

# The Experimental Investigation of the Effect of TiC Nanoparticles on the Thermal Behavior and Specific Strength of LDPE and HDPE

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**Abstract**—To assess the influence of Titanium Carbide (TiC) nanoparticles on the thermal stability and the specific strength of Low-Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE), the 2% weight fraction of TiC was added into LDPE and HDPE matrices. The thermal stability, rheological behavior, and specific strength of the pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC samples were studied through Thermogravimetric Analysis (TGA), rheology, and tensile testing. The results obtained show that the 2 wt% of TiC nanoparticles are not good reinforcing agents in terms of improving the thermal stability of pure LDPE and pure HDPE. The rheology results demonstrated an improvement in the storage modulus and the complex viscosity of LDPE compared to HDPE reinforced with TiC. However, TiC nanofiller proved to influence the mechanical properties of LDPE and HDPE. The 2% weight fraction of TiC increased the specific strength of pure LDPE by 4% and pure HDPE by 11%. The tensile strength of the pure LDPE and pure HDPE improved by 9% and 15% with the addition of 2 wt% of TiC. The obtained results showed that TiC can enhance the mechanical properties of LDPE and HDPE.

**Keywords**—polymer-based nanocomposites, polyethylene, specific strength, thermal stability, titanium carbide

## I. INTRODUCTION

Polymer-based Nanocomposite (PNC) materials have attracted the attention of many researchers in various fields and industrial applications. This is due to their growing demand in industries such as automotive, aerospace, biomedical, packaging water pipelines, water storage tanks, and others [1–3]. The reason for the demand for PNC materials is owing to their remarkable ability to be enhanced with the nanofillers to achieve improved mechanical, thermal, chemical, and other properties [4, 5]. The techniques of enhancing the polymer matrices with the nanofillers depend entirely on the choice of the polymer matrix, the nanofiller type, nanofiller weight fractions, the mixing procedure applied, as well as the processing techniques [6]. There are various studies conducted on the improvement of mechanical and thermal properties of different polymers by adding various nanofillers which resulted in successful results; however, some were not successful [7, 8]. Other studies proved that the better way of mixing the polymer with nanofillers, or processing and shaping PNC components is through heating and melting [9]. The heating of the polymer can be applied in different ways depending on the processing technique and have different effects on the resulting polymer products. It is vital to study and understand the behavior of

polymers, and polymer nanocomposites undergoing a heating process and the effect of heating rate on their mechanical and thermal properties. This current study focuses on the thermal stability, viscous behavior, and specific strength of Low-Density Polyethylene (LDPE), and High-Density Polyethylene (HDPE) reinforced with 2% Titanium Carbide (TiC) nanoparticles. LDPE and HDPE are known for their low weight, ease of shape, cheapness, and other properties that have gained their popularity in the automotive, and aerospace, industrial applications where low weight-to-strength ratio and thermal stability are targeted [10]. The challenging part with the LDPE and HDPE is that they have low strength and lower melting point temperatures [3]. To enhance such properties, nanofillers can be introduced in this polymer material as the reinforcement. The effect of various nanofillers on the different polymer matrices' thermal stability, melting point, or mechanical properties has been investigated and several solutions were obtained. Leszczyńska *et al* [11] studied the effect of layered silicate-montmorillonite on the thermal stability of High-Impact Polystyrene (HIPS). The results obtained from their study showed that layered silicate-montmorillonite improves the thermal stability of HIPS. Chen *et al* [12] studied the thermo-mechanical properties and phase behavior of Polypropylene (PP)–Polyethylene Terephthalate (PET) reinforced with inorganic fullerene tungsten sulfide IF-WS<sub>2</sub> nanofillers. The observation of their study showed that an increase in the weight fraction of IF-WS<sub>2</sub> up to 1 Wt% improves the tensile strength of PP-PET polymer. Their thermogravimetric results displayed a slight improvement in the thermal stability of PP-PET with an increase in IF-WS<sub>2</sub> which demonstrates that IF-WS<sub>2</sub> has the potential to improve both the mechanical and thermal properties of the polymers. Further studies on the enhancement of mechanical, thermal, and other properties of polymers using various nanoparticles were conducted by researchers such as Fattahi *et al* [13], Salmoria *et al* [14], Vlasveld *et al* [15], Loh *et al* [16], and others; where their work and recommendations show that more studies need to be done to gain more knowledge and advance better techniques to develop advanced polymer-based nanocomposite materials for automotive, aerospace and other similar industrial applications. The work covered in this study will add knowledge and contribute to the existing literature related to the study field.

