PP/ZnO composites were prepared by melt mixing method. It was then spun into fibers by melt spinning and subsequent drawing. Mechanical properties of the fibers were measured using Favimat tensile testing machine with a load cell of 1,200cN capacity. Thermal behaviour of the fibers was studied using differential scanning calorimetry and thermogravimetric analysis. Surface morphology and cross section of the fiber was studied using scanning electron microscopy. Mechanical properties of the PP fiber was improved by the addition of ZnO nanoparticles. Thermogravimetric analysis shows significant improvement in thermal stability of PP fiber. Improvement in crystallinity is observed by the addition of ZnO nanoparticles. Antibacterial properties of fiber was studied using Bacillus aereus (gram positive) and Escherichia coli (gram negative) bacteria.
4.1 Introduction

PP is a widely used thermoplastic for hygienic applications such as food packaging, surgical masks, diapers etc. It is also used for fibers and films. PP fibres have been widely used in apparel, upholstery, floor coverings, geotextiles, car industry, automotive textiles, various home textiles etc [1, 2]. Because of the low cost, high toughness, strength and resistance to chemicals, PP fibers find a broad spectrum of use in industrial and home furnishing sector [3]. PP comprises a major portion of the materials used for spun bound and melt blown fabrics in hygiene and medical products [4-16]. It has a relatively low melting point of 160-175°C and it is an ideal polymer for making fibers. Three different crystalline forms of PP have been identified: α-monoclinic, β-trigonal and γ-orthorhombic. All the three forms are the helical conformation of the constituent PP chains. The α- form is the most stable and also the most important in making of PP fibers. Its monoclinic lattice has unit cell dimensions of a=0.665 nm, b=0.2096 nm, c=0.650 nm, α=γ=90°, β=99.3° and PP chains lie in the direction of the C – axis. The structure includes both left-handed and right handed helical PP chains and any given helix for the most part lies next to helices of the opposite chirality [17-19]. Isotactic α-PP also exhibits a lamellar branching, which is unique in polymer crystallography [20]. PP provides nearly half of base fiber for non-wovens fabrics [21]. Some synthetic and natural fibers are replaced by PP fibers are replaced by PP fibers due to its excellent properties and processability.

Modification of PP can improve the properties of the fiber. New materials are used today in PP fibers to increase the functionality and enter new markets. Conventional methods used to modify fibers and fabrics do not lead to permanent effects and lose their functions after laundering or wearing. However, because of their high surface energy, nanoparticles present better
PP/ZnO nanocomposite fibers through melt spinning

affinity for fibers and fabrics and increase the durability of their function. Thus, the studies related to the modification of polymeric textile fibers and fabrics by nanoparticles has increased recently [22, 23]. Incorporation of fillers in polymer generally shows improvement in strength, thermal stability and crystallization behaviour of PP fibers [24-29]. Anton Marcin et al reported the positive influence of boehmite Disperal 40, organoclay Cloisite C15A, nano TiO2 and MWCNT nanofillers in oriented PP composite fibers on their UV barrier properties at low content of the nanofiller [30]. Effect of silica particles on crystallization behaviour of PP fibers were studied by Natee Srisawat et al [31].

Melt spinning, electrospinning and wet spinning are the commonly used method for the production of fibers [32, 33]. Among these methods melt spinning is the least complex method and it involves forcing a polymer melt through a spinneret and into air to cause the polymer to solidify. It does not involve any problems associated with the use of solvents and is therefore the preferred method provided that the polymer gives a stable melt. The homogenized melt is extruded the spinneret and solidify anywhere from a few centimetres from the spinneret plate to as far away as several meters.

This chapter reports the preparation of PP/ZnO nanocomposite fibers by melt spinning and drawing. Mechanical, thermal, morphological, x-ray diffraction analysis and antibacterial properties of these fibers were studied.

4.2 Experimental

4.2.1 Preparation of PP/ZnO nanocomposite fibers

PP/ZnO (0-3wt% of ZnO) composites were prepared by melt mixing method. The hot mix were then made into sheets using a hydraulic press and cut in to small pieces to prepare fibers. The fibers were spun using a small scale spinning machine manufactured by Bradford University Research Ltd.,
UK, using a single hole spinneret of 1 mm diameter at 175°C with ram speed 3.10 m/min and winding speed 35 m/min. Subsequent drawing was done at 100°C at a draw ratio of 1:6. Schematic representation of melt spinning machine is given in figure 4.1 and specifications are given below.

