5.1 INTRODUCTION

Thiol-ene photo polymerization involves a reaction between multifunctional thiol and ene monomers. The inherent flexibility of the thioether linkages present in the structure of thiol–ene networks result in low glass transitions which are generally observed at or below room temperature. In this direction, several approaches have been reported with the aim of improving thermo mechanical properties including thiol-alkyne networks (Tg ~60°C) and hybrid, dual-cure thiol–ene/thiol-epoxy networks (Morgan et al 1977, Hoyle et al 2004, Cramer et al 2006 and Carioscia et al 2007). Photo polymerization has been the basis for the production of numerous industrial products viz., coatings, adhesives, inks and printing plates, etc (Kloosterboer 1998, Roffey et al 1997, Bunning et al 2000 and Yagci et al 2010). An attempt has been made in the present work to apply dual synthetic compact for developing multicomponent hybrid networks that exhibit properties unachievable with traditional thiol–ene reaction routes.

Polybenzoxazines are a class of thermosetting phenolic resins obtained from benzoaxidine through ring opening polymerization of oxirane ring in the absence of a catalyst, releasing no byproducts during curing. Polybenzoxazines have many advantages like near-zero shrinkage upon polymerization, low water absorption, high char yield, excellent dimensional
stability, flame retardance, stable dielectric constants, and low surface free energy. Despite these advantageous properties, polybenzoxazines suffer from certain disadvantages including inferior mechanical properties and limited processing behaviour particularly into thin films and coatings. To address these shortcomings, benzoxazines have been incorporated with pendant moieties. Lu and coworkers (2008) recently reported an interpenetrating polyacrylate/polybenzoxazine networks that could be sequentially cured by photochemical polymerization of a multifunctional acrylate followed thermal polymerization of a bisfunctional benzoxazine.

Benzoxazine resins have also been modified through blending with other polymers viz., epoxy, polyurethane, poly (N-allyl-2-pyrrolidone), inorganic species (e.g., clays), polyhedral oligomeric silsesquioxane (POSS), and carbon nanotubes to improve properties for high performance industrial applications (Chernykh et al 2009a, Chen & Xu 2006, Lee et al 2006 and Sherrington & Taskinen 2001). The polymer/inorganic hybrid nanocomposites developed possess an attractive property that has made much research interest in the recent past.

Polyhedral oligomeric silsesquioxane (POSS) contain an inner inorganic cage made up of silicon and oxygen where outer surface is substituted by organic tethers. The POSS organic-inorganic hybrid nanocomposites can be easily achieved through copolymerization with various monomers or blended with other common polymers. Polymers hybridized with POSS generally possess an improved thermal stability, dimensional stability, high glass transition temperature and low dielectric constant (Ni et al 2004, Lee et al 2005b, Devaraju et al 2012 and Chandramohan et al 2013a) that have attracted considerable interest in several applications.
Number of POSS-based photo curable resins has also been studied, such as epoxy, cinnamate, methacrylate, coumarin, and thiol-ene functionalized POSS systems (Sellinger & Laine 1996, Fujiwara et al 2003). The POSS moiety has a unique and well-defined structure that can be used for preparing hybrid materials with well defined structures. To improve the miscibility and interactions between the inorganic Si₈O₁₂ core of the POSS and the organic polybenzoxazine matrix, the POSS moiety must be terminated with the polymerizable functional group which in turn reacts with the benzoxazine unit. Reports are available with regards to photo polymerization behavior as well as thermal polymerization of monomers using thiol-ene system (Narayanan et al 2012, Beyazkilic et al 2012 and Bai et al 2014). Benzylidene based benzoxazine monomers were synthesized and their photo polymerization behavior as well as thermal polymerization were studied (Vengatesan et al 2012).

In the present work, allyl terminated benzoxazine and thiol functionalized POSS were synthesized and were photo polymerized using thiol-ene reaction followed by thermal polymerization to obtain hybrid composites with improved glass transition temperature, thermal stability, UV shielding behavior and low dielectric constant suitable for high performance industrial and engineering applications. Data obtained from thermal, dielectric, UV shielding and morphological behavior of the hybrid samples are discussed and reported.