## II. MATERIALS AND METHODS

### A. Materials

Low-Density Polyethylene (LDPE), High-Density Polyethylene (HDPE), and polyester-block-polyether were purchased from Sigma-Aldrich Chemistry, South Africa, and the Titanium Carbide (99.5% TiC) was produced from Weartech (PTY) LTD, welding, thermal, and specialty metals division, South Africa

### B. Material Processing

The LDPE and HDPE were supplied as clear white pellets. To mix them with TiC nanoparticles, they were first ground into smaller granules using a grinder and then placed into the oven at the temperature of 6 °C for 16 hours to remove the moisture. 150 g of LDPE and HDPE were processed through the twin-screw extruder. The mixture of LDPE and HDPE with TiC was achieved by measuring 141.6 g of LDPE and HDPE in separate beakers, 3 g of TiC and 5 ml of polyester block was added into each beaker and stirred to yield the mixture of LDPE/2wt% TiC and HDPE/2wt% TiC nanocomposite. The polyester block was added to achieve better dispersion of TiC nanoparticles through LDPE and HDPE matrices. The prepared mixtures were then processed with the twin-screw extruder for better mixing. The extruder parameters were set to the speed of 120 rpm for LDPE, and 100 rpm for HDPE, with a torque of 2.7 Nm and 40 Nm, pressure of 8.1 MPa, and 8.6 MPa, the die temperature of 160 °C and 190 °C respectively. The extruded pure LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC, came out of the extruder as a filament that was cooled with water at a temperature of 27 °C. The filaments were ground and dehumidified in the oven for 16 hours at a temperature of 60 °C. The prepared material then proceeded according to the next section.

### C. Samples Preparation

The Rheology samples were prepared through the compression molding technique with a compression mass of 2 tons, compression temperature of 160 °C for LDPE and 190 °C for HDPE, 4 minutes of heating time, 4 minutes of holding time, and a cooling time of 5 minutes. The processed samples were then analyzed for thermal stability using TGA, viscous behavior using a rheometer, and dynamic mechanical analysis, as well as the tensile test.

## III. RESULTS AND DISCUSSION

### A. Thermal Stability

The thermal stability of the LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC samples were examined according to ASTM E1131 standards using the Thermogravimetric Analysis (TGA) Q500 machine. The initial mass of the samples was measured to be roughly 9 to 10 mg, the analysis temperature was from 25 °C to 700 °C, and the ramp rate of 10 °C/min. The obtained Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) results for the stated samples are presented in Figs. 1 and 2 respectively.

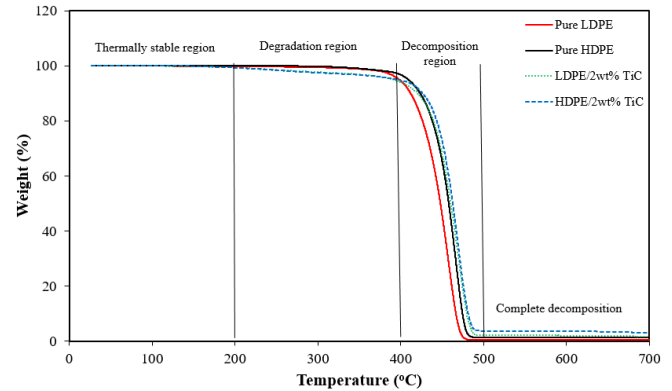


Fig. 1. The TG curves of LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC.

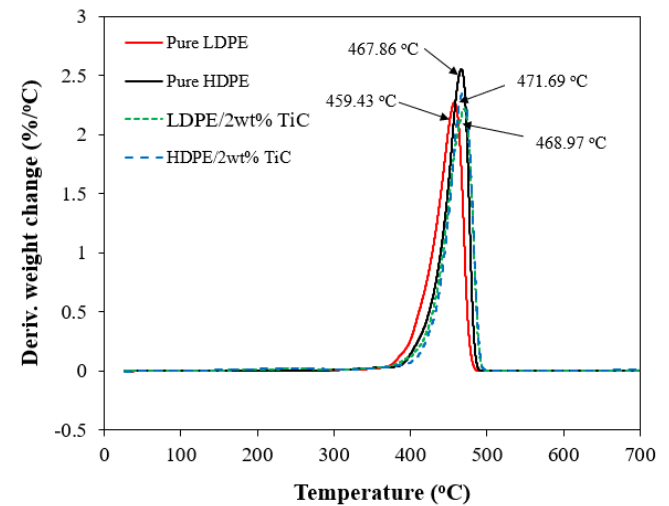


Fig. 2. The DTG curves of LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC.

