CHAPTER-4

ENHANCED THERMAL PROPERTIES OF HIGHLY MONODISPERSED ZnO NANOPARTICLES / POLY (STYRENE-CO-ACRYLONITRILE) NANOCOMPOSITE
4.1 Introduction

The polymer-inorganic composite after addition of inorganic filler in polymer matrix have attracted wide attention in comparison to conventional polymers due to their synergistic effects [1]. ZnO has been chosen as the filler in polymer matrix out of TiO$_2$, Al$_2$O$_3$, CaCO$_3$ etc., because of its wide band gap (3.30 eV) and high exciton binding energy (60 meV). The addition of ZnO in polymer matrix will enhance the properties of polymer nanocomposite (PNs) as UV-absorber, photo catalyst and gas sensors [2-9] etc. Addition of ZnO nanoparticles (NPs) in polymer matrix results to uniform dispersion and interfacial adhesion between filler and polymer [10]. The incorporation of ZnO nanofillers in polymer matrix improves its mechanical and thermal stability [11,12,13]. In order to make effective and appropriate dispersion of filler in polymer matrix, a optimum low content of fillers (1-10) wt.% should be added in comparison to high filler addition (15-40 wt.%) [14]. The selection of inorganic filler into polymer matrix in place of existing carbon based different fillers such as nanotubes, nanofibres, nanoparticles etc. is due to their properties and cost factor. The final properties achieved in PNs depends on the physical and chemical interaction between polymer and nanofillers together. Minimizing the agglomeration between the fillers is a crucial and challenging issue which needs to be optimized through proper synthesis techniques of nanocomposite in order to improve thermal, mechanical and tribological properties etc. [11, 12, 13, 15].

The requirement of flexible, easy processing, low weight based products is fulfilled by thermoplastic based materials and are able to replace the existing metal based products. The selection of polymer matrix among the existing polymer materials such as Poly(phenylenesulphide) [16], Poly(methylmethacrylate) (PMMA) [17], Polystyrene (PS) [18], Poly(acrylate) [19] etc., is very important factor in order to achieve improved thermal and mechanical properties of PNs. The properties of PS and polyacrylonitrile (PAN) are complementary to each other, hence can be used to develop functionalized nanocomposites. While PS has optical transparency and easy processing [20], thermal and chemically stable nature of PAN [21] directs the development of their co-polymer i.e. poly(styrene-co-acrylonitrile) (PSAN). Thus limited optical, chemical, thermal and mechanical properties of PS and PAN improved through their copolymerization [22]. Earlier, the fabrication of ZnO filler based poly(ether-ether-ketone)(PEEK)[23], poly(lactic-acid)[24, 25], poly(3-hydroxybutyrate) [26],
polyacrylate [27], poly(phenylenesulphide)[16] etc., polymer matrices have been studied to improve the mechanical, thermal and antibacterial properties of polymer composite. To ensure the effective dispersion and interfacial adhesion of NPs with polymer, insitu emulsion polymerization techniques [28, 29] has been preferred over other polymerization like suspension [30], dispersion [31] etc. In the present work, insitu emulsion polymerization based PSAN/ZnO nanocomposite has been reported with unique structural, morphological and thermal properties.

4.2 Experimental

4.2.1 Preparation of Poly (styrene-co-acrylonitrile)/ZnO (PSAN/ZnO) nanocomposite

PSAN/ZnO PNs were synthesized by insitu emulsion polymerization. The detail procedure of PSAN/ZnO synthesis has been explained with detail chemical reaction mechanism in chapter-2, section 2.2 and 2.3. The prepared PNs were characterized by different characterization techniques viz. FTIR, XRD, FESEM with EDAX, TEM, TGA and DSC.

