Phenyl Pendant Carbazole End Capped Pyridine Core Imine Skeletal Based Polybenzoxazine-Nanosilica (nSiO₂/PBZ) Hybrid Nanocomposites

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Abstract - *A new series of nanosilica reinforced polybenzoxazine (nSiO₂/PBZ) hybrid nanocomposites were structurally designed and developed using nanosilica (nSiO₂) and carbazole end capped phenyl pendant pyridine core imine skeletal benzoxazine monomer (PhCBZ) via in-situ sol-gel method. The formation of the nanosilica/ polybenzoxazine hybrid nanocomposites was confirmed by physico-chemical studies. The increment in the thermal stability is due to the inorganic nanosilica content in the nanocomposites. The zipping of the imine skeletal phenyl pendant pyridine ring owing to the end capped carbazole increases the char yield to higher value. The restricted movement of polybenzoxazine network along with the incorporated nanosilica particles elevated the glass transition temperature. The hydrophobicity and less polar nature of nano SiO2 in the nanocomposites reduces the water absorption behaviour to lower percentage The shift in the both absorption and emission value supported the uniform molecular level dispersion of nSiO₂ particles in the PBZ matrix. The homogeneous dispersion of nano SiO₂ onto PBZ networks was evidenced by scanning electron microscopic images. The transmission electron microscope images confirmed the reinforcement of nSiO₂ onto the polybenzoxazine matrix.*

Key Words: Carbazole terminal benzoxazine; nanosilica; polybenzoxazine; thermal stability; dielectric constant; photoluminescence; morphology.

1. INTRODUCTION

Organic-inorganic hybrid nanocomposite materials have charmed substantial attentiveness from both academia and industry. These nanocomposites have been regarded as a new generation of high performance materials, since they combine the advantages of the inorganic materials (high stability, rigidity) and the organic polymers (ductility, flexibility, dielectric and processibility). In the recent past years, scientists have developed assorted techniques for synthesizing hybrid nanomaterials. The design and synthesis of nanomaterials with controlled properties is a challenging problem. An intensive research on the development of hybrid composite materials at a nanoscale level is sketching attention for the past few years [1-4].

Polybenzoxazines as a new category of thermosetting [5] polymers have received much attention due to their magnificent performance and larger flexibility in molecular design. Various raw materials used for the synthesis of benzoxazine monomer authorize significant molecular-design flexibility. Generally, benzoxazine was synthesized [6] by using phenol and/or bisphenol with primary amine and formaldehyde solution through Mannich condensation. They were formed by the ring-opening polymerization of cyclic benzoxazine monomers by thermal curing, with or without using a catalyst and forming no byproducts. Incorporation in polybenzoxazines reveal better enchanting properties such as cost effectiveness, heat resistance, flame retardance and electronic properties on top of the conventional composites in many respects. Furthermore, they furnish additional distinctive characteristics such as low water absorption, high dimensional stability and near-zero volumetric shrinkage or expansion upon curing [7].

Over the past decennary, an appreciable amount of studies on the hybridization of polybenzoxazine with different inorganic nanoparticles to develop polybenzoxazine nanocomposites has been reported. Other higher level properties of polybenzoxazine nanocomposites contain barrier resistance and flame retardancy as well as improved in optical and electrical properties. Agag et al 2008 reported the first polybenzoxazine nanocomposites using nanoparticles such as organoclay and polybenzoxazine matrix forming polybenzoxazine clay nanocomposites with excellent thermal mechanical properties [8] Polybenzoxazine-POSS hybrid composites have been also developed using polyhedral oligomeric silsesquioxane [9].

Polybenzoxazine hybrids were prepared by sol-gel process, bearing hybrid materials with excellent thermal stability. It is well known that the sol-gel process make it prepossessing for application in the synthesis of organic-inorganic hybrid nano materials. A number of valuable hybrid polymers have been prepared through the sol-gel process [10-12]. The sol-gel process is one of the most acceptable methods to develop silica through Si-O-Si linkages by the hydrolysis of alkoxysilanes. The properties of the organic-inorganic hybrid materials are considerably based on the interaction between the organic portion and the siloxane matrix [13], and their homogeneous distribution along the hybrid systems. The factors which affect the efficient interaction between the components involved, are hydrogen bonding [14], covalent bonding [15], p-p and ionic

interactions [16], stereo regular complex [17]. The characteristics of the organic-inorganic hybrids are highly hanging on the interaction between the organic polymers and the siloxane matrix [18-21] and their complete distribution within the hybrid systems. Agag et al 2004 developed a polybenzoxazine-TiO₂ based hybrid, with enhanced thermal properties [22]. Devaraju et al 2011 reported a novel polybenzoxazine-silica hybrid nanocomposite using a new benzoxazine monomer with improved thermal stability and high char yield. [23] Recently, Gunasekaran et al 2017 reported a new polybenzoxazine-silica hybrid nanocomposite using a new benzoxazine monomer with improved thermal stability and increased char yield [24].