The TG results in Fig. 1 present the weight loss % for LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC as temperature increases at a constant rate. The thermal behaviour of all samples is almost similar from 25 °C to roughly 200 °C which shows no weight % change. This means the produced polymers and polymer nanocomposites still retain their thermal properties at that temperature range. However, as the temperature increases from 200 °C to roughly 400 °C, LDPE/2wt% TiC and HDPE/2wt% TiC began to degrade by demonstrating a slight weight % loss compared to pure LDPE and HDPE which are still thermally stable. This trend might have been influenced by the TiC thermal storage capacity or the newly developed bond between the polymer matrices (LDPE and HDPE) and the reinforcement (TiC). Furthermore, at temperatures between 400 °C and 500 °C all the polymers and their corresponding nanocomposite TG curves display a typical one-step decomposition through drastic weight loss. Although HDPE, LDPE/2wt% TiC and HDPE/2wt% TiC tend to lose weight at a slightly higher temperature compared to LDPE, the actual decomposition temperatures ( $T_{max}$  the maximum peak temperature of each weight loss %) of the materials are 459.43 °C for pure LDPE, 467.86 °C for pure HDPE, 468.97 °C for LDPE/2wt% TiC, and 471.69 °C for HDPE/2wt% TiC as illustrated by DTG curve in Fig. 2. At temperatures from 500 °C to 700 °C the TGA curve displays the total decomposition of LDPE and HDPE with the remaining small amount of LDPE/2wt% TiC and

HDPE/2wt% TiC weight %. This demonstrates the remaining 2% weight fraction of TiC added into the polymer matrices, given that TiC has a higher melting and degradation point compared to the LDPE and HDPE. In general, the TGA results indicate that TiC is not a suitable nanofiller for the enhancement of the LDPE and HDPE thermal stability.

### B. Rheological Behavior

Rheology is a technique used to analyze the behaviour of polymers or polymer-based nanocomposites relative to shear forces at various temperature ranges [17, 18]. This technique can be conducted through an amplitude sweep where the frequency is constant, while the amount of strain/deformation increases, or a frequency sweep where the amount of strain is constant while the frequency increases [19, 20]. The rheological results presented in this work are based on the frequency sweep analysis conducted at the angular frequencies between 0.1 rad/s and 100 rad/s according to the ASTM D4440-15 standards using a Modular Compact Rheometer (MCR 302e) set to a temperature of 190 °C.

#### 1) Frequency sweep

Previous studies have demonstrated that enhancing polymer matrices with nanofiller changed their rheological behavior [21, 22]. In this study, TiC nanofiller was used to reinforce LDPE and HDPE matrices. The rheological results in Fig. 3 (a) and (b) present the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) of the LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC versus angular frequency.

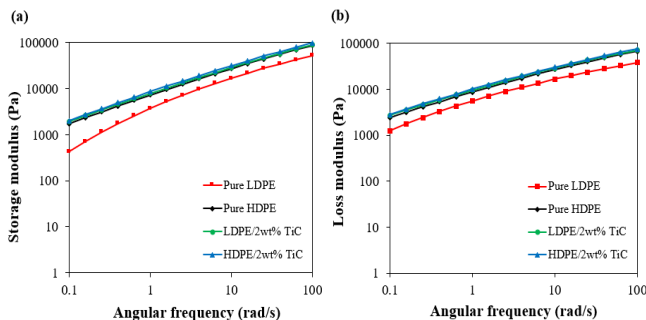


Fig. 3. (a) storage modulus and (b) loss modulus against angular frequency for Pure LDPE, Pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC at 190°C.

Trends in Fig. 3(a) and (b) display an increase of both storage modulus and loss modulus of LDPE/2wt% TiC compared to pure LDPE. However, pure HDPE and HDPE/2wt% TiC show almost similar trends in storage and loss moduli. Besides, the curves for pure HDPE and HDPE/2wt% TiC almost overlap with those for LDPE/2wt% TiC at all angular frequencies. The TiC nanofiller improved the storage modulus and the loss modulus of both pure LDPE and HDPE though, a significant improvement was observed for pure LDPE related to LDPE/2wt% TiC. In general, the results in Fig. 3(a) and (b) demonstrate that pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC possess the domination of storage modulus over loss modulus for all frequencies.

