Tuijin Jishu/Journal of Propulsion Technology
ISSN: 1001-4055
Vol. 47 No. 02 (2026)

Comparative Study of Green and Chemically Synthesized ZnO Nanoparticles Reinforced Waste Polyethylene Nanocomposites

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Abstract:- The mechanical properties of Reinforced waste polyethylene nanocomposites were study. In this work, zinc oxide (ZnO) nanoparticles synthesized via chemical (CS) and green routes (GS) using garlic bark extract were incorporated into waste polyethylene to fabricate polyethylene/ZnO nanocomposites. The influence of nanoparticle synthesis route and filler loading on mechanical properties - including hardness, tensile strength, flexural strength, Young's modulus, and elongation at break - were systematically investigated. The nanocomposites were prepared via in-situ polymerization and ZnO particles were characterized using mechanical testing, scanning electron microscopy (SEM), X-ray diffraction (XRD) and FTIR. Results revealed that chemically synthesized ZnO nanoparticles enhanced hardness and stiffness due to their higher crystallinity, while green-synthesized ZnO nanoparticles exhibited superior flexural performance owing to improved dispersion and interfacial interaction. Tensile strength and elongation at break generally decreases with increasing ZnO loading due to nanoparticle agglomeration at higher concentrations.The average crystalline size obtained 115.10 nm GS and 195.88 nm CS ZnO nanoparticle and Zn-O prominent absorption was observed between 673.18 to 437.18 cm^{-1} GS ZnO and 678.73 to 472.77 cm^{-1}CS ZnO .The findings demonstrate that green synthesis provides a sustainable alternative for producing effective ZnO-reinforced polyethylene nanocomposites from plastic waste.

Keywords: *Waste polyethylene, ZnO nanoparticles, green synthesis, nanocomposites, mechanical properties.*

1. Introduction

Polymer nanocomposites have attracted significant research attention due to their enhanced mechanical, thermal, and functional properties, enabling applications in packaging, electronics, energy storage, adhesives, and structural materials(Mahmoodi & Soleimani, 2023). Polyethylene is among the most widely used polymers because of its low cost, chemical resistance, and ease of processing. However, its relatively low mechanical strength restricts its application in advanced engineering systems. Reinforcement with metal oxide nanoparticles has proven effective in improving the mechanical and barrier properties of polyethylene through enhanced stress transfer and interfacial bonding (Dogara *et al.*, 2023a).

Zinc oxide (ZnO) nanoparticles are particularly attractive as fillers due to their high stiffness, thermal stability, radiation absorption capacity, and multifunctional properties. Studies have demonstrated that polyethylene reinforced with ZnO, TiO_2, Fe_2O_3, and Ag_2O nanoparticles exhibits improved hardness, tensile strength, and barrier performance (Dejene, 2025). Specifically, ZnO nanoparticles have been shown to enhance elongation at break and radiation shielding properties in polyethylene nanocomposites (Ahmed et al., 2017 ; Alshipli et al., 2023). Consequently, ZnO is considered an effective structural and functional reinforcement for polyethylene matrices. An investigation into the effects of green synthesized silver nanoparticles (AgNP) on thermoplastics revealed that the resulting polymer composite demonstrated exceptional adhesion between AgNP and the matrix, enhancing the polymer composite's barrier qualities, mechanical strength, flexibility, and thermal stability (Ceballos et al., 2021). In comparison to graphene nanosheets, a higher fracture toughness and tensile strength were found when the mechanical properties of the polymer-based nanocomposites were examined using another green synthesized graphene nanoplatelet made from lemon juice (Safari et al., 2021). Mechanical properties such tensile strength, flexural behavior, microhardness, and impact resistance were investigated in hybrid biopolymercompsites made from green produced bamboo fiber, eggshell, and coconut shell powder. The results show that, when compared to their untreated counterparts, composite fibers exhibit higher mechanical performance as measured by tensile, flexural, hardness, and impact strength(Natrayan et al., 2024). It has been reported that adding TiO2 nanoparticles to acrylic improves its mechanical properties; nevertheless, as the amount of nanoparticle addition rises, the acrylic resins' flexural strength values fall (Özkan Ata et al., 2022). Another report, showed that a dual-screw extruder, zinc oxide (ZnO) nanoparticles were compounded with polypropylene (PP) to create hybrid materials, the ZnO nanoparticle significantly influence the morphology, mechanical characteristics, and chemical structure led to a decrease in tensile strength and an improvement in mechanical characteristics including young modulus and percentage elongation at break(Prasert et al., 2020). Using a twin-screw extruder for the creation of polymeric blends and their composites, a polymeric blend of polypropylene (PP) and high-density polyethylene (HDPE) was created with varying weight percentages of ZnO. The impact of this mixture on the mechanical properties of the PP/HDPE blends was investigated.Due to immiscibility, the results of PP/HDPE blends demonstrate that as the percentage of HDPE increases, both tensile strength and hardness decrease.(Ban Jawad Kadhim et al., 2024)

