30 (*s*, 2 H), 6.67 (*s*, 2 H), 5.67 (*s*, 2 H), 5.54 (*s*, 2 H), 4.74 (*s*, 4 H), 3.23 (*s*, 6 H).

¹³*C NMR* (400 MHz, DMSO-d₆, δ): 159, 158, 150, 143, 138, 135, 132, 131, 129, 127, 122, 117, 113, 112, 90, 56 (aromatic carbon).

3.1.4. UV-Vis Absorption Properties of BZ-al Monomers Absorption (nm): 321 (BZ_a-al), 308 (BZ_a-al), 346 (BZ_aal).

3.1.5. PL Properties of BZ-al Monomers

Emission (nm): 467 (BZ_a-al), 446 (BZ_b-al), 450 (BZ_c-al).

3.2. Characterization of PBZ-SiO₂ Nanocomposites

Figure 1 shows the FT-IR spectra of the neat PBZs and PBZ-SiO₂ hybrid nanocomposites. The ring opening polymerization was evidenced by the disappearance of the absorption peaks at 948 cm⁻¹ (oxazine ring) and at 1505 cm⁻¹ (trisubstituted benzene), which confirms the formation of neat polybenzoxazines matrices (PBZs).

The appearance of the new absorption peaks at 1480 and 1120 cm⁻¹ (Si–O–Si linkages) also specified the ring opening polymerization of the PBZ-SiO₂ nanocomposites.⁴⁷ The strong bands at 838 and 712 reveal the occurrence of C–S stretching of thiophene ring present in the PBZ and PBZ-SiO₂ systems. The absence of the bands at 3421, 2500 (S–H stretching) and 1652 cm⁻¹ (C=C stretching) and indicates the formation of covalent bonding between MPTMS and BZ-al at 180 °C, resulted from the ring-opening polymerization of benzox-azine along silica precursors.

3.3. Thermal Properties

3.3.1. Differential Scanning Calorimetry

Differential scanning calorimetric analysis was carried out to determine the glass transition temperature of the neat PBZs and PBZ-SiO₂ hybrid nanocomposites and the DSC thermo grams were shown in Figure 2. The values of the



Figure 1. FT-IR spectra of neat PBZ and $PBZ-SiO_2$ hybrid nanocomposites.

glass transition temperature (T_g) of neat PBZs and PBZ-SiO₂ hybrid nanocomposites are presented in Table II.

From the DSC thermograms (Fig. 2), it is observed that the PBZ-SiO₂ hybrids showed higher T_g values than those of the neat PBZs. This may be attributed to the incorporation of silica components into the PBZ matrices. Furthermore, the enhancement in the T_g values may be due to the hydrogen bonding interaction between silica and PBZ matrices, which restricts the mobility of the polymer chains.^{15,21} In addition, the sulfide product formed during Michael addition (thiol-ene) led to increase the glass transition temperature of the resulted nanocomposites.

3.3.2. Thermo Gravimetric Analysis

The thermo grams of all the PBZ-SiO₂ systems are shown in Figure 3. The PBZ-SiO₂ hybrids showed enhanced thermal stability (as evidence from the thermal degradation temperature) when compared to that of the cured neat PBZs (Table II), due to the presence of highly thermally stable silica networks.¹² Especially, the hybrids containing 2.0 wt% silica particles exhibit higher initial degradation temperature of 330 °C and char yield of 60.2% for 2.0 wt% PBZ_a-SiO₂, 63.1% for 2.0 wt% PBZ_b-SiO₂ and 62.7% for 2.0 wt% PBZ_c-SiO₂ respectively. This may be due to the presence of sulfur, partial ionic nature, high bond energy of Si-O-Si network and higher silica content.

In addition, this enhanced thermal stability could be attributed to better adhesion between the polymeric matrix and inorganic Si–O–Si network domains via the construction of hydrogen bonding between the polar groups from the thiol functional silane and the free –OH groups of the polybenzoxazine matrix. Moreover, the formation of Michael adducts between the benzoxazine monomers and thiol end silane coupling agents afford the higher initial degradation temperature for the hybrids. The increasing char residue can reduce the exothermic nature of the pyrolysis reaction, which in turn, lowers the thermal conductivity and inhibits the combustion of the burning moieties, led to the higher thermal stability than those of neat PBZ systems.^{21, 34, 46, 47}

3.3.3. Limiting Oxygen Index

The flame retardant behavior of the neat PBZs and PBZ- SiO_2 nanocomposites was studied for their char yield at 700 °C in terms of LOI values and is presented in Table II. The LOI values were found to be in the range of 49.0–63.0 (Fig. 4). The burning behavior was correlated to the higher char yield. Furthermore, the flame retardancy was increased due to the presence of sulfur content as well as inorganic Si–O–Si network formed during the thermal ring opening polymerization. Thus, the formation of inorganic network hinders the hybrid materials from combustion.