The next rheological analysis is based on the complex viscosity of the pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC, versus frequency as presented in Fig. 4.

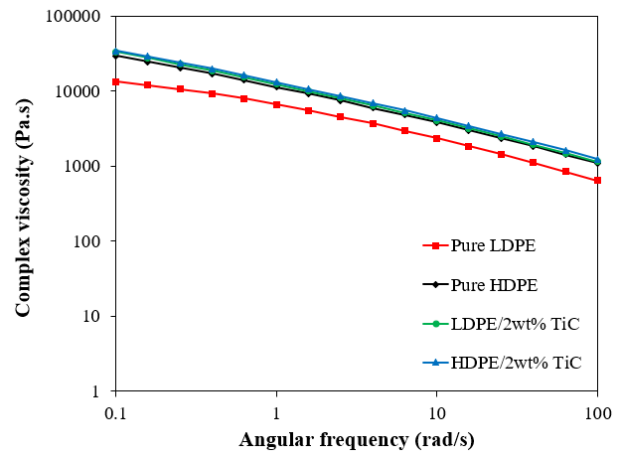


Fig. 4. Complex viscosity plot versus angular frequency of pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC at 190°C.

The plot of complex viscosity ( $\eta^*$ ) against angular frequency in Fig. 4 shows that the introduction of a 2% weight fraction of TiC nanoparticles in both LDPE and HDPE increases their complex viscosity. However, a significant increase in complex viscosity was observed between the LDPE/2wt% TiC and pure LDPE as compared to the increase between HDPE/2wt% TiC and pure HDPE. This means the TiC nanofiller provides the polymers (especially LDPE) with the resistance to flow at 190 °C as a function of angular frequency. The overall results demonstrate that the viscosity of the polymers is higher at lower frequencies and decreases with an increase in frequency.

### C. Specific Strength

The specific strength of LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC were analysed by determining the density and the tensile strength of the produced samples. The densities of the samples were calculated by weighing their masses as illustrated in Table 1 and then dividing them by the volume of the specimen (0.687 cm<sup>3</sup>). Three samples for pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC, were measured and their average mass was considered for the calculation of their densities as summarized in Table 3.

Table 1. The Masses of the Pure LDPE, pure LDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC Samples

Nanocomposites	Sample Masses [g]			Average Mass [g]
	Mass 1	Mass 2	Mass 3	
Pure LDPE	0.637	0.639	0.632	0.636
Pure HDPE	0.652	0.647	0.650	0.650
LDPE/2wt% TiC	0.667	0.670	0.664	0.667
HDPE/2wt% TiC	0.676	0.687	0.675	0.679

The tensile strength of the pure LDPE, pure HDPE, and their corresponding nanocomposite samples were determined by conducting the tensile tests according to the ASTM D 638-02a standard using an Instron 1195 tensile testing machine. Fig. 5 displays the stress-strain curves for pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC through their stress-strain curves. To get reliable results for the stress-strain behavior of the polymer and polymer-based nanocomposites, three tensile tests were performed for each polymer sample and their strengths are summarised in Table 2.

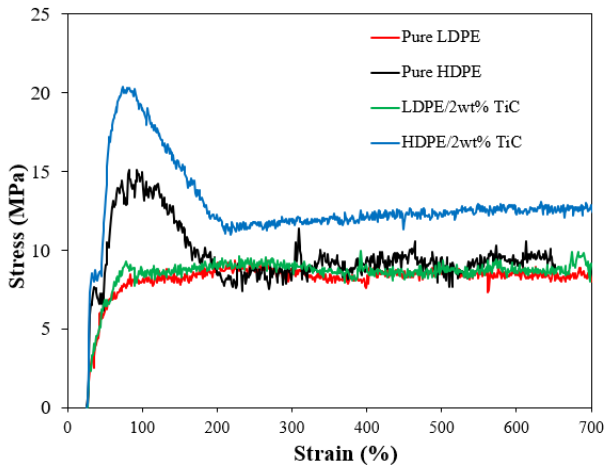


Fig. 5. The stress-strain curves for pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC.