In the present research work, sol-gel process has been used to develop polybenzoxazine-nanosilica hybrid nanomaterials using the newly synthesized carbazole end capped phenyl pendant pyridine core imine skeletal benzoxazine monomer as the organic network and $nSiO_2$ as inorganic components respectively. The resulting $nSiO_2$/PBZ hybrid nanocomposites were characterized for their optical, electrical, physicochemical, thermal and morphological properties.

2. EXPERIMENTAL METHODS

2.1 Synthesis of pyrenyl pendant pyridine core aromatic diamine

The hydroxy terminal phenyl pendant pyridine core aromatic diamine was synthesized according to procedure reported elsewhere [25]. The product was characterized the structure and confirmed the by ^{1}H-NMR, ^{13}C-NMR and FT-IR data [26].
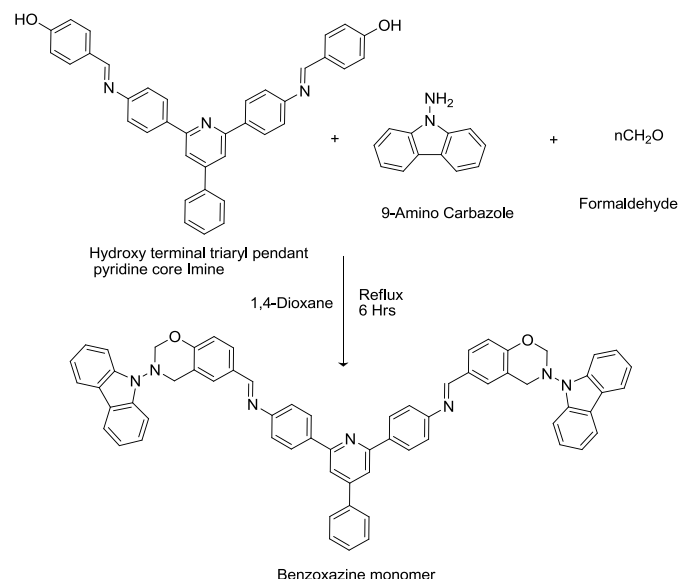
2.2 Synthesis of hydroxy terminal phenyl pendant pyridine core imine

Hydroxy terminal phenyl pendant pyridine core Imine derivative was synthesized as per the procedure [27] as shown in Scheme 1. In a 500 mL flask, 4-hydroxy benzaldehyde (HB) (0.002 mol, 5.4 g) and phenyl pendant pyridine core aromatic diamine (0.001 mol, 10.0 g) were mixed with ethanol and refluxed for 4 h. The resultant mixture was quenched with water and washed using aq.NaHCO₃ (200 ml). Then, the product was filtered and dried using anhydrous sodium sulphate for 10 h. Finally, hydroxyl terminal phenyl pendant pyridine core imine (PhPI-OH) was obtained after removing residual solvent under vacuum. The yield was 89 %.

2.3 Synthesis of hydroxy terminal phenyl pendant pyridine core imine benzoxazine monomer (PhCBZ)

Benzoxazine monomer from hydroxy terminal phenyl pendant pyridine core imine (PhCBZ) was synthesized as per reaction procedure [28] as shown in Scheme 1. In a 250 mL round bottomed flask, 50 ml of dioxane, hydroxy terminal

phenyl pendant pyridine core, PhPI-OH (0.015 mol, 10.0 g), carbazole amine (CA) (0.030 mol, 5.46 g) and formaldehyde (0.06 mol, 2.0 ml) were refluxed at 115°C for 7 h. The product mixture was washed with water and filtered with 1 M NaHCO₃ aqueous solution. The obtained product was dried using vacuum for 10 h. The brown powder was yielded to 90 %.