The synthesis route of ZnO nanoparticles significantly influences their size, morphology, crystallinity, and surface chemistry, which directly affect dispersion and interfacial interaction with polymer chains. Conventional chemical synthesis methods often involve hazardous reagents, high energy consumption, and environmental concerns (Dhoke, 2023). In contrast, green synthesis approaches utilizing plant extracts or biological materials offer environmentally benign, cost-effective, and sustainable alternatives. The biocoumpounds that are employed are binding molecules that primarily alter the size, shape, and surface chemistry. The availability of phytochemicals in the plant or biological components such flavonoids, phenolic, and alkaloids that facilitate metal ion reduction and stabilize the particles during synthesis makes them an appealing substitute for traditional nanoparticle synthesis(Edo et al., 2025). By introducing organic capping agents, these techniques enhance compatibility with polymer matrices and control the development of nanoparticles. dispersion of the nanoparticles and inhibit the aggregation of particles (Sidhu et al., 2022). Additionally, by precisely controlling and optimizing the characteristics of the nanoparticles, the capping gents make them more appropriate for the creation of polymer composites (Rutherford et al., 2025).

This study compares ZnO nanoparticles synthesized via chemical and green routes using garlic bark extract and evaluates their reinforcing effects in waste polyethylene nanocomposites. Mechanical properties including hardness, tensile strength, flexural strength, Young’s modulus, and elongation at break were assessed to determine the influence of synthesis route and filler loading. The aim is to identify an effective and sustainable approach for producing high-performance polyethylene nanocomposites from plastic waste.

2. Materials and Methods

2.1. Materials

All chemicals used are of analytical grade and were used without further purification. Sodium hydroxide (NaOH, 95–97%), benzoyl peroxide, hexane (97%), methanol (99.8%), ethanol (99.8%), $ZnSO_4 \cdot 7H_2O$, xylene, and dimethyl sulfoxide (DMSO) were sourced from Sigma-Aldrich and British Drug House (BDH) (I think it is best to put the supplier for each reagent in front of it like this - NaOH, 97% BDH, etc). All solutions were prepared using distilled water.

2.2. Preparation of Waste Polyethylene

Waste polyethylene sachet water bags were collected from a domestic waste bin and were thoroughly washed, air-dried, and shredded into small particles to increase surface area and facilitate dissolution.

2.2.1. Dissolution of Polymer Waste

The method reported by Achilias *et al*. (2015) was adopted with slight modification. 4.0 g of shredded polyethylene waste were placed in a round-bottom flask equipped with a condenser, and 20 mL of xylene was added. The mixture was then heated at elevated temperature until complete dissolution was achieved.

2.3. Green Synthesis of ZnO Nanoparticles

The green synthesis of ZnO nanoparticles was carried out following the method of Amutha and Sridhar (2018) with a few modifications. 1.0 g of $ZnSO_4·7H_2O$ was dissolved in 100 mL of distilled water and heated at 80 °C under continuous stirring. Subsequently, 20 mL of garlic bark extract was added as a reducing agent. After 10 minutes, 20 mL of 0.1 M NaOH was then added dropwise to adjust the pH of the mixture to 6.0. The mixture was sonicated, resulting in the formation of a white precipitate. The nanoparticles were centrifuged, washed repeatedly with ethanol then with distilled water and allowed to dry at 70 °C overnight.

2.4. Preparation of Polyethylene/ZnO Nanocomposites

Polyethylene/ZnO nanocomposites were prepared using the method described by (Alsharaeh, 2016; Omar et al. 2020) with a slight modification. About 0.2–0.8 g ZnO nanoparticles and 1.0 g of benzoyl peroxide were added to 80 g of waste polyethylene and stirred for 1 hour. (How many mL?) DMSO solvent was added to the mixture and stirring was maintained for 20 hours at 80 °C to promote in-situ polymerization. The product was precipitated using methanol, washed with water and ethanol, filtered, and dried at 30 °C.

2.5. Mechanical Testing

Compression-molded samples were prepared according to ASTM standards. Tensile and flexural properties were evaluated using an Instron Universal Testing Machine at a crosshead speed of 10 mm/min and temperature of 25 ± 3 °C. Hardness measurements were conducted using a Shore durometer following ASTM D2240 standard technique. Three replicate specimens were tested, and average values were reported.

2.6. Morphological and Structural Characterization of ZnO Nanoparticles

The morphology of ZnO nanoparticles was examined using scanning electron microscopy (SEM) morphology was recorded using a JEOL JSM-7600F machine and particle size distribution was determined using ImageJ software. X-ray diffraction (XRD) analysis was performed (X-ray diffractometer operated at 0 kV and 0 mA (Rigaku-binary) to identify crystalline phases and estimate crystallite size using the Debye–Scherrer equation. Fourier transformed infrared spectroscopy (FTIR) spectrum was recorded with a Shimadzu FTIR-8400s Fourier transform infrared spectrophotometer in the scanning range of 4000-400 cm^{-1} using a cold-pressed pellet of potassium bromide (KBr, Merck) containing 1% hydroxyapatite (HAp) sample to determine the functional groups present.