5.2 EXPERIMENTAL
5.2.1 Synthesis of Thiol Terminated POSS (SH-POSS)

Thiol terminated POSS was prepared as per reported procedure (Fu et al 2008, Liu et al 2005). In a 250 mL flask equipped with a magnetic stirrer, 2.7 mL of deionized water, 20 mL of ethanol, 0.2 mL of concentrated
hydrochloric acid (37%), and 23 mL (0.1 mol) of 3-mercaptopropyl-triethoxy silane (MPTEOS) were charged together with an argon blanket. The reactants were refluxed for 36 h at 60°C to ensure the completion of hydrosilylation reaction. A viscous liquid product was obtained after the removal of the solvent by the reduction of pressure by vacuum pump and subsequently it was washed with methanol to remove the traces of MPTEOS if any and dried in a vacuum oven. The tentative structure of thiol terminated POSS is shown in Figure 5.1.

![Figure 5.1 Structure of SH-POSS](image-url)

5.2.2 Synthesis of Allyl Terminated Benzoxazine

The allyl-terminated benzoxazine was synthesized as per the reported procedure (Oie et al 2010, Agag 2006 and Agag & Takeichi 2008). Bisphenol- A (160 mmol, 32.04 g) and paraformaldehyde (640 mmol, 19.2 g) in toluene (200 mL) were mixed for 15 min in a 500 mL round bottomed flask in an ice bath. After this, ally amine (320 mmol, 18.269 g) was added in drop wise to the reaction mixture for another 15 min with stirring at 0°C. The
temperature was gradually raised to 80°C, and stirring was continued at 80°C for 6 h. After cooling to room temperature, the toluene was removed using a rotary evaporator. Then, the resultant product was dissolved in diethyl ether (200 mL), washed three times with aqueous 1N sodium hydroxide (200 mL) and three times with distilled water (200 mL), and then dried with anhydrous sodium sulfate. After the evaporation of diethyl ether in an evaporator at 40°C, the sticky yellowish fluid product was dried under vacuum at 40°C for 24 h to yield 36.8 g (62%) of allyl terminated benzoxazine. (Scheme 5.1).

\[
\text{Bisphenol A} + 2\text{H}_2\text{N} + 4(\text{CH}_2\text{O})_n \rightarrow \text{Allyl terminated benzoxazine}
\]

Scheme 5.1 Synthesis of allyl terminated benzoxazine

5.2.3 Photo Initiation Followed by Thermal Polymerization of Benzoxazine with POSS

The dual cured hybrid networks were developed by sequential thiol–ene photo polymerization followed by thermal ring-opening of benzoxazine as represented in Scheme 5.2. The allyl functionalized benzoxazine monomer was dissolved in 10 ml of CHCl₃ solutions followed by the addition of 10, 30 and 50 wt. % of SH-POSS separately and were then exposed to UV photo reactor separately at 0,10,20,30,40,60,90,120 and 150 min intervals to carry out the curing reaction.

The photo chemical activity of benzoxazine monomer was studied using UV spectroscopy in each time interval. After UV irradiation, the
solution was slowly evaporated, and cured step-wise at 100°C, 120°C, 140°C for 1 h each, and at 160°C, 180°C for 2 h each and at 200°C, 220°C for 1 h each in an air circulating oven. The samples were then post cured at 240°C for 1 h in an air circulating oven (Scheme 5.2).

Scheme 5.2  Schematic representation for the preparation for dual cured POSS-PBZ composites

5.3 RESULT AND DISCUSSION

5.3.1 Fourier Transform-Infra red Spectroscopy

The FTIR spectra of allyl terminated benzoxazine and SH-POSS are shown in Figure 5.2(a) and 5.2(b)). From the spectrum the peaks appeared at 1230 and 1028 cm$^{-1}$ represent the asymmetric and the symmetric stretching of C–O–C in the oxazine ring respectively. The peak appeared at
927 cm\(^{-1}\) corresponds to the presence of oxirane ring in the benzoxazine (Agag & Takeichi 2000, Agag and Takeichi 2006).

![FTIR spectra of (a) Allyl terminated benzoxazine and (b) SH-POSS](image)

**Figure 5.2** FTIR spectra of (a) Allyl terminated benzoxazine and (b) SH-POSS

The peak appeared at 1497 cm\(^{-1}\) indicates the presence of trisubstituted benzene ring. Characteristic absorption peak correspond to allyl group appeared at 3075 cm\(^{-1}\). In SH-POSS the alkyl -CH\(_2\)- groups appeared at 2923 cm\(^{-1}\) and 2858 cm\(^{-1}\) respectively. Vibration occurs at 2556 cm\(^{-1}\) indicates the presence of S-H stretching, the peak appeared at 1256 cm\(^{-1}\) represents the Si-C asymmetric stretching vibration and Si-O-Si asymmetric stretching occurs at 1124 cm\(^{-1}\).