4.3 Results and discussion

4.3.1 FTIR Study

The FTIR absorption spectrum of filler ZnO NPs and different PNs (PSAN, PSAN0.5, PSAN5) are depicted in figure 4.1. The formation of ZnO NPs has been confirmed after observation of Zn-O absorption vibration at 491 cm\(^{-1}\) and -OH group vibration at 3433 cm\(^{-1}\) respectively as shown in figure 4.1-i(d). The presence of styrene segment in PSAN polymer has been established by presence of aromatic C-H stretching at \(\sim 3010-3100\) cm\(^{-1}\), out of plane hydrogen vibration at 758 cm\(^{-1}\) and benzene ring C=C out of plane bending at 699 cm\(^{-1}\) respectively [32, 33, 34]. The vibration of -CN band observed at 2241 cm\(^{-1}\) confirms the presence of acrylonitrile unit in PSAN structure. Further, the presence of two frequency band at 2930 and 2850 cm\(^{-1}\) directs the presence CH\(_2\) vibration in polymer [32]. While the incorporation of ZnO NPs into PSAN matrix with increase in their content is clearly seen from their absorption spectra (Figure 4.1-i(a, b, c)), Zn-O vibration band is observed at frequency of 540 cm\(^{-1}\). The enhancement in the intensity of vibration of ZnO NPs for PSAN to PSAN5 supports the effective interaction between ZnO and PSAN. In addition, the band shift and decrease in the intensity of Zn-O vibration in PNs compared to bare ZnO clearly confirms the interaction of PSAN with ZnO NPs [16].
Effective interaction between ZnO NPs -OH group and PSAN -CN group has been established with the shifting of -CN vibration peak to lower frequency (2241 to 2236 cm\(^{-1}\)) for PSAN to PSAN5. The interaction between PSAN and ZnO NPs content was also confirmed by decrease in the intensity of -CN vibration peak [35] in PSAN compared to PSAN5 (figure 4.1-ii(a-d)).

### 4.3.2 Crystal Structure

The X-ray diffraction pattern of different PNs named PSAN, PSAN0.5, PSAN2.5, PSAN5 and ZnO NPs are shown in figure 4.2. The presence of hump like pattern from 2\(\theta\) =10\(^{\circ}\) to 25\(^{\circ}\) range infers to more of the amorphous nature of pristine polymer (PSAN) as shown in figure 4.2(a). The incorporation of ZnO NPs into polymer matrix has been clearly seen in their diffraction pattern (figure 4.2 (b, c & d)). The purity of synthesized ZnO NPs has been confirmed with distinctive diffraction peaks observed at 2\(\theta\) = 31.65\(^{\circ}\), 34.47\(^{\circ}\), 36.26\(^{\circ}\), 47.67\(^{\circ}\), 56.64\(^{\circ}\), 62.90\(^{\circ}\), 66.49\(^{\circ}\) and 68.03\(^{\circ}\) for crystalline planes(100), (002), (101), (102), (110), (103), (200) and (112) respectively(figure 4.2(e)). The diffraction data of bare ZnO NPs matches with JCPDS card no.-36-1451 for wurtzite ZnO. The average crystallite size calculation for synthesized ZnO NPs has
been performed using Scherrer formula given by equation (3.2) chapter 3 and the values calculated are summarized in table 4.1.

![Figure 4.2](image)

**Figure 4.2:** (a-e) XRD pattern for PSAN, PSAN0.5, PSAN2.5, PSAN5 and ZnO NPs.

**Table 4.1:** Crystallite size of pure ZnO for different peaks.

<table>
<thead>
<tr>
<th>2θ(°)</th>
<th>31.65</th>
<th>34.47</th>
<th>36.26</th>
<th>47.67</th>
<th>56.64</th>
<th>62.90</th>
<th>66.49</th>
<th>68.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(nm)</td>
<td>45.55</td>
<td>44.00</td>
<td>46.67</td>
<td>39.60</td>
<td>35.53</td>
<td>47.79</td>
<td>28.00</td>
<td>60.26</td>
</tr>
</tbody>
</table>

Average crystallite size = 43.42 nm

The incorporation of ZnO NPs into PSAN matrix was confirmed by decrease in intensity of peaks in diffraction pattern of ZnO NPs in comparison to pristine ZnO NPs. The presence of ZnO diffraction pattern in amorphous polymer clearly indicates the presence of crystalline phase in polymer matrix. The crystallinity level \( (X_c) \) has been calculated with the help of equation (4.1)[16]:

\[
X_c = \frac{I_c}{I_c + I_a}
\]  

(4.1)
where $I_a$ and $I_c$ are integrated intensities of the amorphous and crystalline phases respectively. Increased content of ZnO NPs from 0.5, 2.5 and 5 wt % in PSAN matrix leads to enhance the overall crystallinity level to 29.4, 58.4 and 60.0 % respectively. This also infers the enhanced crystalline nature of PSAN/ZnO nanocomposite in comparison to pristine polymer (PSAN) [36].

