Anti-bacterial High density Polyethylene/Nano Titanium Dioxide Composite Synthesis and Characterization

Ansam A. Hashim*, Watheq K. Salih*

Abstract— High density Polyethylene (HDPE)/Titanium dioxide (TiO2) nano-composite was prepared by melt compounding with a twin screw extruder to detect the anti-bacterial efficiency (E.coli & S.aureus types) and the mechanical properties (tensile stress & E-modulus) of this composite. Different weight fractions of Titanium dioxide (2%, 4%, 6% wt) were used. The activity of TiO2/HDPE composite against bacteria types was investigated using disc diffusion method. The results showed that highest tensile and E-modulus values (33.35, 266 MPa) were recorded for 4%wt sample and it has the highest activity against the bacteria. Also the results showed that TiO2/HDPE composite is more effective against E.coli bacteria than against S.aureus type. Microscopic images of the prepared samples assured that 4% wt. sample is characterized by a high degree of homogeneity which contributed in this activity and in improving mechanical properties.

Index Terms—anti-bacterial composite, polyethylene, nano TiO2, E-modulus, tensile strength, polymer, Photovoltaics effect

1 INTRODUCTION

In recent years, antibacterial polymers acquired extra importance in the different medical and industrial fields and in various applications such as biomedical products, packing materials, and filters of air-conditioning systems, water reservoirs and so forth.

Antimicrobial polymers are the up and coming new class of disinfectants, which can be used even as an alternative to antibiotics in some cases. Interestingly, antimicrobial polymers can be tethered to surfaces without losing their biological activity, which enables the design of surfaces that kill microbes without releasing biocides [1].

Antimicrobial polymers have been known since 1965, when Cornell and Dunraruma described polymers and copolymers prepared from 2-methacryloyloxytroponones that kill bacteria [2]. In the 1970s several groups synthesized various polymeric structures that showed antimicrobial action, e.g., Vogl et al., who polymerized salicylic acid [3], or Panarin et al. who synthesized polymers with quarternary ammonium groups [4]. A large number of such macromolecules are known to date. Their function is not always understood. Nevertheless, the number of FDA-approved disinfecting polymers has significantly increased in the past decade, which indicates the need for alternatives to antibiotics and antibiotics and environmentally critical disinfectants. Recently, several reviews have summarized the state of the art [5–8].

The development in nanotechnology opened new horizons to use these materials in anti-bacterial polymers. The vital properties of nano material are their activity in killing bacteria, fungi and microbes with different mechanisms depend on nano material type.

Nanoparticles (their size between 0.2-100 nm) seem to be a very good option for antimicrobial additives, mostly thanks to their size, which is similar to the size of the cells and particles and can pass through the membrane easily. The main mechanism of toxicity of nanoparticles is thought to be via oxidative stress that damage lipids, carbohydrates, proteins, and DNA. Lipid peroxidation is considered the most dangerous as it leads to alterations in cell membrane properties which in turn disrupt vital cellular functions [9].

So, there are many nano metals and oxides were used as antibacterial materials such as a sliver, gold, Magnesium oxide, Copper oxide, Aluminum, Titanium dioxide, Zinc oxide. Every substance has a specific technique to kill bacteria depending on its physical and chemical properties.

1.1 photocatalytic mechanism of nano TiO2:

Owing to the photocatalytic activity of TiO2, it is an effective catalyst to generate a strong oxidizing agent- hydroxyl radical which is much stronger than chlorine, ozone and peroxide oxidizing agents. In general, donor molecules such as H2O are absorbed and react with a hole in the valence band and acceptors such as O2 are also absorbed and react with the electron in the conduction band. The mechanism of generation of hydroxyl radical is known below [10]:

1. Absorption of photons (hν=3.2 V) by titanium dioxide

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2^*(e^- + h^+) \quad (1)
\]

2. Neutralization of OH- groups by photo holes produces OH

\[
\text{TiO}_2h^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad (2)
\]

3. Oxygen insorption(oxygen reduction where oxygen's oxidation state changes from 0 to 1/2)

\[
\text{TiO}_2e^- + \text{O}_2 \rightarrow \text{O}_2^- \quad (3)
\]

4. Neutralization of O2- by photon

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \quad (4)
\]
5. Transient hydrogen peroxide formation and dismutation of Oxygen

\[
2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (5)
\]

6. Decomposition of H\textsubscript{2}O\textsubscript{2} and reduction of oxygen

\[
\text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{HO}^- + \text{OH}^- \quad (6)
\]

The present work aims to investigate the possibility of using nano Titanium dioxide as anti-bacterial filler of high density polyethylene (HDPE). Different loadings of nano titanium dioxide are used. The antibacterial and tensile tests are done to assess the performance of this composite.