Figure 5.3 show the FTIR spectra of dual cured POSS-PBZ. From the spectra the peak appeared at 2556 cm\(^{-1}\) represents the thiol group and its disappearance confirms that the occurrence of polymerization. The disappearance of peak at 927 cm\(^{-1}\) also confirms the occurrence of ring opening polymerization and the peak appeared at 1473 cm\(^{-1}\) further confirmed the formation of tetra substituted polybenzoxazine ring.
Figure 5.3  FTIR spectra of dual cured POSS-PBZ composites. P_{10}-PBZ - 10wt % SH-POSS Polybenzoxazine hybrid composite, P_{30}-PBZ - 30wt % SH-POSS Polybenzoxazine hybrid composite and P_{50}-PBZ - 50wt % SH-POSS Polybenzoxazine hybrid composites

5.3.2 NMR Spectral Analysis

Figure 5.4 shows the $^1$H NMR spectrum of allyl terminated benzoxazine; the two resonance peaks appeared at 5.20 and 5.89 ppm are represent the protons of CH$_2$ and CH– in the allyl group, respectively. The peak appeared at 3.35 ppm corresponds to the protons located between the allyl group and the nitrogen atom. The peaks appeared at 3.94 ppm (–Ar–CH$_2$ –N–) and 4.81 ppm (–O–CH$_2$ –N–) are attributed to protons in the methylene bridge of the oxazine ring. The peaks appeared at 3.66 and 6.65–6.96 ppm
indicate the presence of CH₂ between the benzene ring and the aromatic protons.

**Figure 5.4** ¹H NMR spectrum of allyl terminated benzoxazine

The ¹³C NMR spectrum of allyl terminated benzoxazine is presented in Figure 5.5. The signals of the carbon atoms of the terminal olefin unit appear at 116 and 138 ppm. The characteristic signals appeared at 52 and 82 ppm represent to the carbon atoms of the oxazine ring.

The ¹H NMR spectrum of SH-POSS is presented in Figure 5.6. The peak appeared at 0.62 ppm is attributed to Si-CH₂ – proton, the peak at 1.20 ppm represents the proton of –SH and the peaks appeared at 1.55 and 2.47 ppm correspond to protons of -CH₂- and -CH₂-S respectively. ²⁹Si-NMR spectrum of SH-POSS is presented in Figure 5.7. A broad peak appeared at -66.02 confirm the Si atom present in the POSS core.
Figure 5.5 $^{13}\text{C}$ NMR spectrum of Allyl terminated benzoxazine

Figure 5.6 $^1\text{H}$ NMR spectrum of SH-POSS
5.3.3 Photo Cross Linking Studies of Thiol-ene system

The sample of allyl terminated benzoxazine with 10, 30 and 50 wt % SH-POSS were separately dissolved in chloroform and was irradiated in a UV photo reactor and the structural changes occurred were monitored by UV spectrophotometer. The representative spectral changes involved in the photolysis of samples are shown in Figure.5.8 (a-c).

The UV spectra of allyl terminated benzoxazine with 10, 30 and 50 wt % SH-POSS in a chloroform solution showed that there is a decrease in the intensity of absorption at 337 nm. This may be due to cross linking reaction occurred between thiol group of POSS and ene group of the benzoxazine monomers (Lee et al 2005a). The reaction proceeds via propagation of a thyl radical through an allyl functional group. This reaction is followed by chain
transfer of the radical to a thiol functional group, regenerating a thyl radical, which in turn restarts the process.

This successive propagation/chain transfer mechanism is the basis for step-growth thiol-ene polymerization (Cramer et al 2002). As the irradiation time is increased from 0 min to 150 min the intensity of the peak is decreased. The 50wt% POSS reinforced sample at 150 min in Figure 5.8(a) shows the lowest intensity when compared to that of other samples.