Scheme - 1: Synthesis of Carbazole terminal phenyl pendant pyridine core imine based benzoxazine monomer

2.3 Preparation of nanosilica reinforced polybenzoxazine nanocomposites

The neat polybenzoxazine (PBZ) and nanosilica reinforced polybenzoxazine ($nSiO_2$/PBZ) hybrid nanocomposites were prepared as per reported procedure [28] as shown in Scheme 2. The benzoxazine monomer was first dissolved in 1, 4-dioxane and cured initially at 120°C for 120 min and then further curing was done for 120 min at 180°C to get neat PBZ system. The curing cycle time is mentioned in Table 1. The $nSiO_2$ particles were added to benzoxazine monomer solution and the resultant homogeneous solution poured onto a precoated glass plate and then thermal ring opening polymerization was carried out at 120°C for 120 min and also cured at 180°C for 120 min to get nanosilica reinforced polybenzoxazine nanocomposites.
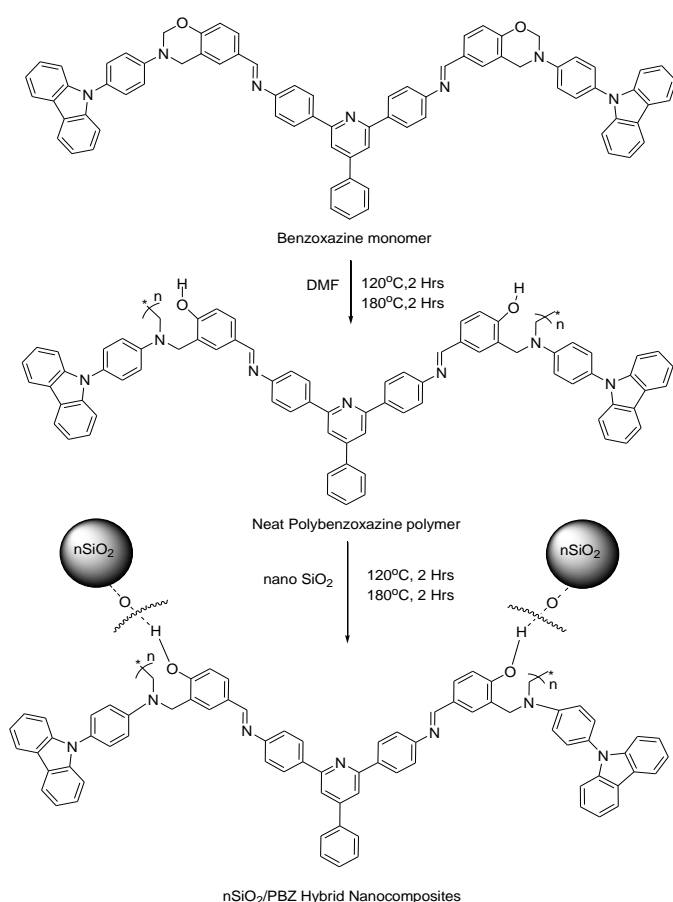
Scheme - 2: Schematic representation for the synthesis of phenyl pendant pyridine core imine skeletal polybenzoxazine-nanosilica (nSiO$_2$/PBZ) hybrid nanocomposites

2.4 Characterization

About 100 mg of potassium bromide was finely grounded with enough quantity of the solid sample to make 1.0 wt % mixture for making KBr pellets. After the sample was loaded, a minimum of 10 scans was collected for each sample at a resolution of ±4 cm^{-1}, FT-IR spectra were recorded on a Perkin Elmer 6X FT-IR spectrometer. Then, the neat polybenzoxazines and nanosilica incorporated polybenzoxazine nanocomposites were characterized by UV-Vis- spectrophotometer (UV-Vis) (U-4100, Hitachi, Japan). The absorbance of the solution was measured with a wavelength ranging from 200 to 1300 nm. All ^{1}H-NMR and ^{13}C-NMR analyses were done in d-CHCl$_3$ and DMSO-d$_6$ recorded on a Bruker 500 NMR spectrometer. The emission properties of the PBZ and PBZ-SiO$_2$ nanocomposites were also studied using Fluorescence spectrophotometer (Cary Eclipse, FL1201M002, Japan) with an excitation wavelength. 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. 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. Scanning electron microscope (SEM) (Desktop Mini-SEM with EDS, ALFATECH), 5Kv to 30kV variable accelerating voltage was used to observe the surface morphology of the PBZ and nSiO$_2$/PBZ nanocomposites. The transmission electron microscope (TEM) observations were carried on a JEOL JEM-2100 plus, SRM IST, Chennai, India, with an accelerating voltage of 200 KV, Emission gun-Thermionic emission (LaB$_6$). And Raman spectra were recorded by Micro-Raman spectrometer (785 nm laser source, HORIBA France, LABRAM HR Evolution).

