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PREPARATION AND CHARACTERIZATION OF HIGH-DENSITY POLYETHYLENE WITH TiO_2 MODIFIED PEG 6000 FILLER AS A LANDFILL LINER MATERIAL

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ABSTRACT

High-density polyethylene is an engineering polymer that is used in bottom liners of landfills. However, to be used in the environment application, it needs to have good mechanical and thermal qualities. Incorporation of inorganic fillers such as titanium dioxide into a polymer aimed at enhancing several features such as mechanical strength, thermal stability, and resistance to surface wear. In this study, HDPE preparation was carried out by adding TiO_2 nanoparticles. TiO_2 nanoparticles were synthesized using the precursor $TiCL_4$ and then modified with the addition of PEG 6000. Furthermore, the resulting TiO_2 was used as a filler in thermoplastic HDPE. Characterization of high-density polyethylene with TiO_2 filler as a landfill liner material shows an increase in mechanical and thermal properties. The HDPE sample containing 8%wt filler had the highest tensile strength, measuring at 84.72 Mpa. In contrast, the use of 6wt% filler resulted in the lowest recorded tensile strength, measuring at 56.24 Mpa. The elastic modulus had its highest increase at 8 wt% TiO_2, reaching a value of 729.33 MPa. However, the addition of 6 wt% TiO_2 resulted in a notable decrease in elastic modulus, with a value of 522.79 MPa. Additionally, it was observed that the highest elongation at break was achieved with a 4% weight filler, resulting in a value of 49.37%. Similar to the reduction observed in the elastic modulus value, the elongation at break exhibited a substantial decrease of 39.22% upon the addition of 6wt% TiO_2. DSC scan curves for both the fabricated nanocomposite systems clearly show that they are affected by the nanofiller and its percentage fraction. There was an increase in Tm_1 in the composition of 8wt% TiO_2, while an increase in Tm_2 occurred in 2wt% TiO_2. Therefore, HDPE which is given TiO_2 filler has the potential to be used as landfill liner material.

Keywords: nanocomposite; mechanical properties; thermal stability; $TiCL_4$.

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1. INTRODUCTION

Polymer composite materials are utilized in many industrial and private sectors due to their advantages, including their lightweight nature, high-specific strength, and cost-effectiveness. To optimize the performance of polymer composites, the utilization of a suitable. nanofiller is imperative. Polymer composites, through the utilization of natural fibers and nanofillers, have a synergistic effect that enhances their characteristics and environmental compatibility, rendering them appropriate for a wide range of applications (Das *et al.,* 2021). High density polyethylene (HDPE) is an engineering polymer that is widely used in many industrial commodities, including landfill liners, power and telecom cable conduits, sewage and drainage pipe, and automotive parts(N. Bukit *et al*., 2018; Mendes *et al*., 2003; Nguyen *et al*., 2020). Covering systems of landfills involve partial or complete isolation of waste from the surrounding environment. engineers and researchers were mainly concerned with the final covers of landfills, and materials have been widely used, high density polyethylene (HDPE) geomembranes(Chen *et al*., 2011; Eith & Koerner, 1997; Ikpe *et al*., 2019; Muralikrishna & Manickam, 2017).

In order to be used in the environment application, it needs to have good mechanical and thermal qualities. Incorporation of inorganic fillers into a polymer matrix is a common practice aimed at enhancing several features such as mechanical strength, thermal stability, optical characteristics, magnetic behavior, electrical conductivity, and resistance to surface wear. Extensive research has been conducted on the utilization of high density polyethylene (HDPE) mixed with metallic nanoparticles due to its mutual advantages (Akhil *et al*., 2019; Frida, Bukit, *et al*., 2022; Frida, Rahmat, *et al*., 2022). The commercial manufacture of titanium dioxide (TiO_2) emerged in the early twentieth century, and since then, it has found extensive application in several domains such as gas sensing, white pigmentation, optical coatings, solar cells, and more(B. F. Bukit *et al*., 2022b; Sadu *et al.,* 2014; Wojciechowska *et al*., 2022; Zeng *et al*., 2019). The applications can be categorized as energy and environmental, with their efficacy primarily reliant on the inherent qualities of TiO_2.