3. Results and Discussion

3.1. Mechanical Properties

3.1.1. Hardness Shore D

Figure 1(a) shows that for chemically synthesized ZnO nanoparticles used for the preparation of the polyethylene/ZnO nanocomposite, the hardness shore D increases almost linearly with increasing amount of the ZnO nanoparticles from 94.2 N/mm^2 when there is no ZnO nanoparticles to 99.0 N/mm^2 when the amount of the ZnO nanoparticles increases to 0.8 g. On the other hand, for the green synthesized ZnO nanoparticles, the hardness shore D decreases with increasing amount of the ZnO nanoparticles from 94.0 N/mm^2 to 92.0 N/mm^2 as the amount increases from 0.0 g to 0.8 g.

The divergent trends in Shore D hardness between chemical and green synthesized ZnO nanoparticles (NPs) within the waste polyethylene matrix imdicates the critical role of nanoparticle surface characteristics in composite reinforcement. The progressive increase in hardness for chemically synthesized ZnO (97.0 to 99.0 N/mm²) is consistent with established materials science literature, which posits that rigid inorganic fillers effectively restrict the mobility of polymer chains and enhance the resistance to localized plastic deformation (Abbas *et al.*, 2019). This reinforcement suggests a high degree of interfacial adhesion and uniform dispersion within the matrix. In contrast, the decrease in hardness observed with green synthesized ZnO (94.0 to 92.0 N/mm²) may be attributed to the "plasticizing effect" of residual biogenic capping agents (such as alkaloids or phenolic compounds) which serve as reducing agent during synthesis. These agents are then inherited from the plant extracts (Dhaka *et al.*, 2023). According to Van Ravensteijn *et al.*, 2019, these organic residues can interfere with the polymer's crystalline structure and act as lubricants, thereby increasing chain flexibility and reducing surface hardness. Furthermore, at higher concentrations (up to 0.8 g), green nanoparticles often exhibit a higher tendency for agglomeration due to the different method of extraction, solvent and temperature leading to an inconsistency in reduction kinetics, capping efficiency, and ultimately the size,, creating stress concentrators that weaken the mechanical integrity of the composite compared to their chemically synthesized counterparts (Ayub et al., 2025).

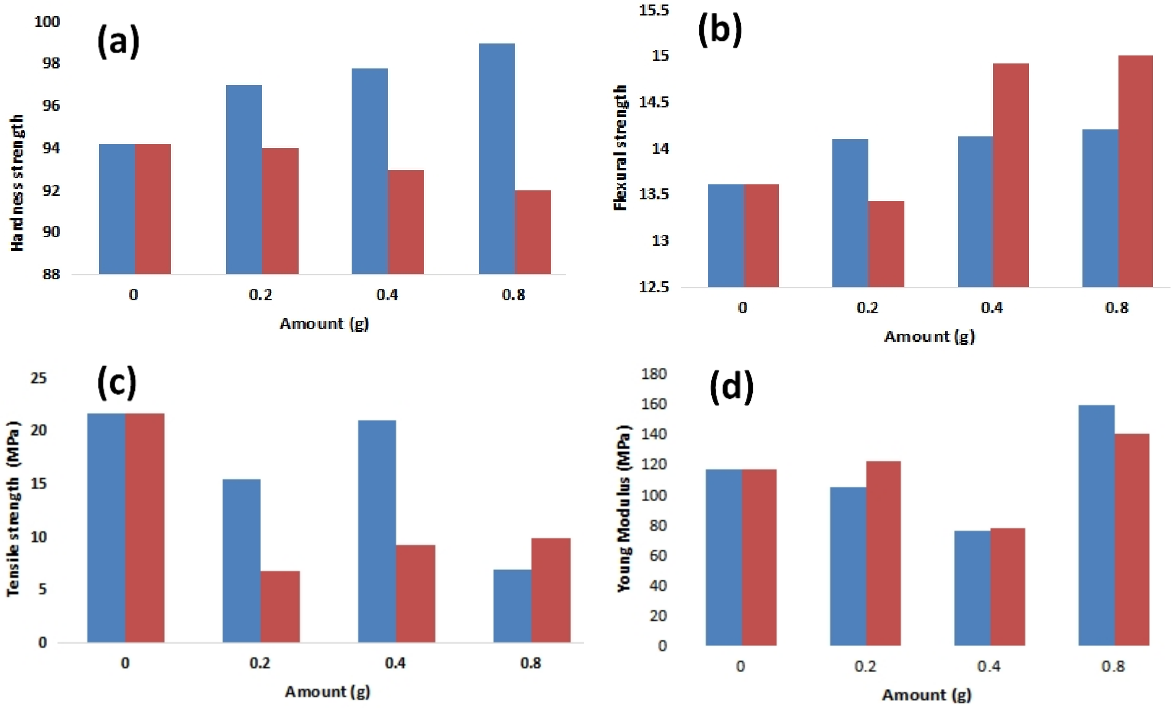

Figure 1. Mechanical properties of the polyethylene/ZnO nanocomposite prepared using chemically (🟦) and green synthesized (🟥) ZnO nanoparticles: (a) hardness shore D, (b) flexural strength, (c) tensile strength, and (d) Young modulus.