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3.4. Dielectric Constant

The development of new low k materials is warranted for advanced microelectronic applications. In this direction, new types of PBZ-SiO₂ hybrid material were developed and its insulating behavior has been assessed. The values of dielectric constant of the neat PBZs and PBZ-SiO₂ hybrid nanocomposites at the frequency range of 1 MHz in room temperature are presented in Table II. In the present work, the lowest values of dielectric constant were obtained for a maximum (2.0 wt%) loading of silica in the PBZ matrices (Fig. 5). It is inferred that the incorporation of silica into the PBZ matrices lowered the values of the dielectric constant, compared to that of neat PBZs. This is attributed to the presence of the low polar nature of Si–O–Si networks present in the nanocomposites.

Table II. Thermal and dielectric data of neat PBZ and PBZ-SiO $_2$ hybrid nanocomposites.

Systems	$T_{\rm g}$ (°C)	10% weight loss (°C)	20% weight loss (°C)	Char yield (at 700 °C) (%)	Dielectric constant (ε)	LOI at 700 °C $0.4(\sigma) + 17.5$
Neat PBZ _a	210	360	408	49.1	3.70	37.1
0.5 wt% PBZ _a -SiO ₂	217	350	412	51.2	3.42	38.0
1.0 wt% PBZ _a -SiO ₂	223	375	414	52.3	3.01	38.4
1.5 wt% PBZ _a -SiO ₂	227	390	422	57.6	2.57	40.5
2.0 wt% PBZ _a -SiO ₂	234	401	430	60.2	2.39	41.6
Neat PBZ_{h}	213	370	406	49.5	3.65	37.3
0.5 wt% PBZ _b -SiO ₂	219	350	410	52.0	3.22	38.3
1.0 wt% PBZ _b -SiO ₂	225	390	422	58.0	2.71	40.7
1.5 wt% PBZ _b -SiO ₂	230	400	451	61.6	2.42	42.1
2.0 wt% PBZ _b -SiO ₂	236	412	468	63.1	2.13	42.7
Neat PBZ_c	211	356	410	48.8	3.75	37.0
0.5 wt% PBZ _c -SiO ₂	220	380	413	52.0	3.46	38.3
1.0 wt% PBZ _c -SiO ₂	223	360	420	56.0	2.82	39.9
1.5 wt% PBZ _c -SiO ₂	229	395	450	60.1	2.50	41.5
2.0 wt% PBZ_c -SiO ₂	232	410	464	62.7	2.21	42.6

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Figure 3. TGA thermograms of PBZ-SiO₂ hybrid nanocomposites.

3.5. Optical Properties

3.5.1. UV-Vis Absorption Spectra

The UV-vis absorption studies of the neat PBZ matrices were illustrated in Figure 6. It was found that



Figure 4. LOI values of neat PBZ and PBZ-SiO₂ hybrid nanocomposites.

the neat PBZ matrices display a characteristic absorption band corresponding to the benzoxazine moieties. Hence, this study confirms the successful formation of polybenzoxazines.



Figure 5. Dielectric behaviour of PBZ-SiO₂ hybrid nanocomposites.



Figure 6. UV-vis absorption spectra of PBZ matrices.

3.5.2. Photoluminescence Spectra

Figure 7 shows photoluminescence spectra of the neat PBZs and PBZ-SiO₂ hybrid nanocomposites at an excitation wavelength of 365 nm. The strong fluorescent peaks were observed in the wavelength region of 459 nm (PBZ_a), 449 nm (PBZ_a-SiO₂), 460 nm (PBZ_b), 441 nm (PBZ_b-SiO₂), 449 nm (PBZ_c) and 441 nm (PBZ_c-SiO₂)

respectively. The blue shift was occurred due to the presence of silica particles in the form of Si–O–Si networks within the matrix. Hence, such these emission peaks reveal the photoluminescence properties and in turn, it ascertains the successful formation of PBZ-SiO₂ nanocomposites.

3.6. Morphology of the PBZ-SiO₂ Nanocomposites *3.6.1.* Scanning Electron Microscopy

The surface morphology of the neat PBZs and PBZ-SiO₂ hybrid nanocomposites was investigated by SEM techniques. Figures 8(a)–(f) shows a uniform and smooth surface morphology of neat PBZ matrices. The surface of the hybrid thin film is quite smooth, indicating that the synthesized hybrids have a molecular-level dispersion of silica particles, distributed uniformly over the organic phase.²¹ In addition, the excellent structural uniformity is resulted from both the covalent bonding and Michael addition of thiol end silane coupling agent and benzoxazine matrix.