The stress-strain plots in Fig. 5 show that LDPE/2wt% TiC and HDPE/2wt% TiC, have higher ultimate tensile strength compared to pure LDPE and pure HDPE. This means TiC has enhanced the tensile strength of LDPE and HDPE even though the substantial improvement is shown by HDPE/2wt% TiC when compared to HDPE. The average tensile strength for polymer and polymer nanocomposites presented in Table 2 shows the tensile strength improvement of 9% for LDPE/2wt% TiC compared to pure LDPE, and 15% for HDPE/2wt% TiC compared to the pure HDPE.

Table 2. The average tensile strength for pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC

Nanocomposites	Tensile Strength [MPa]			Average Tensile Strength [MPa]	Improvement %
	Test 1	Test 2	Test 3		
Pure LDPE	10.260	09.347	10.267	09.958	--
Pure HDPE	17.710	15.081	16.640	16.477	--
LDPE/2wt% TiC	11.613	11.215	09.979	10.936	08.943
HDPE/2wt% TiC	19.331	20.111	18.391	19.278	14.530

The results in Tables 1 and 2 were used to determine the specific strength of the produced LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC as presented in Table 2.

Table 3. The specific strength of pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC

Nanocomposites	Tensile Strength [MPa]	Density [g/cm <sup>3</sup> ]	Specific Strength [kN.m/kg]	Improvement %
Pure LDPE	09.958	0.925	10.765	--
Pure HDPE	16.477	0.946	17.418	--
LDPE/2wt% TiC	10.936	0.971	11.263	04.422
HDPE/2wt% TiC	19.278	0.988	19.512	10.732

The results in Table 2, show the tensile strengths, densities, and specific strengths for pure LDPE, pure HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC respectively. The obtained specific strengths show an improvement as the TiC nanoparticles are added to the polymer matrices. Statically, the 2% weight fraction of TiC improved the specific strength of LDPE by 4% and HDPE by 11%, respectively. This indicates that TiC nanofillers are good as reinforcing agents for the mechanical properties of the polymers.

#### D. Other Recommendations

Investigate the influence of different weight fractions of TiC on the thermal, and rheological properties, and the specific strength of HDPE.

Study of the influence of TiC on the thermal and mechanical properties of various polymer matrices such as Polyamide 6 (PA6), and Polypropylene (PP).

#### IV. CONCLUSION

This study covered the investigation of the effect of a 2% weight fraction of Titanium Carbide (TiC) nanofillers on thermal performance and tensile properties (specific strength) of Low-Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE). The Thermogravimetric Analysis (TGA) and Rheology were conducted to examine the thermal behavior of the polymers while the tensile test was conducted to aid in determining the specific strength of the material. The overall results are found to be as follows:

- The TGA results show that LDPE, HDPE, LDPE/2wt% TiC, and HDPE/2wt% TiC are thermally stable from 25 °C to roughly 200 °C, and start to degrade from 200 °C to 400 °C where decomposition starts to take place. The total decomposition of the polymers and polymer nanocomposites was obtained at a temperature above 450 °C. Moreover, TiC nanofillers were shown to have no significant effect on the thermal stability of the LDPE and HDPE.
- The rheology results indicated an improvement in the storage modulus and the complete viscosity of LDPE and HDPE when enhanced with the TiC nanoparticles. However, a significant improvement was demonstrated by LDPE.
- The addition of a 2% weight fraction of TiC into pure LDPE and pure HDPE enhanced their tensile strengths by 9% and 15% respectively.
- In terms of mechanical properties, the tensile test results showed an improvement in LDPE and HDPE ultimate stress when reinforced with TiC. The specific strength of the reinforced LDPE and HDPE improved by 4% and 11% respectively, with the introduction of the TiC nanofibers.
- In general, TiC nanofillers are good reinforcing nanoparticles for mechanical properties rather than the thermal properties of polymers.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

#### AUTHOR CONTRIBUTIONS

All authors contributed to the study's conception and design. Ronny T. Tebeta performed Material preparation and data collection; Ronny T. Tebeta and Daniel D. Madyira performed Data analysis; Ronny T. Tebeta wrote the first draft of the manuscript; Daniel M. Madyira supported resources and financial support; Ronny T. Tebeta, Daniel M. Madyira, and Harry M. Ngwangwa revised the original manuscript to the current version; all authors had approved the final version.



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