The hardness results revealed that chemically synthesized ZnO nanoparticles significantly increased the Shore hardness of waste polyethylene composites, whereas green-synthesized ZnO nanoparticles caused a slight reduction in hardness with increasing filler loading. The enhanced hardness observed for chemically synthesized ZnO is attributed to its higher crystallinity, intrinsic stiffness, and ability to restrict polymer chain mobility, thereby improving load transfer within the polyethylene matrix (Zhou et al., 2023).. Acting as rigid nucleating agents, chemically synthesized ZnO nanoparticles promote ordered crystalline regions and can increase hardness by approximately 20–50% at optimal loadings. In contrast, green-synthesized ZnO nanoparticles are capped with biogenic organic compounds that lower crystallinity and promote amorphous, plasticized structures, leading to reduced hardness values (Ying et al., 2022). These organic coatings can hinder effective interfacial bonding and nanoparticle dispersion, producing lubricating effect that weakens the stress transfer and decreases the surface resistance.

3.1.2. Flexural Strength

Flexural strength of green synthesis and chemical synthesized waste polyethylene ZnO nanocomposite is presented in Figure 1(b). The result shows that the flexural strength of the waste polyethylene/ZnO nanocomposite prepared with both a chemically synthesized and green synthesized ZnO nanoparticles increases as the amount of the nanoparticle loading increases. It also shows that the flexural strength of the nanocomposite prepared with green synthesized ZnO nanoparticles is higher than those of the chemically synthesized ZnO nanoparticles.

The contrast in flexural strength between waste polyethylene (WPE) reinforced with chemically synthesized (CS) and green synthesized (GS) ZnO nanoparticles reveals distinct mechanical reinforcement behaviors. While both synthesis methods ultimately improve the flexural strength with increasing amount of the nanoparticles, the GS ZnO nanoparticles demonstrate a more significant enhancement at higher concentrations, reaching up to 15.01 MPa compared to the 14.21 MPa achieved by CS ZnO nanoparticles. In literatures, the steady increase in flexural strength for CS ZnO is typically attributed to the high surface area to volume ratio of the nanoparticles, which facilitates effective stress transfer from the polymer matrix to the rigid fillers by creating a protective layer (Mohammed et al., 2023). However, the superior performance of the GS ZnO composites at concentrations above 0.2 g suggests that the plant extract such as phenols, flavonoid and saponins used during green synthesis of ZnO nanoparticles may act as effective coupling agents, significantly influence the compatibility between the ZnO and the polyethylene chains (Chanthapong et al., 2025). Unlike the hardness results where green synthesis residues acted as plasticizers, the flexural data implies that these residues may enhance the elastic interface and energy absorption capacity of the composite under bending loads (I. S. Mohammed et al., 2023). The slight dip for GS ZnO at 0.2 g (13.44 MPa) before its sharp rise may indicate a threshold concentration required to overcome initial particle-matrix mismatch.

Flexural strength of waste polyethylene nanocomposites increases with ZnO nanoparticle loading, confirming the reinforcing role of ZnO under bending deformation (Chang *et al*., 2014). GS ZnO nanoparticles exhibited superior flexural performance due to enhanced dispersion and stronger interfacial adhesion provided by phytochemical surface functional groups, which improved stress transfer efficiency and crack resistance during flexural loading (Hanna *et al*., 2025; Şomoghi *et al*., 2024). In contrast, CS ZnO nanoparticles shows slight reductions in flexural strength at lower loadings as a result of particle agglomeration and stress concentration effects, which limited effective load transfer within the polymer matrix (Raha & Ahmaruzzaman, 2022; Dey *et al*., 2025). At higher ZnO nanoparticle content, flexural strength increased for both synthesis routes, indicating that an optimal filler threshold was reached where the reinforcing effect of ZnO outweighed dispersion-related limitations through the formation of a semi-continuous filler network (Fu *et al*., 2008; Chang *et al*., 2014).

3.1.3. Tensile Strength

It can be seen from Figure 1(c) that the tensile strength of the control waste polyethylene is higher than those loaded with the ZnO nanoparticles prepared using both synthesis route. The waste polyethylene with chemical synthesized ZnO nanocomposites showed a decrease in the tensile strength from 6.959 Mpa to 15.51 Mpa as the concentration of the nanoparticles was increase from 0.2 to 0.8. Also the waste polyethylene with green synthesized ZnO nanocomposites showed a decrease in the tensile strength from 6.814 to 9.932 Mpa as the concentration of the ZnO nanoparticles increases from 0.2 to 0.8.

For the control WPE (at 0 g of ZnO nanoparticle loading), the tensile strength peaks up to 21.67 MPa. Upon adding nanoparticles, both chemical synthesized (CS) and green synthesized (GS) nanocomposites show an initial drop followed by an increase in tensile strength as concentration increases from 0.2 g to 0.6 g, then decreases at the highest loading of 0.8 g. This general reduction compared to the control is often attributed primarily to the nanoparticle agglomeration and weakened interfacial stress transfer by disruption of the polymer continuous phase (M. Mohammed et al., 2023). Chemically synthesized ZnO nanoparticles exhibited greater reductions in tensile strength as a result of their high surface energy, which promotes particle clustering and creates stress concentration sites within the polymer matrix (Baronins et al., 2023; Adlie et al., 2023). In contrast, the flexural strength shows a consistent improvement for both types over the neat WPE (13.62 MPa), with GS ZnO outperforming CS ZnO at 0.8 g by reaching 15.01 MPa compared to 14.21 MPa. This suggests that while nanoparticles may create stress concentration points that lower tensile strength, they effectively enhance the material's stiffness and resistance to bending (Ali et al., 2025).

