ISSN 2229-5518

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 (TiO_2) 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 TiO_2/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 TiO_2/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-methacryloxytroponones 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.

* Directorate of materials research - Ministry of Science & Technology – Baghdad, Iraq
Corresponding Author: Email: alwathiq316@yahoo.com

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 TiO_2:

Owing to the photocatalytic activity of TiO_2, 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 H_2O are absorbed and react with a hole in the valence band and acceptors such as O_2 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 (hv =3.2 V) by titanium dioxide

$$TiO_2 \longrightarrow TiO_2\,(e\text{-}cb + h + vb) \qquad \text{--- (1)}$$

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

$$TiO_2h + vb + H_2O \longrightarrow H^+ + OH^{\cdot} \qquad \text{----- (2)}$$

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

$$TiO_2e\text{-}cb + O_2 \longrightarrow O_2^{-\cdot} \qquad \text{--------- (3)}$$

4. Neutralization of O_2- by photon

$$O_2^{-\cdot} + H^+ \longrightarrow H_2O^{\cdot} \qquad \text{-------- (4)}$$

ISSN 2229-5518

5. Transient hydrogen peroxide formation and dismutationof Oxygen

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad \text{----- (5)}$$

6. Decomposition of H_2O_2 and reduction of oxygen

$$H_2O_2 + e^- \longrightarrow HO. + OH^- \text{ ------ (6)}$$

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_2): the properties and Xrd diffraction pattern of this material are listed in Table 1 and Figure 1 :

Table 1: Nano Titanium dioxide specifications

Titanium Dioxide phase	Anatase
Particle size	< 50 nm
Purity	99.8%
Color	White powder
Manufacturer	Hongwu nanometer company /China

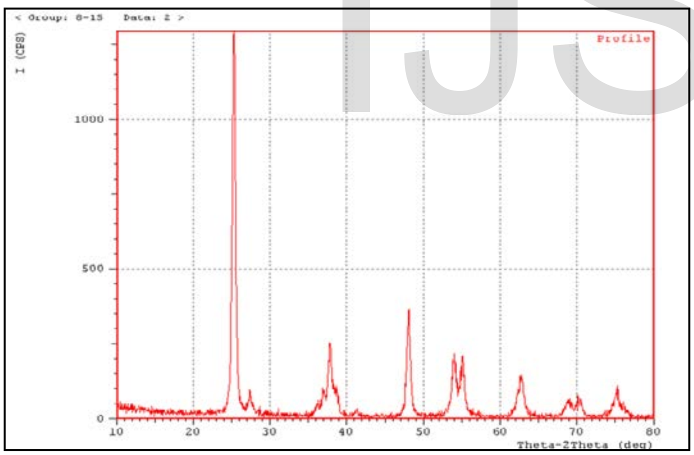

Figure 1 X-ray diffraction pattern of Titanium dioxide

The X-ray test was done via (XRD-6000 – Shimadztu - Japan , Cu target – 1.54060 A°) 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 2 Properties of HDPE polymer

Properties	Unit	Value	Test Method
Melt flow rate	g/10min	8	ASTM D1238
Density	Kg/m³	963	ASTM D1505
]Tensile strength @ yield	MPa	26	ASTM D638
Hardness (shore D)		62	ASTM D2240
Manufacturer	Sabic company / Saudia Arabia		

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:

Model	Origin	L/D	Motor model	Motor speed
RD11- 100 – 0254	China	20/25	SJSZZO / 4	0 - 40 rpm

Figure 2: Extruder machine

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

Sample No.	Materials		
	HDPE (g)	TiO_2 (g)	TiO_2 % wt.
Sample 1 [PURE]	200	-	0%
Sample 2 [2% wt]	196	4	2%
Sample 3 [4% wt]	192	8	4%
Sample 4 [6% wt]	188	12	6%

Figure 3: HDPE/ TiO_2 composite sheet

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

Sample No.	Tensile force (MPa]	% tensile force improvement	% max. of elongation at Strain	Elastic modulus [MPa]
Sample 1 [PURE]	20.04	-	34	58.9
Sample 2 [2% wt]	29.79	48.65	32.8	78.5
Sample 3 [4% wt]	33.35	66.42	12.54	266
Sample 4 [6% wt]	30.4	51.7	14.5	209.655

Depending on the results of all samples .The results showed that a sample which contains 4% of nano TiO_2 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

$$\text{E-modulus} = \frac{\text{tensile stress}}{\text{strain}} \quad \text{------------ (7)}$$

$$\text{Strain} = (\Delta L/L) * 100\ \% \quad \text{------------- (8)}$$

Where:
ΔL = 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 uninfected

ISSN 2229-5518

surface using rule. The results were recorded as in following:

Table 6: Anti-bacterial test results

Sample no.	Zone of inhibition (mm)					
	Bacteria E.coli			Bacteria S.aureus		
	24 hr	**48 Hr**	**72 hr**	**24 hr**	**48 Hr**	**72 hr**
Sample 1 [pure]	Nill	Nill	Nill	NILL	NILL	NILL
Sample 2 [2% wt]	7	10	12	7	11	11
Sample 3 [4% wt]	20	22	22	17	20	20
Sample 4 [6% wt]	11	16	16	14	17	17

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 TiO_2 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 TiO_2/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:

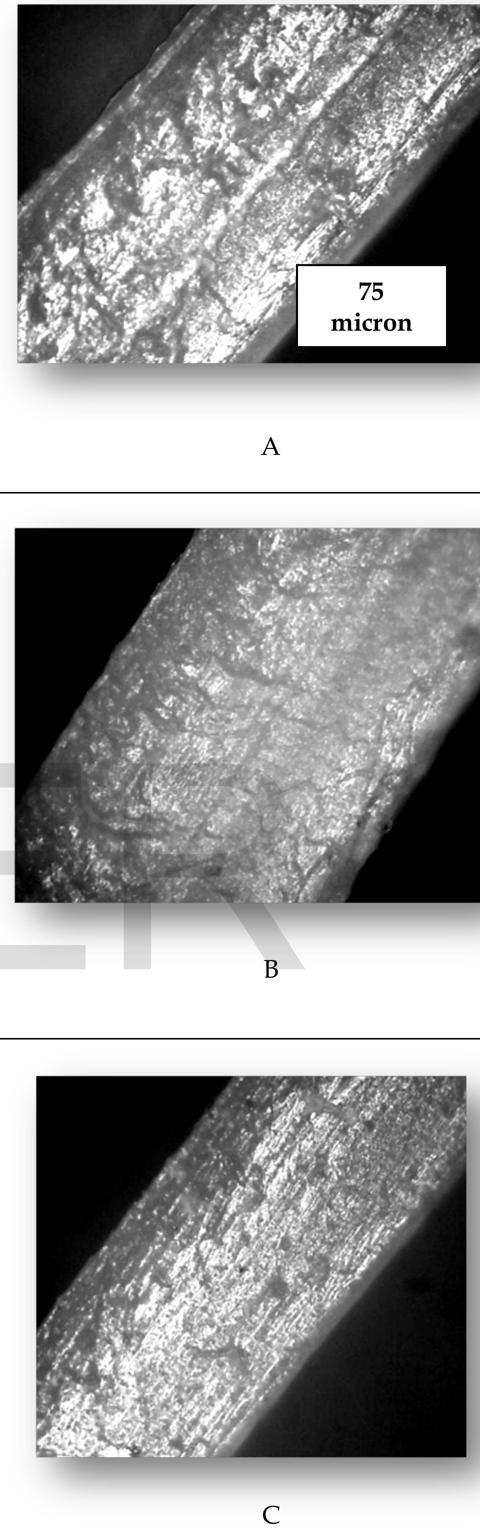

Figure 3: Microscopic images of prepared samples
Sample 2 (A) - Sample 3 (B) – Sample 4 (C)

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 TiO2/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

[1] S Felix. and C. Joerg Tiller, "Antimicrobial Polymers in Solution and on Surfaces: Overview and Functional Principles" , Polymers 2012, 4, 46-71; doi: 10.3390/polym4010046

[2] R.J. Cornell,; L.G. Donaruma, "2-Methacryloxytroponones. Intermediates for Synthesis of Biologically Active ", Polymers. J. Med. Chem. 1965, 8, 388-390.

[3] O. Vogl and D., "Tirrell, Functional Polymers with Biologically-Active Groups. ", J. Macromol. Sci.-Chem. 1979, A13, 415-439.

[4] E.F. Panarin, M. Solovski., O. Ekzemply, "Synthesis and Antimicrobial Properties of Polymers Containing Quaternary Ammonium Groups",. Khim.-Farm. Zh. 1971, 5, 24-28.

[5] G.N. Tew, R.W. Scott; M.L. Klein; W.F. De Grado ,"De Novo Design of Antimicrobial Polymers, Foldamers, and Small Molecules: From Discovery to Practical Applications". Account. Chem. Res. 2010, 43, 30-39.

[6] E.-R. Kenawy, S.D Worley.;. R. Broughton, "The Chemistry and Applications of Antimicrobial Polymers: A State-of-the-Art Review", Biomacromolecules 2007, 8, 1359-1384.

[7] L. Timofeev and N. Kleshcheva, "Antimicrobial Polymers: Mechanism of Action, Factors of Activity, and Applications", Appl. Microbiol. Biotechnol. 2011, 89, 475-492.

[8] I . Banerjee ,Pangule, R.C.; Kane, R.S. ,"Antifouling Coatings: Recent Developments in the Design of Surfaces That Prevent Fouling by Proteins, Bacteria, and Marine Organisms", Adv. Mater. 2011, 23, 690-718.

[9] M. Heinlaan and A. Ivask, "Toxicity of nanosized and bulk ZnO, CuO and TiO2 to bacteria Vibrio", Chemosphere, 2008, Vol. 71, pp. 1308–1316,.

[10] S. G. Velhal, S. D. Kulkarai and R.G. Jaybhaye," novel particles for water and waste water treatment" , Res. J. Chem. Environ. , June 2012,Vol. 16 (2)

[11] SY Fu , G. Xu, Y.W. Mai , "On the elastic modulus of hybrid. Particle/short fiber/polymer composites", Compos B , 2002, 33:291–299

[12] A D. Drozdov , A . Dorfmann, "The stress–strain response and ultimate strength of filled elastomers", Comput Mater Sci, 2001, 21:395–417

[13] N. A. Saad , N. J. Hadi, and I. M . Zahraa , "Investiagtion of rheological , thermal and mechanical behavior of micro and nano carbon black filled LDPE" ,JMES , 2014, VOL 1 issue 2

[14] J . Veronika, H. Libuše, and V. Jarmila ,"TiO2 and ZnO Nanoparticles in Photocatalytic and Hygienic Coatings", HindawiPublishing Corporation International Journal of Photoenergy Volume 2013, Article ID 795060, http://dx.doi.org/10.1155/2013/795060