3. RESULTS AND DISCUSSION

3.1 Structure of Benzoxazine Monomers

The structural formation of the benzoxazine was characterized and confirmed from FT-IT spectra [31] by the presence of the peaks at 948 cm^{-1} and 1221 cm^{-1} (C-O-C). The ^{1}H NMR and ^{13}C NMR spectra also confirmed the structure of BZ [24, 28-30]. The UV-Vis and PL spectra also confirmed the optical behaviour of benzoxazine monomer.

3.1.1 FT-IR absorption properties of monomers

FT-IR: (KBr, cm^{-1}): 3046(=CH-), 1679 (C=C), 1322 (C-N), 1221 (C-O-C), 948 (N-CH$_2$-O), 735 (C-H).

3.1.2 NMR absorption properties of monomers

^{1}H NMR: (400MHz, DMSO-d^6) δ (ppm): 8.66 (s, 2H), 8.54 (s, 2H), 8.18 (t, 3H), 7.90 (d, 4H), 6.81 (d, 2H) 6.42 (d, 4H), 4.70 (s, 4H) 4.68 (s, 4H).

^{13}C NMR: δ (ppm): 160, 158, 149, 143, 137, 131, 129, 128, 127, 126, 121, 114, 110, 93, 68, 59 (aromatic carbon).

3.1.3 UV-Vis absorption properties of monomers
Absorption (nm): 310 (BZ)

3.1.4 PL properties of monomers
Emission (nm): 411 (BZ)

3.2 Curing behavior of Benzoxazine monomers

The curing behaviour of benzoxazine was characterized by DSC analysis as shown in Table 1. The DSC thermogram showed an exothermic peak, which confirms the presence of benzoxazine hydroxyl group [24]. The onset and peak top temperature of the major peak was observed at 187°C corresponding to benzoxazine, which is lower than that of the already prepared benzoxazine monomer. The peak curing temperature of the resulting monomer was at 230°C and the polymerization temperature was 260°C as it can be seen from Table 1.

Table – 1: Curing behaviour of Benzoxazine monomers

Sample code	T_i (ºC)	T_p (ºC)	T_f (ºC)
BZ	187	230	260

T_i = initial polymerization temperature; T_p = peak curing temperature; T_f = final polymerization temperature.

3.3 Characterization of *n*TiO$_2$/PBZ Nanocomposites

The FT-IR spectral analyses were done for the neat PBZ and nSiO$_2$/PBZ nanocomposites as shown in Figure 1. The absorption peak at 3425 cm^{-1} corresponding to the hydrogen bonded phenolic OH in and also a new peak at 1496 cm^{-1} owing to the tetra substituted benzene ring confirm the successful formation of polybenzoxazine matrix. The ring opening polymerization of benzoxazine was confirmed from the disappeared peaks at 940 and 1510 cm^{-1} (oxazine) and 1222 cm^{-1} (C-O-C) [30]. The stretching vibrations of symmetric C-N and imine linkage were characterized by the peaks obtained at 1320 and 1650 cm^{-1} respectively [27,29-30]. The incorporation of nSiO$_2$ onto PBZ matrix was evidenced from the peak formed at 1070 cm^{-1} resulted from the -Si-O- linkages of nSiO$_2$ particles.
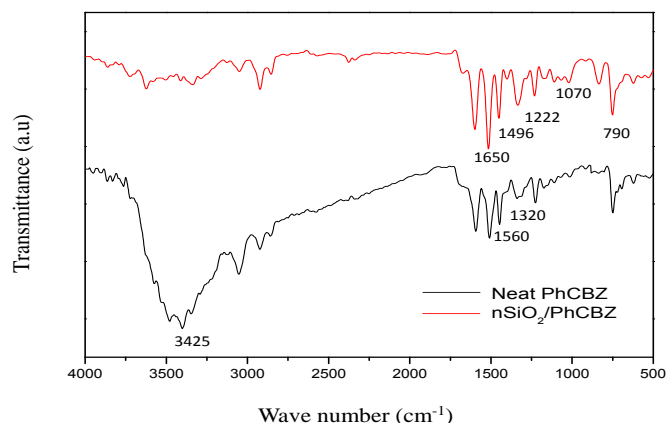