4.3.3 FESEM and Elemental Analysis

The morphological investigation of synthesized material has been carried out by using FESEM and images are shown in figure 4.3 and 4.4. The morphology of bare ZnO NPs has been observed to be nearly uniform with average particle diameter of ~ 75 nm. ZnO NPs due to their small size and high surface energy leads to agglomeration between them as seen in figure 4.3. The addition of ZnO NPs into polymer matrix (PSAN) transforms the morphology of polymer composite drastically as observed in figure 4.4(b & c) as compared to figure 4.4(a). The incorporation of 0.5 wt. % ZnO in PSAN matrix induces the formation of monodispersed spherical particles of ~100 nm size (Fig. 4.4 b). Further, PSAN5 shows the formation of homogenous mono-dispersion PNs with particles interconnected network having average particle diameter of 70 nm.

Thus the reduction in PNs size establish the proper interaction of fillers NPs (ZnO) with polymer matrix directly improving the properties viz. thermal, mechanical, electrical etc. [26, 27, 28].

Figure 4.3: FESEM image of ZnO nanoparticles.
Figure 4.4: FESEM images of (a) PSAN (b) PSAN0.5 (c) PSAN5.
Figure 4.5: EDS Micrograph of (a) PSAN (b) PSAN5.

The elemental quantification of synthesized material has been analyzed using EDAX technique. Figure 4.5(a & b) shows the spectra of PSAN and PSAN5 sample. In figure 4.5(a), observed spectrum shows the presence of Carbon (C), Nitrogen (N), Sulfur (S) and Oxygen (O) elements in the PSAN whereas PSAN5 nanocomposite contains zinc (Zn) elements peak in addition to C, N, S and O elements in figure 4.5(b).
Mapping mode in EDAX has been used to find the homogeneity of PSAN5 sample. In figure 4.6(a-e) specifically located positions of different elements in scanned area are shown in order to confirm their homogeneity in polymer matrix. The presence zinc (Zn) element shown in figure 4.6(d) endorses uniform dispersion of Zinc in PSAN matrix.

**Table 4.2** The elements atomic % in pure polymer (PSAN), PSAN5 polymer with 5 wt% ZnO composite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSAN</td>
<td>82.6</td>
<td>5.2</td>
<td>10.7</td>
<td>1.5</td>
<td>----</td>
</tr>
<tr>
<td>PSAN5</td>
<td>80.2</td>
<td>4.4</td>
<td>9.3</td>
<td>1.4</td>
<td>4.7</td>
</tr>
</tbody>
</table>

**Figure 4.6:** (a-e) EDAX mapping of PSAN5 for carbon(C), nitrogen (N), Sulfur(S), Oxygen (O) and Zinc (Zn) elements respectively.
4.3.4 TEM Study

The ultra structural morphological information of pristine ZnO NPs, PSAN & PSAN5 nanocomposite is observed by TEM as shown in figure 4.7, 4.8 & 4.9.

Figure 4.7(a) shows the spherical shape ZnO NPs with average particle size of 45 nm (figure 4.7-a1). The ZnO NPs particle size clearly matches with XRD results (section 4.3.2). Figure 4.8(a) supports the results of FESEM study (section 4.3.3), which confirms the presence of asymmetrical spherical microspheres with average particles size 105 nm (figure 4.8-a1). In figure 4.8(a), there is formation of some core-shell based formulation which may be explained on the basis of polymer (styrene)-polymer (acrylonitrile) interaction. Further, the core-shell formation of PSAN can be explained with initial formation of core followed by coating of second polymer called the shell. This classifies as swelling mechanism prior to polymerization process. The compatibility of acrylonitrile monomer to be at the core of PSAN results in styrene monomer as shell of polymer [29]. Figure 4.9(a) predicts the presence of monodispersed microsphere formation of PSAN5 having average particle size of 70 nm (figure 4.9-a1). The significant decrease in particle size from 105 nm to 70 nm observed from PSAN to PSAN5 may be attributed to the effective insitu polymerization with incorporation of ZnO NPs in polymer matrix. The effective uniform dispersion of ZnO NPs in insitu emulsion will acts as nucleating agent favoring the decrement of particle size [23]. The addition of ZnO NPs into polymer matrix provides effective nucleation sites [23] for proper polymerization due to high surface area of ZnO NPs.