Figure 5.8 Changes in UV spectral characteristics during photolysis of benzoxazine with POSS in CHCl$_3$ at different time intervals (a) $P_{10}$-PBZ (b) $P_{30}$-PBZ and (c) $P_{50}$-PBZ
5.3.4 UV-Visible Transmittance Spectra

The UV-Visible transmittance spectra for the dual cured POSS-PBZ hybrids were taken using Jasco-(V-650) spectrophotometer and are presented in Figure 5.9. The UV shielding effect at 337 nm absorption range of 50wt % POSS- PBZ shows the higher shielding value when compared to that of other samples. The highest UV shielding behavior (87%) for 50wt % SH-POSS reinforced benzoxazine was observed because of higher weight percentage of Si atom present in the sample. Thus, the shielding efficiency of the developed sample covers the whole UV- rays region UV-A (320–400 nm), UV-B (280–320 nm) and UV-C (200–280 nm) (Jacobine et al 1993).

Figure 5.9 UV-Visible transmittance spectra of dual cured POSS-PBZ composites
5.3.5 Effect of Photo Irradiation on the Curing Behavior of Monomers

DSC thermogram were taken for UV cured and dual cured POSS-PBZ hybrid samples at 30, 90 and 150 min of UV irradiation and the data resulted are presented in Figure 5.10. The DSC thermogram of only UV irradiated hybrid samples show two exothermic peaks. The first exothermic peak appeared at 166 °C is associated with the allyl group of benzoxazine and the second exothermic peak appeared at 242 °C represents the ring opening polymerization of benzoxazine. From the Figure 5.10 a, as the UV irradiation time increased from 30 to 150 min the peak representing the allyl group disappears which confirms the occurrence of thiol-ene reaction. Whereas in the case of dual cured samples (Figure 5.10 b) the second peak associated with ring opening polymerization of benzoxazine completely disappeared at 150 min of UV irradiation shows the complete ring opening polymerization of benzoxazine (Narayanan et al 2012, Chang et al 2012).

![DSC profile of (a) UV cured and (b) dual cured POSS-PBZ composites](image)

Figure 5.10 DSC profile of (a) UV cured and (b) dual cured POSS-PBZ composites
5.3.6 Effect of Photo Irradiation on Thermal Properties

The thermal behavior of dual cured samples with 150 min of UV irradiation was evaluated by the TGA in nitrogen atmosphere at the heating rate of 10°C/min and the data are presented in Figure 5.11 & Table 5.1. The value of char yield of dual cured benzoxazine with 10, 30 and 50wt % of POSS samples are 17%, 26% and 37% respectively. The increase in thermal stability value of UV irradiated samples is due to the completion of thiol-ene reaction between POSS and benzoxazine. Therefore thiol and ene groups undergo an effective thermal polymerization resulting in thermally stable polybenzoxazine. The thermal stability of polybenzoxazine was increased linearly with an increase in the irradiation time of the benzoxazine with POSS monomer (Luo et al 2011).

![Figure 5.11 TGA profile dual cured POSS-PBZ composites](image-url)
Table 5.1 Thermal Properties of dual cured POSS-PBZ composites

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Tg (°C)</th>
<th>Weight loss (%)</th>
<th>Char yield at 750°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>P_{10} - PBZ</td>
<td>242</td>
<td>233</td>
<td>343</td>
</tr>
<tr>
<td>P_{30} – PBZ</td>
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<td>354</td>
</tr>
<tr>
<td>P_{50} – PBZ</td>
<td>259</td>
<td>280</td>
<td>390</td>
</tr>
</tbody>
</table>

5.3.7 Dielectric Properties

The values of dielectric constant of dual cured POSS-PBZ composites measured at 1 MHz are presented in Figure 5.12. The value of dielectric constant of the hybrid samples is decreased with an increase in the weight percentage of POSS. The reduction in the value of dielectric constant of POSS-PBZ hybrids is due to the creation of pores and enhanced free volume contributed by the rigid and bulky core structured POSS molecule. The less polar nature of Si-O-Si linkage present in the POSS-PBZ system also contributes to reduce the value of dielectric constant. The lower value of dielectric constant of 50% POSS-PBZ is due to the presence of higher amount of porosity in the POSS reinforced system. Thus the 50wt% POSS -PBZ possesses the lowest value of dielectric constant (k = 2). Additionally, the value of dielectric loss was also found to be the lowest (Figure 5.13) in the case of 50% POSS -PBZ, which also contributes to good insulating behavior (Selvi et al 2014 b).
Figure 5.12 Dielectric constant of dual cured POSS-PBZ composites

Figure 5.13 Dielectric loss of dual cured POSS-PBZ composites
5.3.8 Morphological Studies
5.3.8.1 Surface free energy

The contact angle measurements were performed using a goniometer and the values of dual cured POSS-PBS are presented in Figure 5.14 & Table 5.2(a-c) and Figure 5.14. The values of contact angle of water and diiodomethane have been used to estimate the surface free energy of hybrid composites surfaces. The value of surface free energy (\( \gamma \)) of the composites is calculated according to the geometric mean model (Devaraju et al 2013) using the equations 4.1 and 4.2 and the results obtained are presented in Table 5.2.