- **Spinneret**: Single hole, dia = 1 mm, length = 7 mm
- **Cylinder temperature**: 175 (± 0.5) °C
- **Ram speed**: 3.10 (± 0.02) mm/min
- **Winding speed**: 35 (± 0.2) m/min
- **Filament type**: mono filament

![Figure 4.1: Schematic representation of laboratory scale melt spinning machine](image-url)
The spun fibers were subsequently drawn using a laboratory single zone drawing machine, a schematic representation of which is given in figure 4.2. The specifications and conditions of drawing were as follows:

![Diagram of fiber drawing set-up](image)

**Figure 4.2: Schematic representation of the fiber drawing set-up**

- **Draw ratio**: 1:6
- **Outer diameter of the rollers**: 11.2 cm
- **Length of the heating plate**: 20.5 cm
- **Heater temperature**: 100 ± 0.5 °C

### 4.2.2 Mechanical properties of the fibers

The mechanical properties of the fibers were studied by a Favimat fiber testing machine with a load cell of 1,200 cN capacity with gauge length of 20 mm and test speed 20 mm/min. The pretension was set at 0.50 cN/tex and
the temperature was maintained at 25± 0°C. Ten measurements were taken to represent each data.

### 4.2.3 Thermogravimetric analysis

Thermogravimetric analyzer (TGA Q-50, TA instruments) was used to study the effect of ZnO on the thermal stability of PP fibers. Approximately 10 mg of the samples were heated at a rate of 20°C/min from ambient to 800°C in nitrogen atmosphere. The corresponding weight changes were noted with the help of an ultrasensitive microbalance.

### 4.2.4 Differential scanning calorimetry

DSC studies were carried out using Q-50 TA instruments in nitrogen atmosphere. The samples were heated to 200°C at a rate of 10°C/min, isothermal for 1 minute, followed by cooling to 40°C at a rate of 10°C/min. In DSC, the crystallization characteristics are studied from the heat flows associated with corresponding transitions as a function of temperature. The percentage crystallinity [34] of the samples was calculated using following equation:

\[
X_c = \frac{\Delta H_c}{\Delta H_0^c (1-Wm)} \times 100 \quad \text{-------------------------- (4.1)}
\]

where \(\Delta H_c\) is the enthalpy of crystallization of the tested fiber and \(\Delta H_0^c\) is the extrapolated value of enthalpy corresponding to 100% crystalline PP, which was obtained from literature as \(\Delta H_0^c = 165\,\text{J/g}\) [35] and \(Wm\) is the weight fraction of ZnO in PP fiber.

### 4.2.5 Scanning electron microscopy

Scanning electron microscope JEOL JSM-6390 was used to study the surface morphology and cross section of fibers.
4.2.6 X-ray diffraction studies

X-ray diffraction studies of the fibers were carried out using Rigaku Geigerflex at wavelength CuKα=1.54 Å.

4.2.7 Antibacterial properties of fibers

Effect of bacterial medium on the fibers were studied by putting the fiber in bacterial medium containing Bacillus aereus (gram positive) and E- Coli (gram negative bacteria). Morphology of fibers were studied using SEM after ten days.

4.3 Results and Discussion

4.3.1 Mechanical properties of the fiber

Figure 4.3 is the photographs of PP fibers and PP/ZnO composite fibers after drawing at 100°C and 1:6 draw ratio.

Tenacity or strength of PP fibers is increased by the addition of ZnO, reaches maximum at 0.5wt% and then decreased. The increase in tenacity (figure 4.4) is 71.5wt% at 0.5wt% of NZO and 41.1% for 0.5 wt% CZO added PP fiber. The increase in modulus (figure 4.5) is about 38.567% for
0.5 wt% of NZO and 36.67% in case of 0.5wt% of CZO when compared to that of neat PP fiber. Increase in tenacity may be due to the good orientation of NZO in the fiber. The elongation at break (figure 4.6) of the PP fibers is increased in case of NZO filled fibers, reaches a maximum and decreases. This may be due to the increase in toughness of the fiber. In case of CZO filled PP fibers elongation at break decreases by the addition of CZO particles. Effect of ZnO on the time to rupture of fibers is given in figure 4.7. By the addition of ZnO time taken to rupture increases, indicate reinforcing effect of ZnO in PP fiber. Linear density (figure 4.8) of the PP fiber is increased by the addition of ZnO which indicates increase in fineness of fibers. Properties of the fiber depend on internal structure, degree of crystallinity and conditions of spinning [36].