In comparison to PSAN, enhanced core density in PSAN5 has been observed attributed to the presence of zinc in polymer matrix [31] (confirmed by EDAX (figure 4.5)).

Figure 4.7: (a) TEM image of ZnO NPs and (a1) its particle distribution respectively.
Chapter 4

Enhanced thermal properties

4.3.5 Thermal study

The effect of ZnO with their different contents on the thermal stability of polymer matrix (PSAN) has been studied by TGA technique shown in figure 4.10 and various parameters calculated are listed table 4.3. The PSAN shows initial thermal degradation (T_i) and maximum weight loss (T_max) at 381.5°C and 455.6°C respectively (figure 4.10). The incorporation of ZnO NPs into PSAN matrix increases its range of degradation temperature.

The initial degradation temperature T_i (°C) for different synthesized PNs i.e. PSAN0.5, PSAN2.5 & PSAN5 increased by 4.9, 7.8 and 12.5°C with reference to PSAN. In addition to T_i (°C) and T_max (°C), T_{10} (°C) (degradation temperature at 10 % wt. loss) also shows the same trend as T_i and T_max and the values are summarized in table 4.3. In order to study the major thermal
degradation effect of ZnO NPs on the PSAN matrix, axes of $T_{\text{max}}$(°C) for PSAN, PSAN0.5, PSAN2.5 and PSAN5 have been zoomed and shown as inset in figure 4.10.

![TGA curve under nitrogen for polymer composite named PSAN, PSAN0.5, PSAN2.5 and PSAN5 and inset zoomed view for $T_{\text{max}}$.](image)

**Figure 4.10**: TGA curve under nitrogen for polymer composite named PSAN, PSAN0.5, PSAN2.5 and PSAN5 and inset zoomed view for $T_{\text{max}}$.

It is clearly observed that there is a decrease in weight loss of PNs with the increase content of ZnO (0.5, 2.5 &5 wt. %) \(i.e.\) 99.87, 90.66, 90.22 and 79.89 wt. % respectively. Enhanced thermal degradation of PSAN with incorporation of ZnO NPs facilitated due to their barrier effect through effective dispersion and will restrict the degradation of PNs into gas phases [23]. In addition, high thermal transportation ability of ZnO will direct the heat dissipation in PSAN/ZnO nanocomposite, enhancing thermal stability of PNs [37]. Further, for thermal stability of PNs, flame retardant property of material has also been studied with the help of char residue formation technique [16]. By using D.W. Van Krevelen equation [16], a correlation of the flame retardant nature of NPs with char residue (\(CR\)) and oxygen index (\(OI\)) has been drawn.

\[
OI \times 100 = 17.5 + 0.4 \, CR
\]  

(4.2)

In equation (4.2), \(CR\) is char residue studied in wt. % at 800°C.

The aromatic nature of PSAN with oxygen index (\(OI\)) \(\leq\) 26% makes material less flammable. The fire retardant ability of synthesized polymer nanocomposite with the addition of inorganic filler (ZnO) in polymer (PSAN) can be achieved due to fast propagation of heat of ZnO as compared to
PSAN polymer. The OI values increase with ZnO addition in PSAN from 35.0 % to 36.5 %. The ZnO NPs will dissipate the heat in polymer matrix which impede the ignition point. Moreover, the mass propagation barrier stops the transport of volatile products during degradation and prevent oxygen to reach PSAN matrix [23, 26].

4.3.6 Crystallization and Melting temperature behavior

The addition of inorganic filler (ZnO) into PSAN matrix affects the crystallization and melting behavior and finally tune other properties of nanocomposite. The study of crystallization and melting behavior has been performed with the help of DSC analysis under non isothermal conditions for different synthesized PNs materials shown in figure 4.11. The corresponding values are tabulated in table 4.3.