Figure – 2: FT-IR Spectra of neat PBZ and nSiO$_2$/PBZ nanocomposites

3.4 Thermal Properties

3.4.1 Differential Scanning Calorimetry

Figure 2 shows the DSC thermograms of the neat PBZ and nSiO$_2$/PBZ nanocomposites and the glass transition temperatures (T_g) were presented in Table 3. The ring-opening polymerization of benzoxazine drives to enhance the T_g value to the substantial level (223ºC) accounted from the bulky organic networks. In addition, the augmentation in the glass transition temperature was exerted by the reinforced nanosilica particles into PBZ network. Thus, the T_g value of nSiO$_2$ reinforced PBZ nanocomposite was increased to about 263ºC than that of neat PBZ system (T_g=223 ºC). The constrained mobility of the polymer chain

network on account of the presence of hydrogen-bonding interaction will also increase the glass transition temperature of the nSiO$_2$/PBZ nanocomposites [4,22,30].
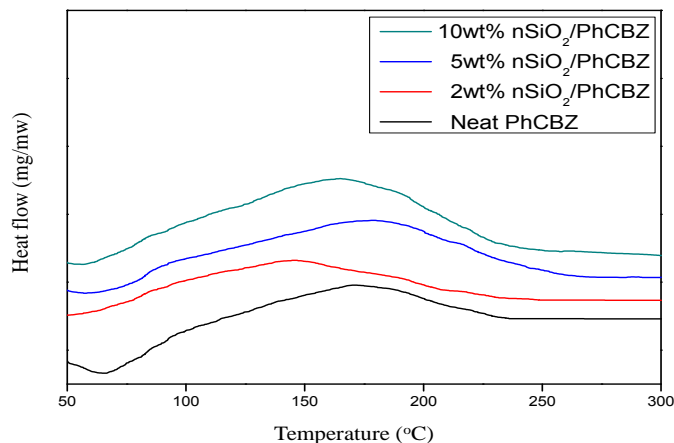

Figure - 2: DSC thermograms of neat PBZ and nSiO$_2$/PBZ nanocomposites

3.4.2 Thermo Gravimetric Analysis

The thermal property and char yield behaviour of the neat PBZ and nSiO$_2$/PBZ nanocomposites were analyzed with the use of thermogravimetric analyzer. The data from TGA studies have evidently described the enhanced thermal stability of the neat PBZ and nSiO$_2$/PBZ nanocomposites and illustrated in Figure 3. The degradation temperature and the char yield at 700ºC were recorded and tabulated in Table 3.
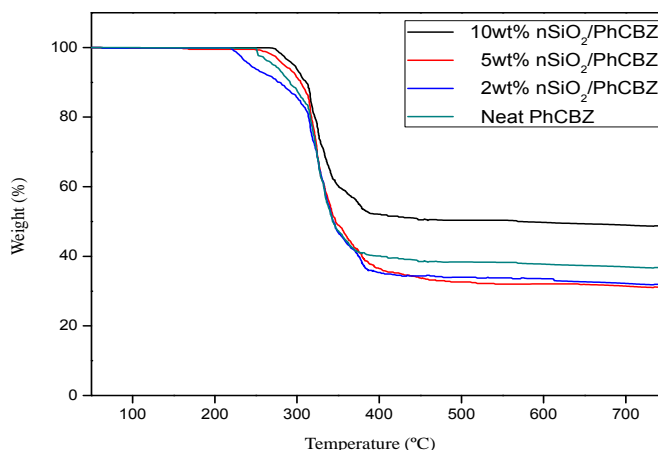

Figure - 3: TGA thermograms of neat PBZ and nSiO$_2$/PBZ nanocomposites

The initial degradation of the neat PBZ system was largely afforded by the existence of both the phenyl and carbazole rings in the matrix. The restricted decomposition was due to the homogeneously dispersed nanosilica particles onto the polybenzoxazine matrix which led to increase the thermal stability of nSiO$_2$ reinforced PBZ nanocomposites [30,31]. This is further supported by the presence of the high bond energy and partial ionic behaviour of the Si-O-Si linkage of

the dispersed $nSiO_2$ in the PBZ matrix. Furthermore, it is concluded that the higher thermal stability was ascertained from the formed hydrogen bonding between the nanosilica particles and the benzoxazine system.

Table – 3: Thermal and dielectric data of neat PBZ and nSiO₂/PBZ hybrid nanocomposites

Exp. code	Systems	T_g (°C)	Char yield at 700°C (%)	Dielectric Constant ($\acute{\varepsilon}$)	LOI At 700°C 0.4 (σ)+17.5	Water absorption (%)
PhCBZ	Neat PhCBZ	223	31	3.85	29.9	0.73
PhCBZ₁	2% nSiO₂/ PhCBZ	247	32	3.56	30.3	0.67
PhCBZ₂	5% nSiO₂/ PhCBZ	258	36	3.20	31.9	0.54
PhCBZ₃	10% nSiO₂/ PhCBZ	263	48	2.48	35.7	0.48