![Figure 4.4: Effect of ZnO on tenacity of PP/ZnO composite fibers](image)

Figure 4.4: Effect of ZnO on tenacity of PP/ZnO composite fibers
Figure 4.5: Effect of ZnO on modulus of PP/ZnO composite fibers

Figure 4.6: Effect of ZnO on elongation at break of PP/ZnO composite fibers
4.3.2 Thermogravimetric analysis of the fibers

The TGA and DTG curves, obtained under nitrogen atmosphere, of pure PP fiber and PP/NZO fibers are shown in figure 4.9 and 4.10 respectively and data is
tabulated in table 4.1. The thermograms of neat PP and composites fibers are found to be similar in nature. All fibers show single step decomposition and this is due to breakdown of polymer chains. TGA shows the shifting of thermograms towards higher temperature region with increase in concentration of NZO. This indicates degradation of composite fibers take place at higher temperature. The enhanced stability of the composite fibers with respect to the neat fibers may be due to the hindering of thermal motion of PP chains by nanoparticles [37], which restrict the degradation of polymer chains. Due to higher compactness of chains, takes much more time to attain the thermal equilibrium and degradation process occurred slowly. Onset of degradation is increased by 31.3°C for fiber containing 3wt% NZO when compared to neat PP. The temperature at which maximum degradation take place is increased by 38.9°C by the addition of 3wt% NZO. There are some recent reports on the increase in polymer stability by the addition of inorganic nanoparticles [38-49].

Figure 4.9: Thermogram of PP/ZnO nanocomposite fibers
4.3.3 Kinetic analysis of thermal decomposition

Kinetics of thermal degradation of PP and PP/ZnO composites fibers is studied by Coats–Redfern method [50] and thermal degradation functions were listed in Table 3.3. Detailed description is given in section 3.3.8. From the table 4.3 it is clear that the activation energy of PP fiber is increased by the addition of NZO. Activation energy (E) obtained for neat fiber is 79.5 kJ/mol, 3% NZO added PP is 139.7 kJ/mol. Significant increase in activation energy indicates high thermal stability. Representative plot of Coats–Redfern equation for neat PP fiber, PP/1.5wt% NZO composite fiber and PP/3wt% NZO composite fiber is shown in figure 4.11.
Table 4.3: Apparent activation energy (E) and correlation coefficients (R) for neat PP and composite fibers by Coats–Redfern method.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>R</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP fiber</td>
<td>0.999</td>
<td>79.57</td>
</tr>
<tr>
<td>PP+0.5% NZO fiber</td>
<td>0.999</td>
<td>93.125</td>
</tr>
<tr>
<td>PP+1.5% NZO fiber</td>
<td>0.999</td>
<td>96.64</td>
</tr>
<tr>
<td>PP+3% NZO fiber</td>
<td>0.999</td>
<td>139.71</td>
</tr>
</tbody>
</table>

Figure 4.11.a: Representative plot of Coats–Redfern equation for neat PP fiber

Figure 4.11.b: Representative plot of Coats–Redfern equation for PP+1.5wt% NZO fiber
4.3.4 Differential scanning calorimetry (DSC)

DSC curves of the neat PP and composite fibers are shown in figures 4.12 and 4.13. From DSC crystallization exotherms (figure 4.12), $T_c$ (the temperature at the crossing point of the tangents of the baseline and the high-temperature side of the exotherm), $T_{cp}$ (the peak temperature of the exotherm) and $\Delta H_c$ (enthalpy of crystallization) can be obtained is reported in table 4.4. Percentage crystallinity ($X_c$) of the fibers can be calculated from the Equation (4.1). Results indicate that there is no significant change in the crystallinity of PP fiber by the addition of NZO.
Figure 4.12: Cooling behaviour of neat PP and PP/NZO composite fibers

Table 4.4: Effect of NZO on the crystallization behaviour of PP/NZO fibers

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Tc(°C)</th>
<th>Tcp(°C)</th>
<th>Tc-Tcp</th>
<th>ΔHc (J/g)</th>
<th>Xc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP</td>
<td>121.43</td>
<td>116.68</td>
<td>4.75</td>
<td>96.5</td>
<td>58.48</td>
</tr>
<tr>
<td>PP+0.5%NZO</td>
<td>121.32</td>
<td>116.12</td>
<td>5.2</td>
<td>94.37</td>
<td>57.48</td>
</tr>
<tr>
<td>PP+1.5%NZO</td>
<td>120.45</td>
<td>114.83</td>
<td>5.62</td>
<td>92.47</td>
<td>56.89</td>
</tr>
<tr>
<td>PP+3%NZO</td>
<td>120.12</td>
<td>114.67</td>
<td>5.45</td>
<td>93.67</td>
<td>58.52</td>
</tr>
</tbody>
</table>