Green-synthesized ZnO nanoparticles also led to reduced tensile strength, attributed to the presence of organic capping agents that introduce a compliant interfacial layer and limit effective load transfer under tensile deformation (Zhang et al., 2025). Similar trends have been reported in ZnO-reinforced polymer systems, where excessive filler loading resulted in poor dispersion, void formation, and premature failure under tensile stress (Dejene, 2024). Overall, the tensile behavior is governed by the balance between nanoparticle dispersion and interfacial bonding, with agglomeration dominating at higher ZnO contents (Dang & Kim, 2023). Hence, the tensile strength of waste polyethylene/ZnO nanocomposites decreased with increasing ZnO nanoparticle loading for both chemically and green-synthesized systems. The tensile strength of waste polyethylene/ZnO nanocomposites decreases with increasing ZnO nanoparticle loading for both the CS and GS systems. This is primarily due to nanoparticle agglomeration and weakened interfacial stress transfer (Mohammed *et al*., 2023). CS ZnO nanoparticles exhibited greater reductions in tensile strength as a result of their high surface energy, which promotes particle clustering and creates stress concentration sites within the polymer matrix (Baronins *et al*., 2023; Adlie *et al*., 2023). GS ZnO nanoparticles also led to reduced tensile strength, attributed to the presence of organic capping agents that introduce a compliant interfacial layer and limit effective load transfer under tensile deformation (Zang et al., 2025). Similar trends have been reported in ZnO-reinforced polymer systems, where excessive filler loading resulted in poor dispersion, void formation, and premature failure under tensile stress (Dejene, 2024). Overall, the tensile behavior is governed by the balance between nanoparticle dispersion and interfacial bonding, with agglomeration dominating at higher ZnO contents.

3.1.4. Young Modulus

The result for the Young modulus presented in Figure 1(d) shows general increase with increasing loading of the ZnO nanoparticles for both chemical and green synthesized ZnO nanoparticle with an exception observed at 0.6 g loading. However, as the loading of both the ZnO nanoparticles increases to 0.8 g, Young’s modulus of the waste polyethylene composites became very high 159.82 and 140.79 MPa respectively.

The mechanical analysis of waste polyethylene (WPE) reinforced with chemically synthesized (CS) and green synthesized (GS) ZnO nanoparticles shows that loading concentration significantly influences the stiffness and elastic properties of the composite. For both synthesis types, an initial increase in concentration from 0 to 0.4 g leads to a notable decrease in Young’s modulus, dropping from 117.38 MPa to 76.8 MPa for CS and 78.46 MPa for GS. This initial reduction in stiffness is frequently documented in literature as being caused by the "dilution effect" or poor initial wettability, where the introduction of particles disrupts the continuous crystalline network of the polyethylene matrix by interrupting the ability of the polymer chains to fold and organize into lamellae before a stable reinforcing network is established (Quan et al., 2005). However, a sharp reversal occurs at the 0.8 g loading level, where the Young’s modulus peaks at 159.82 MPa for CS and 140.79 MPa for GS. Generally, the Young’s modulus of the CS and GS systems exhibited a non-linear dependence on ZnO nanoparticle loading. At low filler contents, a reduction in modulus was observed due to non-uniform dispersion and nanoparticle agglomeration, which disrupted effective stress transfer within the polymer matrix (Silva et al., 2020). As ZnO loading increased, Young’s modulus improved significantly, reflecting the high stiffness of ZnO nanoparticles and their ability to restrict polymer chain mobility and enhance load-bearing capacity when adequately dispersed (Wong et al., 2025; Chang et al., 2014).

Chemically synthesized ZnO nanoparticles produced higher modulus values owing to their greater crystallinity and rigidity, while green-synthesized ZnO nanoparticles showed slightly lower modulus due to the presence of organic capping layers that introduce compliant interfacial regions (Ahmed & Mamat, 2011). Overall, the elastic behavior of the nanocomposites is governed by filler loading, dispersion quality, and particle matrix interfacial adhesion rather than nanoparticle size alone. This substantial gain in stiffness at higher concentrations suggests the particles are overcrowded where the ZnO nanoparticles form a secondary interconnected skeleton that restricts polymer chain mobility and enhances the modulus of elasticity (Lim et al., 2021). While both methods improve stiffness at high loadings, the slightly lower modulus of the GS composite compared to the CS version may be due to the residual organic capping agents from green synthesis, which can introduce a degree of flexibility by creating a hydrated flexible shell or localized plasticization within the rigid inorganic-organic interface (Javed et al., 2020).

3.1.4. Elongation at Break

Figure 2 shows the effect of chemical and green synthesized ZnO nanoparticles on the elongation at break of waste polyethylene. The result obtained shows that increase concentration of the Zno can generally decrease the percentage elongation. However, the result at 0.2 g green synthesized and 0.8 g chemical synthesized showed high increase in the percentage elongation 9.189 and 9.992 %.