Nanocomposites with a polymer matrix present promising avenues for the investigation of novel capabilities that surpass those exhibited by traditional materials. The incorporation of TiO_2 as a reinforcing agent in polymeric nanocomposites has proven to be an effective approach for substantially improving their mechanical properties (Ghazzy *et al*., 2023). The dimensions of the filler significantly influence the mechanical characteristics of the nanocomposite. One characteristic that distinguishes polymer nanocomposites is the enhanced interfacial area resulting from the reduced dimensions of the fillers, in contrast to conventional composites (Ginting & Bukit, 2015; Nurfajriani *et al.*, 2020; Zhang *et al.*, 2021). The presence of interfacial area results in a substantial proportion of interfacial polymer, which exhibits distinct properties compared to the bulk polymer, even at low concentrations of the nanofiller. In this study, TiO_2 nanoparticles were synthesized using the precursor $TiCL_4$ and then modified with the addition of PEG 6000. Furthermore, the resulting TiO_2 was used as filler in thermoplastic HDPE

2. MATERIAL AND METHOD

2.1 Material

Titanium tetrachloride ($TiCl_4$) from Sigma Aldric, ammonium hydroxide (NH_4OH) from Merck, PEG-6000, HDPE, ethanol absolute, distilled water.

2.2 Methods

2.2.1 Preparation of nanoparticle TiO_2

The sol-gel method was employed for the synthesis of TiO_2 nanoparticles. A solution containing 20 ml of $TiCl_4$, 100 ml of NH_4OH, and 100 ml of distilled water was prepared by employing a magnetic stirrer. $TiCl_4$ was dissolved in distilled water using a magnetic stirrer for 2 hours at 200 rpm. Subsequently, NH_4OH was gradually dripped into for 4 hours. The solution obtained was subjected to filtration and subsequent drying at a temperature of 60°C for 24 hours. This was followed by a calcination process carried out at a temperature of 900°C for 2 hours. The TiO_2 was further pulverized using a mortar and subsequently combined with PEG-6000. TiO_2, PEG-6000, and distilled water were measured in the ratios of 35 g, 7.3 g, and 100 ml, respectively then combined using a magnetic stirrer at 400 rpm for 2 hours. The solution undergoes filtration and subsequent mixing with ethanol, followed by a washing process with distilled water and a subsequent round of filtration. Following the completion of the filtration process, the TiO_2 substance was further subjected to a drying procedure at a temperature of 100°C for duration of 2 hours.

2.2.2 Preparation of nanocomposite HDPE with TiO_2

HDPE thermoplastic with filler is prepared using a HAAKE type Rheomixer. The composite was mixed at 60 rpm and 150°C for 10 minutes. Next, the mixture that has been cut into small pieces is then put into an injection molding tool to make ASTM type V dumbbells at a temperature of 180°C and a pressure of 750 bar.

RESULT AND DISCCUSIONS

3.1 Fourier Transform Infrared (FTIR)

The qualitative and quantitative examination of the quantity of side chain branching in HDPE is a notable characterisation that can be effectively conducted using FTIR. The FTIR spectrum can demonstrate how HDPE and filler might react with each other. FTIR HDPE with Filler presented in Figure-1. The transmission band for HDPE samples is shown to be significantly associated with the rocking and scissoring vibrations of CH_2 groups in the methylene groups across all nanocomposite samples within the absorption band (Aggarwal, 2008). The presence of filler in HDPE thermoplastic samples leads to the occurrence of overlapping absorption bands between the matrix and filler components, resulting in similarities in the absorption spectra (B. F. Bukit *et al.*, 2022b, 2022a).