3.4.3   Limiting Oxygen Index

The limiting oxygen index values are calculated from TGA analyses and presented in Table 3. The thermal retardancy behaviour of the neat PBZ and nSiO₂/PBZ nanocomposites was calculated using Van Krevelen's equation (Figure 4). The increment in the crosslinking behaviour and the presence of incorporated nanosilica particles in PBZ matrix made the higher char yielded at 700°C [29,34,37]. Thus, the nSiO₂/PBZ nanocomposites developed in the present work may be considered as good fire-retarding material for high thermal applications.
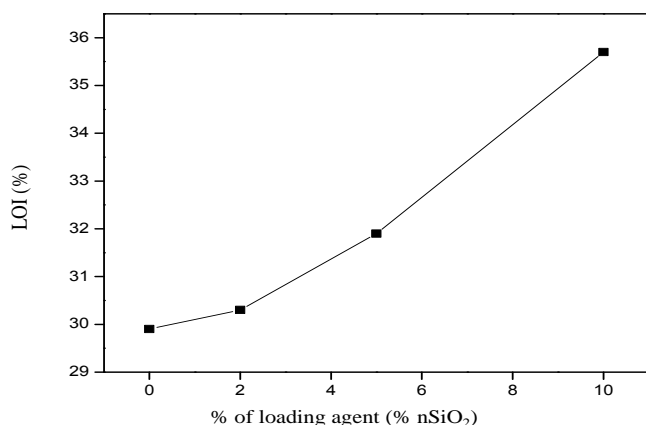

Figure - 4: LOI values of neat PBZ and nSiO₂/PBZ nanocomposites

3.5 Dielectric constant

The dielectric constants of neat PBZ and nSiO₂/PBZ hybrid nanocomposites at 1 MHz in room temperature are represented in Table 3 and Figure 5. The decreasing tendency of the dielectric constant in nSiO₂/PBZ hybrid composites designates that the addition of the amounts of nSiO₂ would make smaller in the dipole-dipole interaction in the developed hybrid nanocomposites [30,32-33]. The decrement in the dielectric constant values *(k*=2.48 for 10% of nSiO₂/PBZ nanocomposites is mainly attributed to the Si-O-Si linkages of nSiO₂ along the hybrids of the polybenzoxazine-nanosilica nanocomposites.
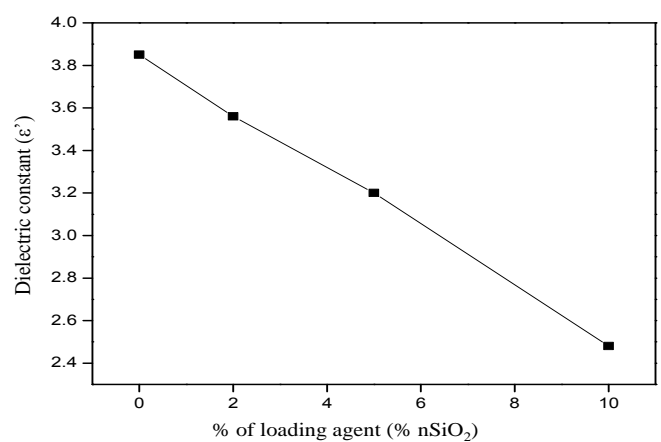

Figure – 5: Dielectric behaviour of neat PBZ and nSiO₂/PBZ nanocomposites

*3*3.6   Optical properties

3.6.1   UV-Vis absorption spectra

The optical properties of the neat PBZ and nSiO₂/PBZ nanocomposites were discussed with the help of UV-Visible spectra and were presented in Figure 6.
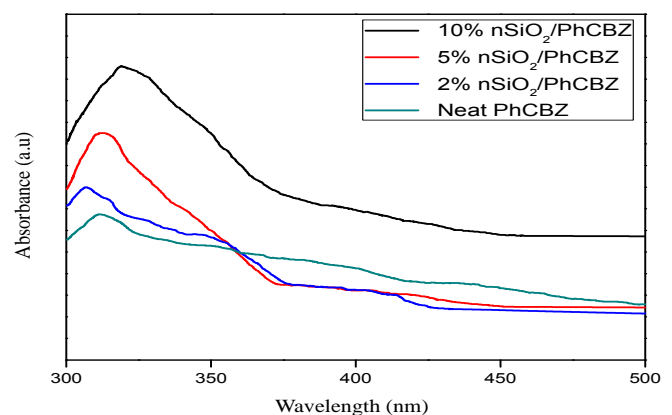

Figure - 6: UV-Vis absorption spectra of PBZ and nSiO₂/PBZ nanocomposites

The absorption at 310 nm was attributed to the neat polybenzoxazine matrix with an unsymmetrical shaped peak. The incorporation of silica particles onto the PBZ matrix slightly shifts the peak to the higher wavelength of 320 nm. This shift confirms the effective reinforcement of nanosilica particles throughout PBZ matrix [30].