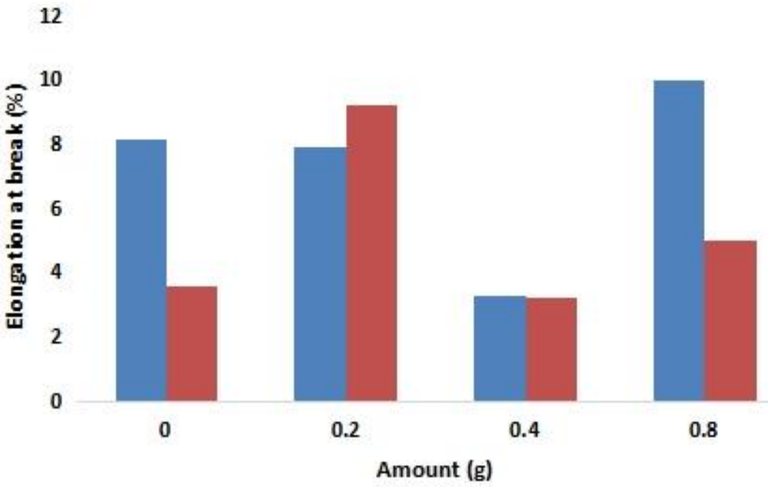

Figure 2. The elongation at break of polyethylene/ZnO nanocomposite prepared using chemically (🟦) and green synthesized (🟥) ZnO nanoparticles.

The impact of ZnO nanoparticles (NPs) on the elongation at break of waste polyethylene (WPE) illustrates a complex relationship between filler concentration and the material's ductility. Generally, the introduction and increasing concentration of ZnO nanoparticles tend to decrease the percentage elongation of the polymer composite. This trend has been observed, as inorganic fillers often restrict the movement of polymer chains and act as stress concentrators, leading to a more brittle material this indicated a reduced ductility due to restricted polymer chain mobility and suppressed strain hardening (Chang et al., 2014). However, notable exceptions occur at specific loadings: green synthesized (GS) ZnO at 0.2 g and chemically synthesized (CS) ZnO at 0.8 g show significant increases in elongation, reaching 9.189% and 9.992% respectively. In the case of GS ZnO at low loading, this localized increase in ductility may be attributed to the "plasticizing effect" of residual biogenic molecules from plant extracts, which can increase the free volume between polymer chains and facilitate greater chain mobility by limiting chain slippage and reorientation, leading to premature fracture, particularly at higher filler loadings where agglomeration further intensified stress concentration effects (Hassanabadi & Rodrigue, 2014); Qu et al., 2025). For the CS ZnO at 0.8 g, the unexpected rise in elongation suggests that a higher concentration may have achieved an optimal distribution that promotes localized shear yielding or energy dissipation mechanisms rather than immediate fracture. However, this slight, suggesting that well-dispersed nanoparticles can act as energy-absorbing sites that delay crack propagation and promote plastic deformation (Dogara et al., 2023b). Overall, the elongation behavior reflects a balance between nanoparticle-induced stiffness and localized toughening mechanisms governed by dispersion quality and filler–matrix interactions.

3.2. XRD of GS and CS ZnO Nanoparticles

X-ray diffraction pattern of GS and CS ZnO nanoparticles are presented in Figure 3. The X-ray diffraction (XRD) patterns for both the green synthesized (GS) and chemically synthesized (CS) ZnO nanoparticles reveal distinct structural profiles that influence the mechanical performance of the waste polyethylene composites. The GS ZnO exhibits a wide range of Bragg angles starting at 8.59° and extending to 58.55°, with eleven prominent peaks representing planes such as (100), (002), and (101). This expanded diffraction profile at lower angles suggests the presence of residual biogenic compounds, which typically act as capping agents that limit crystal growth (Faisal et al., 2021) resulting in a smaller average crystalline size of 115.10 nm for the GS particles. In contrast, the CS ZnO nanoparticles show a more traditional crystalline structure with an average crystalline size of 195.88 nm, indicating a more aggressive growth process during chemical precipitation (Kumar et al., 2013). The smaller crystallite size and surface-active capping agents of the GS ZnO likely contribute to the enhanced flexural strength observed, by improving the interfacial compatibility between the inorganic filler and the polymer matrix (Sabir et al., 2014). Conversely, the larger crystalline size of the CS ZnO (195.88 nm) correlates with a higher surface hardness and a superior Young's modulus, as these larger, more rigid particles provide greater resistance to mechanical deformation and indentation within the waste polyethylene matrix (Talam et al., 2012).

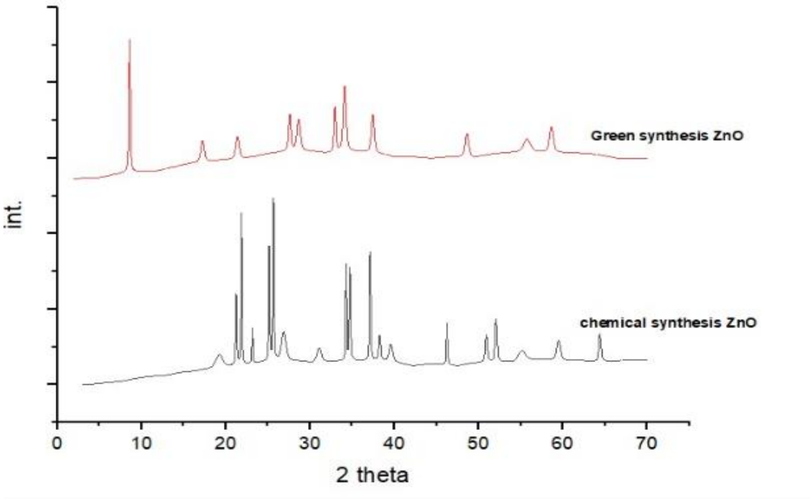

Figure 3. The X-ray diffractions (XRD) of chemically and green synthesized ZnO nanoparticles.