![Figure 5.14 Contact angle images of dual cured P\(_{10}\) – PBZ, P\(_{30}\) – PBZ and P\(_{50}\) – PBZ composites at 150 min. Water (a-c) and Diiodomethane (a1-c1)](image)

The values of surface free energy obtained for P\(_{10}\) – PBZ, P\(_{30}\) – PBZ and P\(_{50}\) – PBZ hybrid samples cured with UV at 150 min are 32.3, 27.6 and 27.4 respectively, which infer that 50 wt % of POSS reinforced benzoxazine
possesses relatively better hydrophobic behavior than that of other hybrid samples. However, with POSS reinforcement the hydrophobic behavior of sample was increased mainly due to the presence of less polar Si-O-Si linkage in the POSS covalently bonded with benzoxazine which in turn reduced the value of the surface free energy of the resulting hybrid composites.

Table 5.2 Surface free energy properties of dual cured POSS-PBZ composites (a) P₁₀-PBZ, (b) P₃₀-PBZ,(c) P₅₀-PBZ composites

<table>
<thead>
<tr>
<th>UV Irradiation Time</th>
<th>Contact angle (°)</th>
<th>Surface free energy (Jm⁻¹)</th>
<th>γ(0)</th>
<th>γ(D)</th>
<th>γ(δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>DIM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>85.0</td>
<td>38.8</td>
<td>42.2</td>
<td>1.8</td>
<td>42.2</td>
</tr>
<tr>
<td>30 min</td>
<td>91.2</td>
<td>47.3</td>
<td>35.8</td>
<td>1.2</td>
<td>36.9</td>
</tr>
<tr>
<td>60 min</td>
<td>93.8</td>
<td>49.5</td>
<td>34.6</td>
<td>0.8</td>
<td>35.4</td>
</tr>
<tr>
<td>90 min</td>
<td>94.1</td>
<td>50.6</td>
<td>33.9</td>
<td>0.9</td>
<td>34.8</td>
</tr>
<tr>
<td>120 min</td>
<td>94.5</td>
<td>51.0</td>
<td>33.7</td>
<td>0.8</td>
<td>34.5</td>
</tr>
<tr>
<td>150 min</td>
<td>96.9</td>
<td>54.6</td>
<td>31.7</td>
<td>0.6</td>
<td>32.3</td>
</tr>
</tbody>
</table>

5.3.8.2 X-ray diffraction analysis

Figure 5.15 illustrates the XRD pattern dual of cured POSS-PBS composites. A broad amorphous peak was observed at 2θ = 18.2° in all the
dual cured samples of POSS-PBZ hybrid composites. The XRD data indicate the absence of crystalline POSS aggregation in the obtained film, which is in good agreement with the appearance of the hybrid composite film.

![XRD pattern of dual cured POSS-PBZ composites](image)

**Figure 5.15 XRD pattern of dual cured POSS-PBZ composites**

5.3.8.3 Transmission electron microscopy

The internal microstructure of dual cured thiol POSS-PBZ hybrid composite film have been analyzed using the HRTEM and the captured images are shown in Figure 5.16 (a-c). The TEM images are clearly illustrates the structure of the hybrid composites. From the high magnification at 20 nm of TEM images it can also be seen that the well separated unidirectional multilayered arrangement. It is well established that the observed dark layers are associated to the POSS molecules and the less intense layers correspond to the benzoxazine segments (Sasi Kumar et al 2014).
5.4 SUMMARY

In the present work an allyl terminated benzoxazine and thiol functionalised POSS were synthesized and were hybridized through photopolymerization as well as thermal polymerization method. Data from thermal, UV-transmittance, contact angle and dielectric studies of dual cured 50 wt % POSS-PBZ hybrids possess the higher thermal stability, higher contact angle, better UV-shielding and the lower value of dielectric constant than those of other samples. It is suggested that the hybrid POSS-PBZ composites developed in the present work can be used as radiation resistant coatings and low k insulating materials for microelectronic applications for better performance and improved longevity.