3.6.2. Transmission Electron Microscopy

The TEM analyses of the $PBZ-SiO_2$ hybrid nanocomposites were performed and their micrographs were presented



Figure 7. Photoluminescence spectra of neat PBZ and PBZ-SiO₂ hybrid nanocomposites.

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Figure 8. SEM images of (a) neat PBZ_a (b) neat PBZ_b , (c) neat PBZ_c , (d) PBZ_a -SiO₂, (e) PBZ_b -SiO₂ and (f) PBZ_c -SiO₂ nanocomposites.



Figure 9. TEM images of (a) PBZ_a-SiO₂ (b) PBZ_b-SiO₂ and (c) PBZ_c-SiO₂ hybrid nanocomposites.

in Figure 9. The incorporation of silica particles led to distinguishable phase morphology, as can be seen from Figure 9. The dark area (the portion of the hybrid) in the polymer matrix represents the dispersions of SiO_2 particles whereas the area surrounding the dark patches indicates the PBZ matrices. Consequently, this study reveals the successful inclusion of the silica network into the polybenzoxazine matrices.

4. CONCLUSION

A new series of novel polybenzoxazine-silica (PBZ-SiO₂) hybrid nanocomposites were successfully prepared from three different types of novel allyl terminal benzoxazine monomers (organic phase) and TEOS (inorganic phase) using MPTMS as a coupling agent through *in-situ* sol-gel method. The developed nanocomposites were then characterized and confirmed by various physico-chemical methods. The values of the dielectric constant were found lower for PBZ-SiO₂ hybrid systems (k = 2.39 for 2.0 wt% PBZ_a-SiO₂, 2.13 for 2.0 wt% PBZ_b-SiO₂ and 2.22 for 2.0 wt% PBZ_c-SiO₂ than those of neat PBZ systems (k = 3.70 for PBZ_a, 3.65 for PBZ_b and 3.75 for PBZ_c). Among the PBZ-SiO₂ hybrids, the hybrids obtained using high

wt% of silica (2.0 wt%) possess higher T_g than that of hybrids prepared using low wt% silica. Theses hybrid polymer networks exhibited good thermal stability and higher char yield (about 60%) than those of neat PBZs, due to the higher content of silica and sulfur present in the hybrids. The blue fluorescent emissions were observed in the wavelength region 439–464 nm for polybenzoxazinesilica hybrid nanocomposites, as evidenced by PL studies. The molecular level dispersion of silica particles in the PBZ matrix was ascertained from morphological studies. Hence, the development of polybenzoxazinesilica nanocomposites with tunable thermal and dielectrical properties is expected to find application in the fields of aerospace and microelectronics.

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References and Notes

- J. C. Huang, C. He, Y. Xiao, K. Y. Mya, J. Dai, and Y. P. Siow, *Polymer* 44, 4491 (2003).
- 2. C. Sanchez, B. Julian, P. Belleville, and M. Popall, J. Mater. Chem. 15, 3559 (2005).
- 3. S. Nagendiran, S. Premkumar, and M. Alagar, J. Appl. Polym. Sci. 106, 1263 (2007).
- Y. Lin, J. Jin, M. Song, S. J. Shaw, and C. A. Stone, *Polymer* 52, 1716 (2011).
- 5. P. Gomez-Romero, Adv. Mater. 13, 163 (2001).
- M. J. Maclachlan, I. Manners, and G. A. Ozin, *Adv. Mater.* 12, 675 (2000).
- 7. S. B. Shen and H. Ishida, J. Polym. Sci. B Polym. Phys. 37, 3257 (1999).
- K. S. Santhosh Kumar, C. P. Reghunadhan Nair, K. N. Ninan, A. D. Kulkarni, and P. P. Wadgaonkar, *Polym. Adv. Technol.* 20, 1107 (2009).
- 9. H. Oie, A. Sudo, and T. Endo, J. Polym. Sci. A Polym. Chem. 48, 5357 (2010).
- 10. L. Qu and Z. Xin, Langmuir 27, 8365 (2011).
- 11. T. Agag and T. Takeichi, Polymer 52, 2757 (2011).
- 12. M. R. Vengatesan, S. Devaraju, A. Ashok Kumar, and M. Alagar, *High Perform. Polym.* 23, 441 (2011).
- S. Jothibasu, A. Ashok Kumar, and M. Alagar, J. Sol–Gel Sci. Technol. 43, 337 (2007).
- 14. C. P. Reghunadhan Nair, Prog. Polym. Sci. 29, 401 (2004).
- 15. T. Agag and T. Takeichi, Polymer 41, 7083 (2000).
- 16. T. Agag, T. Tsuchiya, and T. Takeichi, Polymer 45, 7903 (2004).
- H. Ardhyananta, M. H. Wahid, M. Sasaki, T. Agag, T. Kawauchi, H. Ismail, and T. Takeichi, *Polymer* 49, 4585 (2008).
- 18. Y. Shiina and A. Morikawa, React. Funct. Polym. 71, 85 (2011).
- 19. Q. W. Yuan and J. E. Mark, *Macromol. Chem. Phys.* 200, 206 (1999).
- S. Cheng, D. Shen, X. Zhu, X. Tian, D. Zhou, and L. J. Fan, *Eur. Polym. J.* 45, 2767 (2009).
- S. Devaraju, M. R. Vengatesan, A. Ashok Kumar, and M. Alagar, J. Sol-Gel Sci. Technol. 60, 33 (2011).
- K. Adachi, A. Achimuthu, and Y. Chujo, *Macromolecules* 37, 9793 (2004).
- M. Ivankovic, I. Brnardic, H. Ivankovic, M. Huskic, and A. Gajovic, *Polymer* 50, 2544 (2009).