3.6.2   Photoluminescence spectra

Figure 7 denotes photoluminescence spectra of the neat PBZ and $nSiO_2$/PBZ hybrid nanocomposites. The strong fluorescent emission was resulted from a peak at 305 nm for PBZ and also a peak at 431 nm for $nSiO_2$/PBZ nanocomposites. The red shift in the emission is owing to the presence of homogeneously dispersed nanosilica particles in the PBZ system [30,34-35]. Hence, this type of $nSiO_2$/PBZ nanocomposite delivers a wide range of applications in the fields of opto-electronics manufacturing light-emitting diode materials.
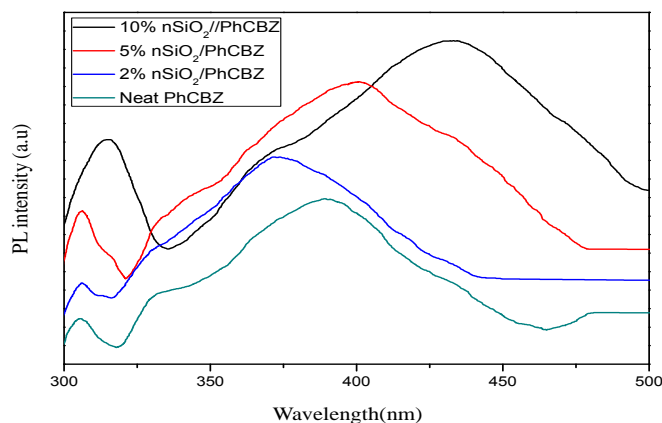

Figure - 7: Photoluminescence spectra of neat PBZ and $nSiO_2$/PBZ nanocomposites

3.7 Water absorption behaviour

Water absorption characteristics of the neat PBZ and $nSiO_2$/PBZ composites are illustrated in Figure 11 and Table 3.
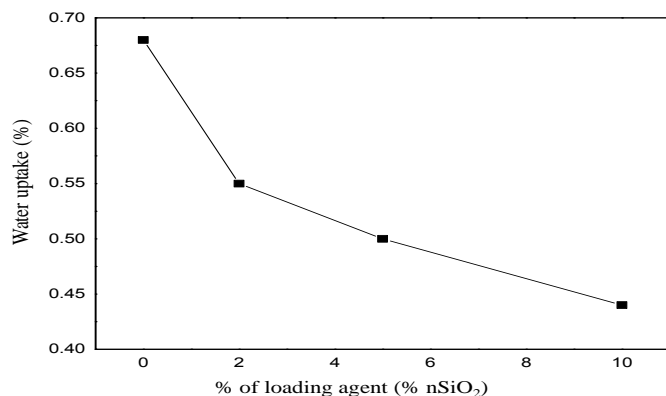

Figure - 8: Water absorption of neat PBZ and $nSiO_2$/PBZ nanocomposites

3.8   Morphological properties

The percentage of water absorption of neat PBZ system is 0.68 %. The incorporation of inorganic nanosilica network into PBZ systems reduced the percentage of water absorption from 0.68 to 0.44. The decrease in percentage of water absorption may be connected with the inherent hydrophobic nature of Si-O- network present in the $nSiO_2$/PBZ composites [30,34]. The surface morphological properties of the neat PBZ and $nSiO_2$/PBZ nanocomposites were analyzed by X-Ray diffraction analysis, scanning electron microscope (SEM) and transmission electron microscopy (TEM) studies.

3.8.1   X-Ray Diffraction analysis

The diffraction patterns were obtained for both the neat PBZ and $nSiO_2$/PBZ hybrid nanocomposites as shown in Figure 9. The amorphous nature of PBZ system can be characterized from a peak observed at 2θ = 19.99 and also an amorphous peak at 21.49º for $nSiO_2$/PBZ nanocomposites, which suggested that the nanosilica particles are entirely distributed in the PBZ systems [30, 36]. The minimal change in the intensity of peak due to the uniform incorporation of $nSiO_2$ particles was markedly seen in Figure 9. Furthermore, the strong covalent bonding interaction between $nSiO_2$ particles and PBZ system played a role in the homogenous distribution and also the retained amorphous surface morphology of the nanocomposites as can be seen in Figure 10.
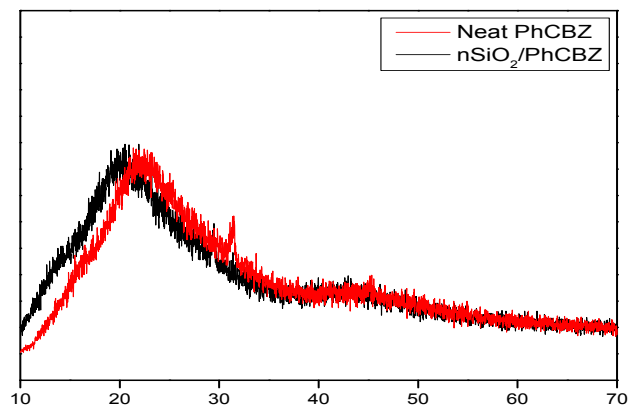