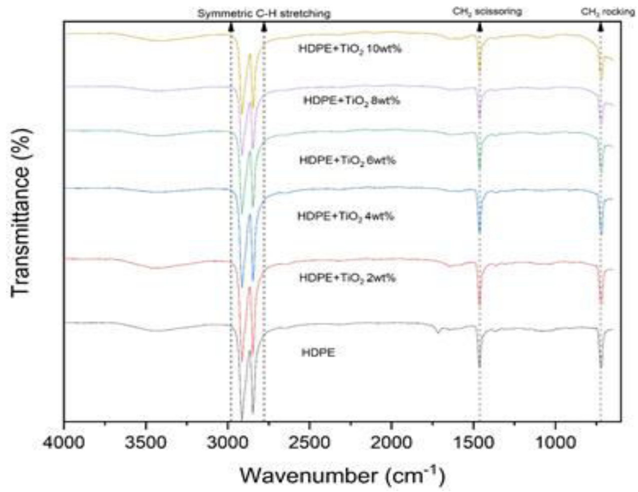

Figure-1. FTIR graph of HDPE-TiO_2 nanocomposite.

3.2 X-Ray Diffraction (XRD) Characterization

The XRD patterns of HDPE incorporated with TiO_2 are illustrated in Figure-02. In terms of XRD analysis, HDPE typically exhibits a semi-crystalline nature.

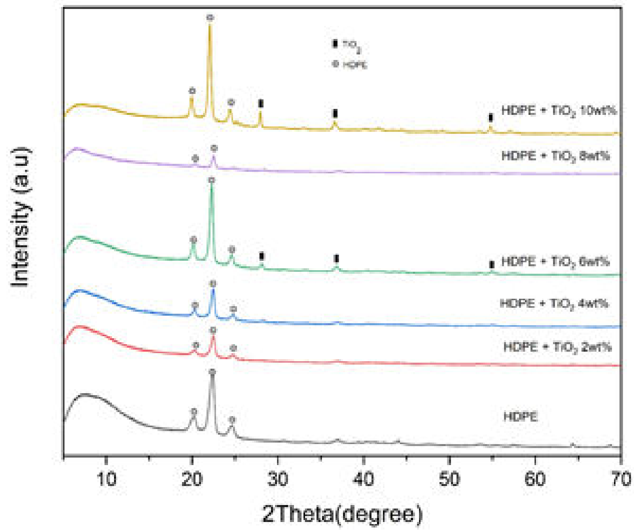

Figure-2. Diffraction peaks of HDPE-TiO_2 Nanocomposite.

The diffraction peaks observed for HDPE are located at 2θ values of 21.4° and 23.7°, which align with the conventional diffraction peak positions. The detection of TiO_2 in the composites was seen at concentrations of 6 wt% and 8 wt%. Based on the existing research, it might be observed that the XRD patterns of TiO_2 exhibit distinct peaks at angles of 25.4°, 37.9°, and 48.1° (Mourad *et al*., 2017; Wang & Zhang, 2014b). From Figure-2 implies that TiO_2 is evenly distributed in the polymer matrix.

3.3 Scanning Electron Microscope (SEM)

The distribution of inorganic fillers inside a polymer matrix is a crucial characteristic. When considering a matrix containing an aggregative particle, it is seen that the stress distribution becomes localized around the aggregation. Consequently, the presence of a crack in this region might lead to material degradation (Bustamante-Torres *et al*., 2021; Wang & Zhang, 2014a).