2. EXPERIMENTAL WORK

2.1 Materials and Equipments

2.1.1 Titanium dioxide (TiO\textsubscript{2}): the properties and Xrd diffraction pattern of this material are listed in Table 1 and Figure 1:

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
<th>Unit</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium Dioxide phase</td>
<td>Anatase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle size</td>
<td>&lt; 50 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>99.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>White powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Hongwu nanometer company / China</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 1 X-ray diffraction pattern of Titanium dioxide](image)

The X-ray test was done via (XRD-6000 - Shimadzu - Japan, Cu target – 1.54060 A\textsuperscript{0}) to identify the type and phase of nano Titanium dioxide. The obtained results are identical with the ICDD standard card (PDF #: 21-1272) which are assured the phase is anatase and the system is tetragonal.

2.1.2 High density polyethylene polymer (HDPE): the properties of HDPE are listed in Table 2:

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt flow rate</td>
<td>8</td>
<td>g/10min</td>
</tr>
<tr>
<td>Density</td>
<td>963</td>
<td>Kg/m\textsuperscript{3}</td>
</tr>
<tr>
<td>Tensile strength @ yield</td>
<td>26</td>
<td>MPa</td>
</tr>
<tr>
<td>Hardness (shore D)</td>
<td>62</td>
<td></td>
</tr>
</tbody>
</table>

![Table 2 Properties of HDPE polymer](image)

Figure 2 Extruder machine

**2.1.3 Extruder machine:**
To mold the nano Titanium dioxide/HDPE composite, a twin screw extruder was used. The extruder specifications are listed in Table 3 and Figure 2:

<table>
<thead>
<tr>
<th>Model</th>
<th>Origin</th>
<th>L/D</th>
<th>Motor model</th>
<th>Motor speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD11-100-0254</td>
<td>China</td>
<td>20/25</td>
<td>SJSZZO / 4</td>
<td>0 - 40 rpm</td>
</tr>
</tbody>
</table>

![Table 3 Extruder machine specifications](image)

**2.2 Sample Preparation Procedure:**
The samples were synthesized according to the following procedure:
1. Weight the specific ratios of Titanium dioxide and HDPE as described in the Table 4.
2. High density Polyethylene-Titanium dioxide nanocomposites were prepared by a melt compounding process, using a twin screw extruder which its specifications are mentioned in Table 3.
3. Selected amount of nano powder was inserted in the compounder and melt-mixed for a temperature of 190 °C and
motor speed of 40 rpm.

4. The compounded materials were then extracted and left to cool down to ambient temperature. Rectangular continuous sheet (10 cm width and thickness 0.5 mm) as it is shown in Figure 3

Table 4: Weight fractions of TiO₂ & HDPE

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Materials</th>
<th>HDPE (g)</th>
<th>TiO₂ (g)</th>
<th>TiO₂ % wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>[PURE]</td>
<td>200</td>
<td>-</td>
<td>0%</td>
</tr>
<tr>
<td>Sample 2</td>
<td>[2% wt]</td>
<td>196</td>
<td>4</td>
<td>2%</td>
</tr>
<tr>
<td>Sample 3</td>
<td>[4% wt]</td>
<td>192</td>
<td>8</td>
<td>4%</td>
</tr>
<tr>
<td>Sample 4</td>
<td>[6% wt]</td>
<td>188</td>
<td>12</td>
<td>6%</td>
</tr>
</tbody>
</table>

3. RESULTS & DISCUSSION :

3.1 Mechanical tests:

3.1.1 Tensile test :

This test is a very important test to assess the mechanical properties of samples with / without titanium dioxide additions. All samples were tested via Tensile Testing Machine (Tinusolsen H50KT/England ). The results were summarized in following Table 5:

Table 5: Mechanical tests results

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Tensile force (MPa)</th>
<th>% tensile force improvement</th>
<th>% max. of elongation at Strain</th>
<th>Elastic modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>20.04</td>
<td>-</td>
<td>34</td>
<td>58.9</td>
</tr>
<tr>
<td>Sample 2</td>
<td>29.79</td>
<td>48.65</td>
<td>32.8</td>
<td>78.5</td>
</tr>
<tr>
<td>Sample 3</td>
<td>33.35</td>
<td>66.42</td>
<td>12.54</td>
<td>266</td>
</tr>
<tr>
<td>Sample 4</td>
<td>30.4</td>
<td>51.7</td>
<td>14.5</td>
<td>209.655</td>
</tr>
</tbody>
</table>

Depending on the results of all samples. The results showed that a sample which contains 4% of nano TiO₂ has the highest values of tensile force and E-modulus (33.35 , 266 MPa). The improvement percentage of tensile is about 66.42% compared with pure sample 1 (without addition). The E-modulus is calculated via using the following equation:

\[ E\text{-modulus} = \frac{\text{tensile stress}}{\text{strain}} \tag{7} \]

\[ \text{Strain} = (\Delta L/L) \times 100\% \tag{8} \]