Figure – 10: XRD patterns of neat PBZ and $nSiO_2$/PBZ nanocomposites

3.8.2   SEM Morphology

Figure 11 illustrates SEM studies of the neat PBZ and $nSiO_2$ reinforced polybenzoxazine nanocomposites. It is noted that the neat PBZ system displayed homogeneous phase morphology (Figure 11a). The strong interfacial interaction of $nSiO_2$ with polybenzoxazine was resulted the distinct surface after the formation of nanocomposites [30] which obeys with XRD analysis as seen from Figure 10.
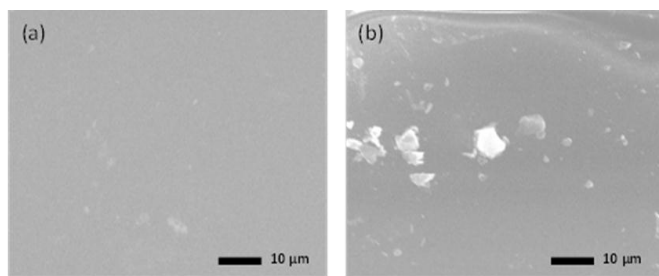
Figure – 11: SEM micrographs of (a) neat PBZ (b) $nSiO_2$/PBZ nanocomposites

3.8.3   Transmission Electron Microscopy

Figure 12 shows the TEM images of neat PBZ and $nSiO_2$/polybenzoxazine nanocomposites. These images clearly show the successful incorporation of $nSiO_2$ onto PBZ hybrid network through thermal curing. The homogeneous molecular level dispersion of nanosilica particles was achieved and revealed the successful formation of $nSiO_2$ reinforced polybenzoxazine nanocomposites [30].
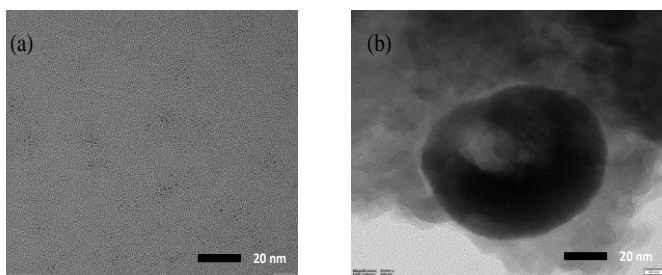

Figure – 12: TEM images of (a) neat PBZ (b) $nSiO_2$/PBZ nanocomposites

4. CONCLUSION

In the present work, $nSiO_2$/polybenzoxazine nanocomposites have been synthesized from nanosilica ($nSiO_2$) and phenyl pendant imine skeletal pyridine core carbazole terminal benzoxazine monomer via thermal curing polymerization. The structure of the polybenzoxazine nanocomposites was characterized and confirmed by various physicochemical methods. The enhanced thermal stability and higher char yield (about 50%) of $nSiO_2$/polybenzoxazine were due to the presence of inorganic nanosilica and the resulted intercross linked network of the polybenzoxazine matrices. The incorporation of $nSiO_2$ into neat polybenzoxazine matrix elevated the glass transition temperature of the $nSiO_2$/PBZ hybrid nanocomposites to 288°C than that of neat PBZ. The dielectric constant is lower owing to the nanosilica present in the newly designed polybenzoxazine system. The successful of inclusion of nanosized silica onto the polybenzoxazine system was revealed by the red shift shown in UV-Vis spectra. The strong fluorescent emission peak was also attributed to the $nSiO_2$ particles in the polybenzoxazine networks. The molecular level dispersion of nanosized silica

in the PBZ hybrid system was ascertained by XRD studies. The SEM and TEM studies evidenced the effective reinforcement of $nSiO_2$ onto the polybenzoxazine system. Thus, this $nSiO_2$/polybenzoxazine nanocomposite may find a wide range of applications in, microelectronics, mechanical and aerospace industries.

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