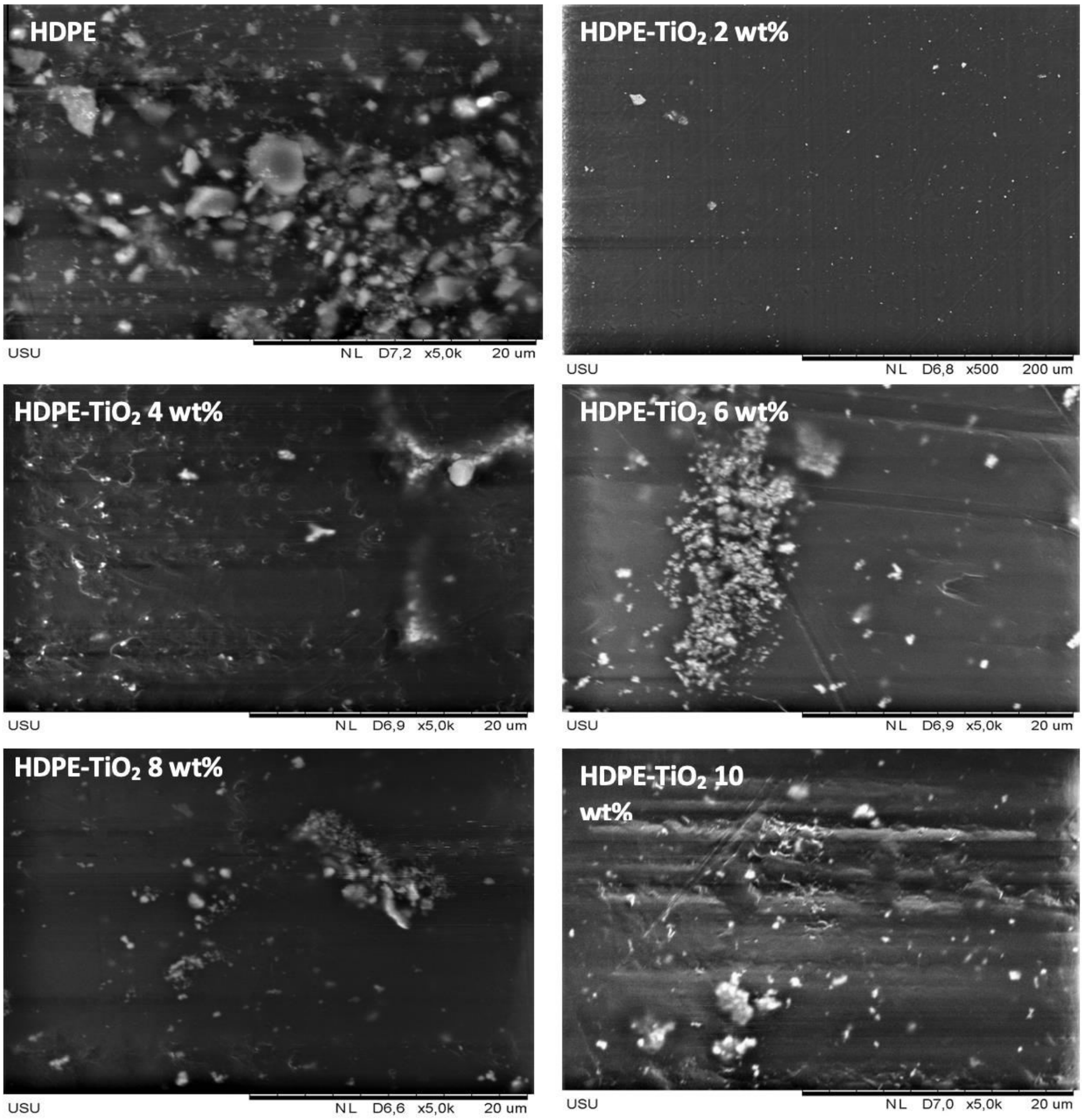

Figure-3. Morphology of HDPE-TiO_2 nanocomposite.

Based on the SEM images in Figure-3, the incorporation of TiO_2 in HDPE leads to a decrease in ductility in specimens as the filler percentages increase. According to the observations made in Figures-3, it can be inferred that an increase in filler percentage leads to a decrease in ductility, as seen by the diminishing presence of fracture neck strands in the failing fracture area. The limited mobility of the polymer chain can be attributed to the presence of fillers that occupy vacant spaces within the chain. The statement above is supported by the correlation between the results of tensile strength and flexural strength, as these mechanical properties are influenced by the chain mobility in the final specimens (N. Bukit *et al*., 2023; Vidakis *et al*., 2022).

3.4 Mechanical Properties

The utilization of titanium dioxide as a filler in various polymeric matrices is attributed to its ability to enhance physical and mechanical qualities. Numerous investigations have demonstrated enhancements in the mechanical strength and modulus of polymeric nanocomposites filled with TiO_2 in comparison to the original matrix material. The internal structure of TiO_2 nanocomposites plays a crucial role in determining their mechanical properties.