Melting behaviour of fibers is shown in figure 4.13 and values are tabulated in table 4.5. From the DSC curves, Tm (designed here as the temperature at the crossing point of the tangents of the baseline and the low temperature side of the curves), Tmp (the peak temperature of the curve), and ΔHm (heat of fusion) can be obtained. The maximum rate of melting (Tmp) take place at 166.6°C for PP fiber and its Tm is 151.5°C. The Tm value of PP fiber with 3 wt% NZO is increased by about 2.1°C compared with neat PP
fiber. In Figure 4.13, it can be seen that there is a small peak at lower melting temperature of PP fiber and 0.5% NZO filled PP fibers and a peak at higher melting temperature. However, PP fiber at high concentration of NZO shows only single peak at high melting temperature. The first peak, with lower melting temperature, indicates the presence of a small amount of β-phase, whereas the second peak indicates the melting of α-phase.

![Figure 4.13: Melting behaviour of PP and PP/NZO composite fibers](image)

Table 4.5: Effect of ZnO on the melting behaviour of PP/NZO fibers

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Tm (°C)</th>
<th>Tmp (°C)</th>
<th>ΔHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP</td>
<td>151.53</td>
<td>166.66</td>
<td>89.5</td>
</tr>
<tr>
<td>PP+0.5%NZO</td>
<td>151.57</td>
<td>164.09</td>
<td>88.91</td>
</tr>
<tr>
<td>PP+1.5%NZO</td>
<td>153.02</td>
<td>164.54</td>
<td>72.17</td>
</tr>
<tr>
<td>PP+3%NZO</td>
<td>153.65</td>
<td>164.28</td>
<td>70.11</td>
</tr>
</tbody>
</table>
4.3.5 X-ray diffraction pattern of fibers

X-ray patterns of neat PP fibers and ZnO filled PP fibers are shown in Figure 4.14. Generally, iPP is a multicrystalline polymer and has five crystalline forms such as $\alpha$, $\beta$, $\gamma$, $\delta$ and pseudohexagonal. The XRD study (Figure 4.14) shows ZnO do not affect the crystalline form of PP fibers. Same crystalline form is observed for both PP and composite fibers. The peaks observed corresponds to (110), (040) and (130) and (041) planes of PP, indicate the $\alpha$–form of iPP.

![Figure 4.14: X-ray diffraction pattern of PP and PP/NZO composite fibers](image)

4.3.6 Morphology of the fibers

SEM images of neat PP and PP/ZnO composite fibers are shown in figure 4.15. Smooth fiber surface is observed in the SEM of PP/NZO composites fiber compared to neat PP fiber and CZO filled PP fiber. The SEM
of cross section of the fibers is given in figure 4.16. Significant difference is observed in the SEM of cross section of PP fibers, CZO filled fiber and NZO filled fiber. This morphological difference may be due to the difference in dispersion state and orientation of filler in PP fiber. NZO filled PP fiber shows good dispersion of filler. This also evident from improvement in mechanical properties compared to neat PP fiber.

Figure 4.15: Scanning electron micrographs of (a) neat PP (b) PP + 3wt% NZO (c) PP + 3wt% CZO fibers
4.3.7 Antibacterial properties of fibers

ZnO shows excellent antibacterial properties and this is evaluated in chapter 2. The resistance of PP textiles to bacterial attack make it possible to use in medical field and defense clothings. Figure 4.17 shows the morphology of the fibers after putting them in bacterial medium for ten days in Bacillus aereus. Fiber surface is more smooth compared to morphology of fibers before bacterial attack (figure 4.15). Figure 4.18 shows the morphology of the fibers after putting them in bacterial medium for ten days in E-coli. Fiber morphology is not significantly changed by the attack of E-coli.
4.4 Conclusion

Melt spinning could be used for the preparation of neat PP fiber and PP/\(\text{ZnO}\) composite fiber. Mechanical properties of the fiber increased by the addition of \(\text{ZnO}\). Significant improvement is shown by \(\text{NZO}\) filled PP fibers when compared to \(\text{CZO}\) filled PP fibers. Thermal stability of the PP fiber is increased significantly in presence of \(\text{NZO}\). \(\text{NZO}\) has no significant effect on
the crystallinity of PP fiber. X-ray diffraction studies indicate similar crystal form of PP fiber and composite fibers. Morphology of the cross section of the neat fiber is different from the morphology of the CZO filled, NZO filled PP fiber indicate difference in dispersion and molecular orientation of filler in the fibers. PP fiber and NZO filled fiber are not attacked by bacteria.

References


Chapter 4