- 24. C. Schramm, B. Rinderer, R. Tessadri, and H. Duelli, J. Sol–Gel Sci. Technol. 53, 579 (2010).
- S. Jothibasu, A. Ashok Kumar, and M. Alagar, *High Perform. Polym.* 23, 11 (2011).
- 26. B. Kiskan, L. Demire, O. Kamer, and Y. Yagci, J. Polym. Sci. A Polym. Chem. 46, 6780 (2008).
- 27. K. S. Santhosh Kumar, C. P. Reghunadhan Nair, R. Sadhana, and K. N. Ninan, *Eur. Polym. J.* 43, 5084 (2007).
- 28. H. Ishida and H. Y. Low, J. Appl. Polym. Sci. 69, 2559 (1998).
- 29. K. K. Ho, M. C. Hsiao, T. Y. Chou, C. C. M. Ma, X. F. Xie, J. C. Chiang, S. H. Yang, and L. H. Chang, *Polym. Int.* 62, 966 (2013).
- 30. D. Pei, Y. Gu, and X. Cai, Acta Polym. Sin. 1, 595 (1998).
- 31. T. Agag and T. Takeichi, Macromolecules 36, 6010 (2003).
- M. R. Vengatesan, S. Devaraju, K. Dinakaran, and M. Alagar, *Polym. Compos.* 32, 1701 (2011).
- 33. T. Agag and T. Takeichi, Polym. Compos. 29, 750 (2008).
- 34. J. Narayanan, M. J. Jungman, and D. L. Patton, *React. Funct. Polym.* 72, 799 (2012).
- 35. M. A. Shahram, M. M. Rezvaneh, and N. Majid, *Eur. Polym. J.* 41, 1024 (2005).
- T. Kanbara, N. Saito, T. Yamamoto, and K. Kubota, *Macromolecules* 24, 5883 (1991).
- 37. S. Dailey, M. Halim, E. Rebourt, L. E. Horsburgh, I. D. W. Samuel, and A. P. Monkman, J. Phys. Condens. Matter. 10, 5171 (1998).
- 38. B. Tamami and H. Yeganeh, J. Polym. Sci. A Polym. Chem. 39, 3826 (2001).
- 39. D. J. Liaw, K. L. Wang, and F. C. Chang, *Macromolecules* 40, 3568 (2007).
- 40. Y. C. Kung and S. H. Hsiao, J. Mater. Chem. 21, 1746 (2011).
- 41. N. Amutha and M. Sarojadevi, J. Polym. Res. 15, 487 (2008).
- **42.** R. Hariharan, S. Bhuvana, M. Anitha Malbi, and M. Sarojadevi, *J. Appl. Polym. Sci.* 93, 1846 (2004).
- 43, S. Yan, W. Chen, X. Yang, C. Chen, M. Huang, Z. Xu, K. W. K. Yeung, and C. F. Yi, *Polym. Bull.* 66, 1191 (2011).
- 44. C. Karikal Chozhan, M. Alagar, and P. Gnanasundaram, *Acta Mater*. 57, 782 (2009).
- 45. T. Takeichi, Y. Guo, and S. Rimdusit, Polymer 46, 4909 (2005).
- 46. H. Ardhyananta, T. Kawauchi, T. Takeichi, and H. Ismail, *High Perform. Polym.* 22, 609 (2010).
- 47. S. Devaraju, M. R. Vengatesan, M. Selvi, A. Ashok Kumar, and M. Alagar, *High Perform. Polym.* 23, 99 (2011).

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