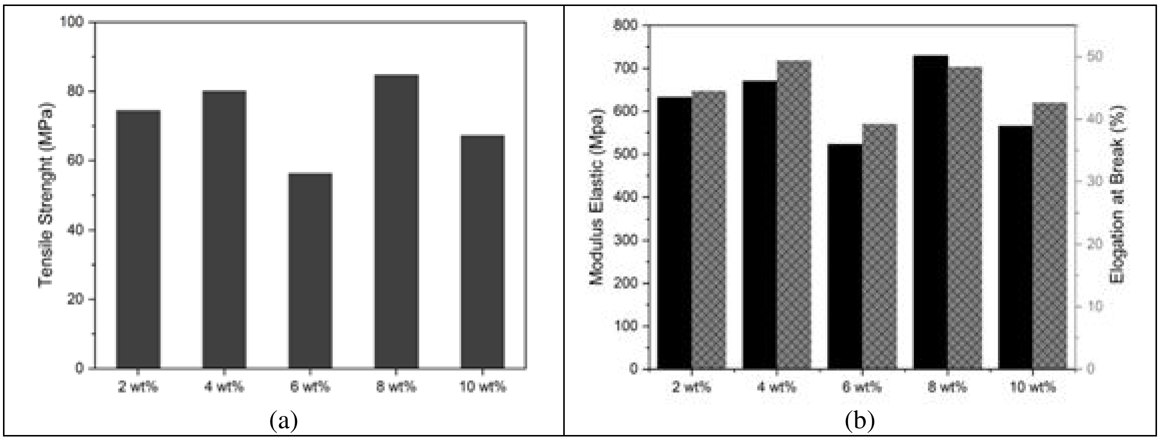

Figure-4. a. Tensile Strength, b. Modulus elastic and Elongation at Break of HDPE-TiO_2 Nanocomposite.

According to the data presented in Figure-4, it can be observed that the HDPE sample containing 8%wt filler had the highest tensile strength, measuring at 84.72 Mpa. In contrast, the use of 6wt% filler resulted in the lowest recorded tensile strength, measuring at 56.24 Mpa. The elastic modulus had its highest increase at 8 wt% TiO_2, reaching a value of 729.33 MPa. However, the addition of 6 wt% TiO_2 resulted in a notable decrease in elastic modulus, with a value of 522.79 MPa. Additionally, it was observed that the highest elongation at break was achieved with a 4% weight filler, resulting in a value of 49.37%. Similar to the reduction observed in the elastic modulus value, the elongation at break exhibited a substantial decrease of 39.22% upon the addition of 6wt% TiO_2. Previous studies have demonstrated HDPE nanocomposites containing 5% TiO_2 by the employment of injection molding. This procedure involved modifying of many processing parameters, such as temperature, pressure, injection velocity, and injection time. The results obtained showed that the mechanical and thermal properties of HDPE-TiO_2 nanocomposites were affected by the processing conditions. The results of mechanical testing demonstrated that the tensile strength exhibited a range of values between 22.5 and 26.3 MPa. Additionally, it was observed that the Young's modulus experienced an increase of 8.6% with the elevation of the molding temperature(Mourad *et al*., 2017).

Polymeric matrix nanocomposites incorporating TiO_2 nanoparticles in order to examine the impact of many variables, such as shape, size, percentage loading, and surface modification. Additionally, the inadequate compatibility between hydrophilic TiO_2 nanoparticles and a hydrophobic polymer matrix might result in the formation of particle aggregates and/or agglomerates. The formation of aggregates inside the nanocomposites results in the emergence of defect sites, which consequently impacts the e mechanical characteristics. It is advisable to achieve a more homogeneous distribution of nanoparticles by employing one-dimensional nanoparticles (Cazan *et al.*, 2021; DeArmitt & Rothon, 2002; Hashimoto *et al*., 2007).