Where:

\( \Delta L \) = change of sample length due the applied force
\( L \) = original length before test

In order to explain the mechanical properties enhancement observed in nano filled samples, many authors in literature hypothesized the presence of an interphase layer around the nanoparticles, promoting the stress transfer at the interface. It is often reported that the particles can restrict the mobility and deformation of the matrix by introducing a mechanical restraint, caused by an effective attraction potential between segments of the chain and the repulsive potential that the polymer is subjected to when it is close to solid particles. The extent of the particle restriction is a function of the properties of the filler and the matrix [11, 12].

So , the results of tests showed increasing improvement of tensile and elastic modulus which is reached, its peak at sample 3 (4% wt titanium dioxide ) whereas the tensile and E-modulus decreased when addition ratio increased (6% wt TiO₂) . The reduction in tensile strength was due to the reduction in particle – matrix interfaces and the increase of particle-particle interfaces with increasing particle content thus changing the failure mechanism.[13]

3.2 Antibacterial test :

Disc diffusion method was used to assess the activity of prepared samples against bacteria(E. Coli) and (S.aureus ) where the samples were prepared as small pieces (disc shape) and it placed in petri dishes contain the bacteria for (24, 48 , 72hr) and then surface around the disc was measured uninfecte
The results were recorded as in following:

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Zone of inhibition (mm)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bacteria E.coli</td>
<td>Bacteria S.aureus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 hr</td>
<td>48 hr</td>
<td>72 hr</td>
<td>24 hr</td>
<td>48 hr</td>
<td>72 hr</td>
</tr>
<tr>
<td>Sample 1 [pure]</td>
<td>Nill</td>
<td>Nill</td>
<td>Nill</td>
<td>NILL</td>
<td>NILL</td>
<td>NILL</td>
</tr>
<tr>
<td>Sample 2 [2% wt]</td>
<td>7</td>
<td>10</td>
<td>12</td>
<td>7</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Sample 3 [4% wt]</td>
<td>20</td>
<td>22</td>
<td>22</td>
<td>17</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Sample 4 [6% wt]</td>
<td>11</td>
<td>16</td>
<td>16</td>
<td>14</td>
<td>17</td>
<td>17</td>
</tr>
</tbody>
</table>

Depending on the results of antibacterial test of all samples, the highest activity was recorded for sample 3 whereas the sample 1 which was contained no TiO2 addition did not record any distinguished area around the sample.

The reason of activity of nano titanium dioxide samples can be attributed to a photocatalytic effect of titanium dioxide which is its mechanisms clarified previously, photo-reduction, photo-oxidation and absorption. The reaction of TiO₂ particles with water produces hydroxyl radicals and in the presence of oxygen leading to super oxidation radicals formation. These radicals attack bacteria, viruses, microbes and germs in terms of inhibiting DNA clonal processing and destroying coenzymes in self generation and enzymes in the respiratory system. As a result, the radical stops the reproduction of bacteria and molds, thereby inhibiting bacteria growth or preventing virus multiplication [14]. The effect of TiO₂/HDPE composite is more effective against E.coli bacteria type than against S.aureus type.

3.3 Microscopic test:

All surfaces of samples are examined using a light microscope (ML-7000/ MEIJI TECHNO /JAPAN) to investigate the topography of samples surfaces and the homogeneity of addition of sample which has highest activity and the highest mechanical properties. The images of samples are shown in the Figure 4 below:

The figures showed the surfaces of the samples with different
weight fractions of nanoTiO$_2$ (2%, 4% and 6% wt.). The surface of sample 3 (image B) shows high homogeneity of Titanium dioxide in polyethylene matrix comparing with other samples (images A & C). The homogeneity is the key word which explains the improvements in anti-bacterial and mechanical properties.

4. CONCLUSIONS

The results were obtained from the experimental work showed the anti-bacteria effectiveness of using anatase titanium dioxide as a filler of polyethylene high density [HDPE]. The mechanical properties of nano TiO$_2$/HDPE composite improved when the nano TiO$_2$ loading increased till 4% wt of TiO$_2$ which was the best antibacterial activity and the highest tensile stress with highest e-modulus while this activity and properties decreased when a higher percentage was used (6% wt.) . The anti-bacterial activity and mechanical properties decreased because of agglomeration of nano particles. The results showed a successful possibility of using this kind of nano anatase titanium dioxide as anti-bacteria filler for high density polyethylene polymer matrix.

REFERENCES

[12] A D. Drozdov , A . Dorfmann, "The stress-strain re-