XRD patterns confirmed the crystalline wurtzite ZnO phase for both synthesis routes, with chemically synthesized nanoparticles displaying sharper diffraction peaks indicative of higher crystallinity and larger crystallite size, while green-synthesized ZnO nanoparticles exhibited broader peaks corresponding to reduced crystallite size and growth inhibition by organic moieties (Ying et al., 2022; Sarkar et al., 2023). These structural differences demonstrate that the synthesis route governs nanoparticle crystallinity, agglomeration behavior, and dispersion, which in turn influence interfacial interactions and the mechanical performance of waste polyethylene/ZnO nanocomposites.

3.3. Morphological Analysis of GS and CS ZnO Nanoparticles

The morphological analysis of the synthesized nanoparticles determined through scanning electron microscopy (SEM) and ImageJ software reveals distinct differences in grain size despite both following a spherical granular pattern. The green synthesized (GS) ZnO nanoparticles exhibit a spherically dispersed granular morphology with an average particle size of 27.48 nm. This size is significantly larger than the chemically synthesized (CS) ZnO nanoparticles, which also show a spherical granular morphology but with a much finer average particle size of 6.0 nm. SEM analysis revealed that CS synthesized ZnO nanoparticles possessed higher crystallinity but exhibited pronounced agglomeration due to their high surface energy, which limited uniform dispersion within the polymer matrix ((Fu et al., 2008; Dey et al., 2025). The larger crystal size of green synthesized particles is often attributed to the improved dispersion and reduced clustering as a result of organic capping agents derived from phytochemicals, which lowered surface energy and provided steric stabilization the complex nature of the biogenic capping agents which can create a thicker organic shell around the metallic core (Hanna et al., 2025; Abuzeid et al., 2023). While the CS ZnO nanoparticles are smaller and well-dispersed, they also exhibit a tendency to aggregate in nature due to their high surface energy (Talam et al., 2012). These morphological findings directly correlate with the observed mechanical properties; for instance, the finer particle size of the CS ZnO nanoparticles allows for more efficient filling of the polymer matrix voids, which contributes to the significantly higher Young's modulus as compared to the GS counterpart (Kumar et al., 2013). Conversely, the larger GS ZnO particles with their organic capping may promote better elastic compatibility under bending loads, explaining the superior flexural strength observed at high concentrations (Sabir et al., 2014).

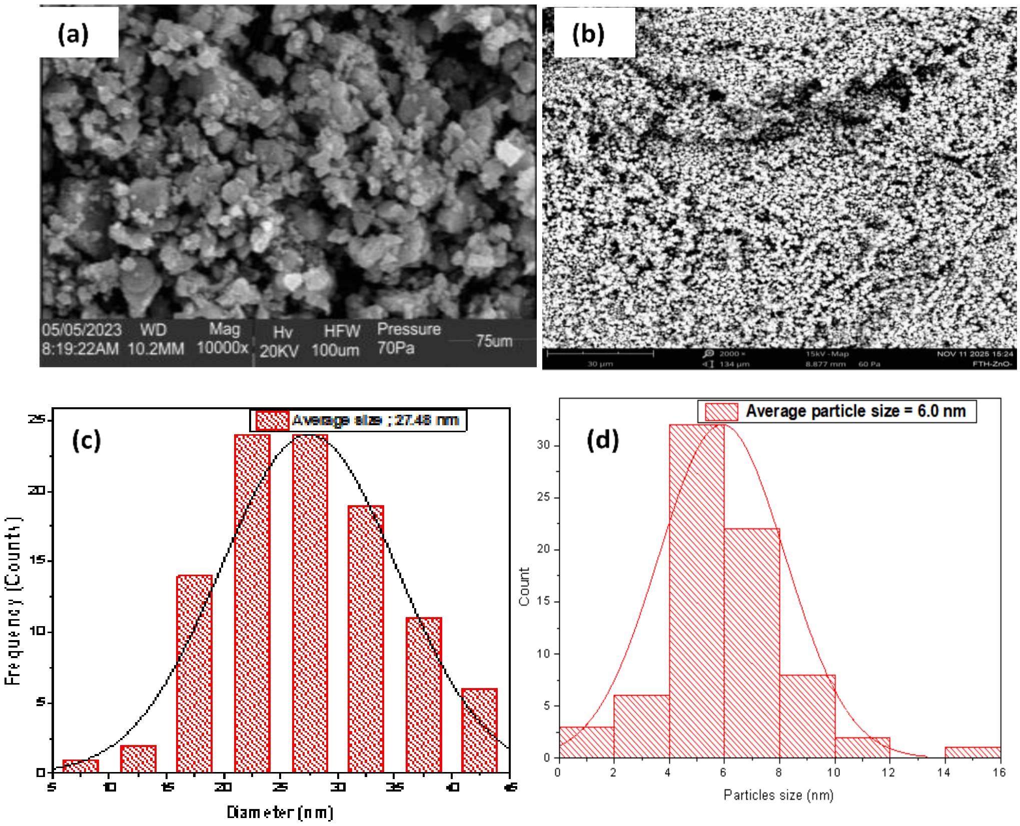

Figure 4. Morphology and particle size distribution of the ZnO nanoparticles prepared following different synthesis route. SEM images and the corresponding particle size distribution of the composite prepared using (a,c) GS ZnO nanoparticles, (b,d) CS ZnO