3.5 DSC (Differential Scanning Calorimetry)

Differential scanning calorimetry (DSC) was used to determine the shift in the melting temperature upon addition of fillers. The melting temperature of the HDPE with filler addition presented in Figure-5.

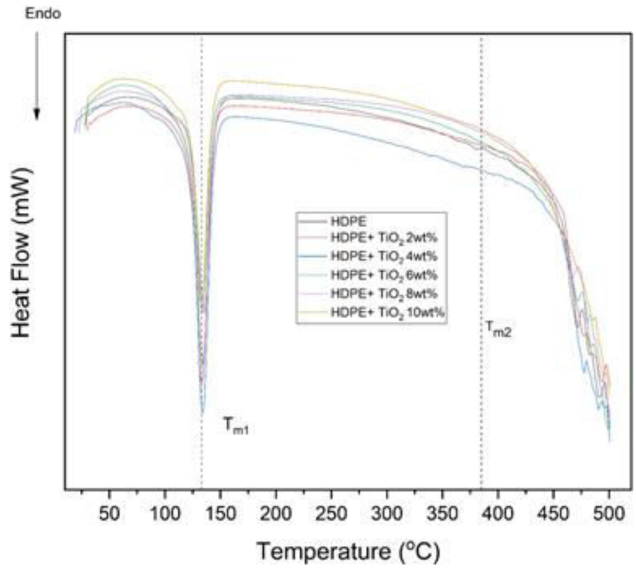

Figure-5. DSC Graph of HDPE-TiO_2 nanocomposite.

Table-1. DSC analysis results.

Sample	Peak 1(°C)	Peak 2 (°C)	On set 1(°C)	On set 2 (°C)	Endset 1(°C)	Endset 2 (°C)	Heat 1 (mJ)	Heat 2 (mJ)
HDPE	133.66	385.50	124.23	668.14	143.49	525.20	-931.51	1.46
HDPE + TiO_2 2wt%	133.22	493.52	123.91	454.59	142.81	499.72	-935.65	977.93
HDPE + TiO_2 4wt%	133.67	381.47	124.33	403.94	144.04	514.52	-1.07	1.43
HDPE + TiO_2 6wt%	133.64	380.59	124.72	262.06	142.68	494.11	-618.25	1.53
HDPE + TiO_2 8wt%	135.09	379.76	124.34	638.48	144.98	486.02	-663.21	1.45
HDPE+TiO_2 10wt%	133.48	380.94	124.87	439.14	142.25	525.61	-705.04	1.27

According to the findings in Table-1, DSC scans show 2 endothermic peaks for melting. DSC scan curves for both the fabricated nanocomposite systems clearly show that they are affected by the nanofiller and its percentage fraction. There was an increase in Tm_1 in the composition of 8wt% TiO_2, while an increase in Tm_2 occurred in 2wt% TiO_2. Melting point characteristics exhibit considerable variability, contingent upon factors such as filler concentration and distribution (Dorigato *et al.*, 2012; Savini & Oréfice, 2020).

CONCLUSIONS

The HDPE sample containing 8%wt filler had the highest tensile strength, measuring 84.72 Mpa. In contrast, the use of 6wt% filler resulted in the lowest recorded tensile strength, measuring 56.24 Mpa. The elastic modulus had its highest increase at 8 wt% TiO_2, reaching a value of 729.33 MPa. However, the addition of 6 wt% TiO_2 resulted in a notable decrease in elastic modulus, with a value of 522.79 MPa. Additionally, it was observed that the highest elongation at break was achieved with a 4% weight filler, resulting in a value of 49.37%. Similar to the reduction observed in the elastic modulus value, the elongation at break exhibited a substantial decrease of 39.22% upon the addition of 6wt% TiO_2. DSC scans show 2 endothermic peaks for melting. DSC scan curves for both the fabricated nanocomposite systems clearly show that they are affected by the nanofiller and its percentage fraction. There was an increase in Tm_1 in the composition of 8wt% TiO_2, while an increase in Tm_2 occurred in 2wt% TiO_2. Therefore, HDPE which is given TiO_2 filler has the potential to be used as landfill liner material.

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