**Table 4.3:** Thermal parameter obtained from DSC and TGA analysis of PSAN and its nanocomposite with ZnONPs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tc(°C)</th>
<th>Tm(°C)</th>
<th>Tl(°C)</th>
<th>T10(°C)</th>
<th>Tmax(°C)</th>
<th>OI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSAN</td>
<td>--</td>
<td>---</td>
<td>381.5</td>
<td>425.1</td>
<td>455.6</td>
<td>35.0</td>
</tr>
<tr>
<td>PSAN 0.5</td>
<td>242.2</td>
<td>265.5</td>
<td>386.4</td>
<td>435.2</td>
<td>463.3</td>
<td>35.2</td>
</tr>
<tr>
<td>PSAN 2.5</td>
<td>244.3</td>
<td>269.8</td>
<td>389.3</td>
<td>444.4</td>
<td>471.6</td>
<td>35.9</td>
</tr>
<tr>
<td>PSAN 5</td>
<td>249.5</td>
<td>271.9</td>
<td>394.0</td>
<td>461.6</td>
<td>485.4</td>
<td>36.5</td>
</tr>
</tbody>
</table>

The addition of ZnO NPs into polymer matrix increases the melting temperature (Tm) by 6.4°C in figure 4.11(a) and crystallization temperature (Tc) by 7.3°C in figure 4.11(b) as compared to pristine polymer. The effective dispersion of filler nanoparticles (ZnO) with strong interaction between ZnO and PSAN via -OH group of ZnO and polar end of polymer, facilitate sufficient nucleating centers for stable material. The impeding re-crystallization of PNs is due to restricted heat mobility of ZnO in polymer matrix. The stable melting and crystallization temperature of PNs with ZnO incorporation is due to high heat capacity of ZnO in comparison to PSAN, which absorbs the heat around it and delays the direct thermal effect on polymer [23].
The thermal stability shown by the polymer with the ZnO NPs is only possible after the perfect and effective interaction between fillers (ZnO) and polymer (PSAN) as confirmed by FTIR study (section 4.3.1).
As per demand and requirement of MIS surgery in medical areas like gynecology surgery, urology, cardiothoracic etc., the synthesized PSAN/ZnO nanocomposite can be used in the fabrication of different MIS tools. This will lead to give minimum post-operative pain, recuperation time and minimal cost [38].

4.4 Conclusion

In present work monodispersed microsphere of PSAN with zinc oxide (ZnO) NPs via insitu emulsion polymerization has been synthesized. The different properties have been explored including structural, morphological and thermal properties using FTIR, XRD, FESEM, EDAX, TEM, TGA and DSC techniques. The effective dispersion of ZnO in polymer matrix has been confirmed by SEM, EDAX, TEM and FTIR study. The high surface area of ZnO NPs through their high interfacial adhesion with reacting monomers (styrene & acrylonitrile) leads to homogenous dispersion of ZnO in polymer (PSAN). The alteration in the -CN vibration of PSAN with ZnO incorporation confirms the chemical bondage of ZnO with PSAN. The presence of ZnO diffraction peaks in PSAN matrix clearly follows their effective incorporation and presence in polymer matrix. The FESEM and TEM study reveals the uniform, monodispersed morphology of PSAN/ZnO nanocomposite. The elemental presence of zinc in polymer matrix in addition to other elements (C, H, N, S, and O) has been confirmed by EDAX study. The addition of ZnO NPs into polymer also affected the heat resistance ability of polymer matrix because of fillers barrier effect towards heat. Crystallization temperature $T_c$($\degree$C) also increased towards higher temperature with ZnO addition due to nucleating ability of nanoparticles. The maximum thermal degradation temperature $T_{max}$(C) also rised by 29.8$\degree$C with respect to pristine polymer(PSAN). The mild improved oxygen index (OI) of PNs from 35 to 36.5% with incorporation of ZnO in polymer matrix can behave as a fire retardant PNs. Thus the improved thermal stability of PSAN/ZnO with flexibility can be utilized in minimal invasive surgery instruments by medical industry (scissor, forceps, microgrips etc.).
REFERENCES


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