3.4. FTIR of GS and CS ZnO Nanoparticles

The spectrum above below the ftir spectra of green synthesized (GS-ZnO) and Chemical Synthesized (CS-ZnO). From the results, O-H bonding of alcohols, water and phenols was observed at 3397.72 cm^{-1} in the green synthesized (GS-ZnO) nanoparticles which further shifted to 3741.85 cm^{-1} chemicaly synthesized (CS-ZnO) nanoparticles.

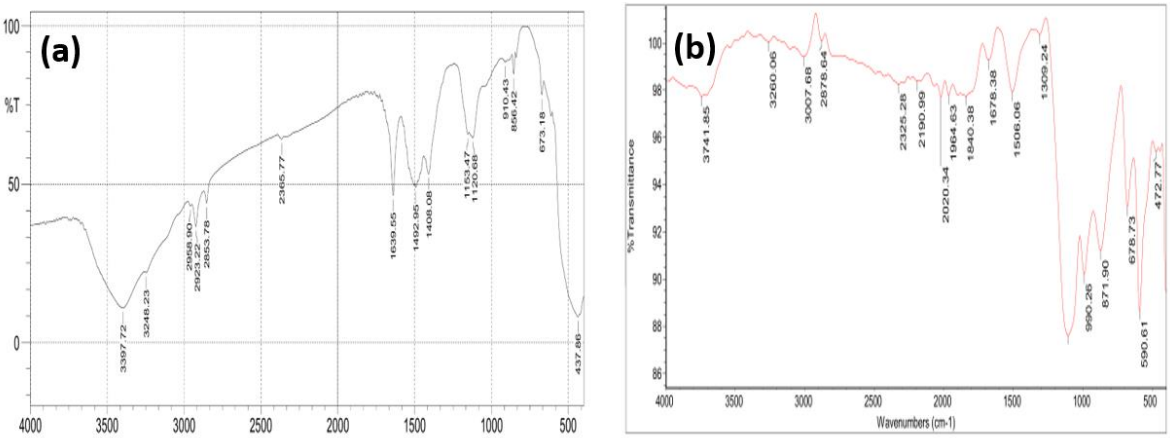

Figure 5. Fourier transforms infrared spectroscopy (FTIR)of the GS ZnO and CS ZnO nanoparticles

The peak observed from 2958.90 to 2853.78 cm^{-1} green synthesized ZnO and 3007.68 to 2878.64 cm^{-1} chemical synthesized ZnO nanoparticles correspond to C-H Sp^3 and Sp^2 stretching of symmetrical and asymmetrical vibrations of aliphatic $-CH_2-$ groups present in the phenolic compounds as reported(Sánchez-Pérez et al., 2023).The band at 1639.55 cm^{-1} GS ZnO and 1678.38 cm^{-1} CS ZnO showed the complex absorptions implying the existence of aldehydes, ketones, and esters characteristic functional groups of C = O stretching as reported by (Bekele et al., 2024). The peak at 1492.95 to 1408.08 cm^{-1}GS ZnO correspond to C=C and C-N of aromatic and amine present in the organic extract of the green synthesis. However, the chemical synthesized ZnO nanoparticles showed absorption band C-O from 1506.06 to 990.26 cm^{-1}are attached to $ZnCO_3$ formation (Salahuddin et al., 2015). The Zn-O prominent absorption was observed between 673.18 to 437.18 cm^{-1} GS ZnO and 678.73 to 472.77 cm^{-1}CS ZnO as shown by (Wang et al., 2024).

4. Conclusion

This study demonstrated that ZnO nanoparticles synthesized via chemical and green routes significantly influences the mechanical performance of waste polyethylene nanocomposites. Chemically synthesized ZnO enhanced hardness and stiffness from 97.0 N/mm² to 99.0 N/mm² 1 to 0.8 g ZnO nanoparticles, while green-synthesized ZnO provided superior flexural performance and sustainability benefits s shown from14.6 to 15.01 Mpa at 8 g ZnO nanoparticles respectively. Green synthesis offers an environmentally friendly and effective alternative for reinforcing waste polyethylene, contributing to sustainable materials development and plastic waste valorization.

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Competing interests

No computing interest

Author contributions

All authors contribute in writing- review and editing of the original draft, methodology, result interpretations, data analysis and funding acquisition.

Funding

No funding to declare

ACKNOWLEDGMENTS

The this work was supported by Department of Chemical Science Gombe State University of Nigeria, Department of Chemistry Abubakar Tafawa Balewa University, Bauchi State of Nigeria and National Research Institute for Chemical Technology, Zaria Kaduna State, Nigeria

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