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INVESTIGATION OF POLYLACTIC ACID AND NANOCLAY EFFECTS ON THE DEGRADATION PROPERTIES OF LOW-DENSITY POLYETHYLENE BIO-COMPOSITES

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ABSTRACT

This study investigated the influence of polylactic acid (PLA), nanoclay, and glycerine as compatibilisers on the degradation properties of virgin and waste low-density polyethylene (LDPE), a primary material in polyethylene bag production. Virgin and waste LDPE, PLA, and nanoclay were sourced locally and compounded using a two-roll mill and compression moulding to fabricate bio-composite samples. The moulded specimens were prepared according to ASTM standards for mechanical and degradation testing, including tensile, flexural, hardness, impact, water absorption, and soil burial tests. Results demonstrated enhanced tensile, flexural, and hardness properties in the bio-composites compared to the control (100% virgin LDPE). The incorporation of PLA, nanoclay, and glycerine facilitated strong interfacial bonding between the matrix and fillers, improving mechanical performance, water absorption, and biodegradation in soil burial tests. However, increased filler content reduced impact strength due to the brittle nature of nanoclay and PLA. These findings highlight the potential of PLA and nanoclay to enhance the mechanical and degradation properties of LDPE-based bio-composites for sustainable applications.

Keywords: *Low-density polyethylene, nanoclay, polylactic acid, glycerol, biodegradation, physico-mechanical properties*

INTRODUCTION

Poly(lactide) (PLA) possesses distinctive properties, including an excellent appearance, high mechanical strength, low toxicity, and favourable barrier characteristics, which have expanded its range of applications (Auras *et al.*, 2004). Numerous studies have investigated the properties of PLA both in its pure form and in combination with other polymers as blends or copolymers. Research conducted by Auras et al. (2004) examined the mechanical, physical, and barrier properties of PLA films, comparing them with those of polystyrene (PS) and polyethylene terephthalate (PET). However, PLA's relatively low glass transition temperature (Tg) restricts its use in thermally processed packaging. Due to its deformation behaviour and slow melting temperature, PLA is better suited for applications such as heat-sealing and thermoforming.

PLA films exhibit superior tensile strength compared to PS but lower than PET, while also possessing a lower melting point (Tm) and Tg than PET, making them more suitable for heat-sealing and thermal processing (Auras *et al.*, 2004). In terms of barrier properties, PLA demonstrates lower permeability coefficients for CO_2 and O_2 than PS, with values comparable to PET. Additionally, PLA exhibits the highest tensile modulus and flexural modulus when compared to PS, polypropylene (PP), and high-density polyethylene (HDPE) (Mbuge, 2017). The environmental concerns associated with non-degradable petroleum-based plastics have increased demand for biodegradable polymers as a means of mitigating ecological impact. PLA is widely utilised in producing loose-fill packaging, compost bags, food packaging, and disposable tableware. Furthermore, owing to its biocompatibility and biodegradability, PLA has garnered significant interest as a polymeric scaffold for drug delivery systems (Nicolas, 2019).

Polyethylene (PE), with the chemical structure $[-CH_2-CH_2-]_n$ (where n denotes the repeating monomeric unit), is synthesised in both low- and high-density forms. Low-density polyethylene (LDPE) exhibits a density range of 0.91–0.93 g/cm³ (Ploypetchara, 2014). PE-based products are ubiquitous in daily life, including food and pharmaceutical packaging films, wire and cable insulation, and piping. Consequently, global PE production is substantial, as it remains one of the most widely used polymeric materials. Polyethylene and polypropylene collectively account for approximately 92% of synthetic plastic production and are extensively employed in manufacturing plastic bags, disposable containers, bottles, and packaging materials (Ploypetchara, 2014). It is estimated that between 500 billion and 1 trillion plastic bags are consumed worldwide annually, disrupting ecosystems and contributing to severe environmental challenges associated with plastic waste management (Li, 2018). Waste plastics degrade into particulate matter via UV irradiation and weathering, increasing their surface area and mobility, thereby facilitating entry into the food chain and posing significant risks to living organisms (Li, 2018). The biodegradation of PE is influenced by its structural morphology, with amorphous regions being more susceptible to microbial degradation than crystalline domains. This review explores recent hypotheses and experimental findings concerning PE biodegradation.

Poly(lactic acid) (PLA) is widely regarded as an environmentally friendly material due to its biodegradability, making it suitable for medical devices, agricultural applications, and packaging (Gupta & Kumar, 2007; Sin *et al.,* 2013). PLA exhibits optimal degradation rates at or above its glass transition temperature (Tg ≈ 55–60°C).

The incorporation of nanoclays in food packaging has attracted considerable interest due to their ability to enhance mechanical and barrier properties (Chaudhary, 2020). Nanoclays are abundant, cost-effective, and biocompatible, with diverse morphologies and chemical compositions, rendering them advantageous over other nanomaterials in materials science (Abulyazied, 2021). These layered silicates consist of single layers measuring 0.7 nm in thickness, while double layers are approximately 1 nm thick. The interlayer spacing can be modified using surfactants to improve plasticity and swelling capacity. The surface properties of nanoclays are determined by nanosheet charge distribution, surface atom characteristics, and interlayer exchangeable cations. Owing to the isomorphous substitution of Al^{3+} or Mg^{2+} ions with silicon, nanoclay surfaces typically exhibit a negative charge (Abulyazied, 2021).

MATERIALS AND METHODS

Virgin Low-Density Polyethylene (Albarka Plastic, Kaduna), waste low-density polyethylene (water satchet bags) from Kaduna Polytechnic, Kaduna, Polylactic Acid (JHD, China), nano clay (NILEST, Zaria), Glycerine (J. Chemicals Limited, Kaduna). Two roll mills (Model: 5183 North Bergen, U.S.A), Wenzhouzhiguang Compression Moulding Machine (Model: 0557), Hounds Field Tensometer (Model: W6466), Izod Impact tester model: 6757 Pianezz-terino Italy), Vickers hardness testing machine (Model: MV1-PC), and Analytical Digital Weighing Balance.

Samples Preparation

Using the formulation table below, six composites were produced using the two-roll mill machine in counter counter-clockwise motion for 5 minutes at a temperature of 170°C, upon achieving a band and bank formation of the LDPE on the front roll, polylactic acid was introduced and allowed to mix for 3 minutes with effective cross mixing. Nanoclay was added gradually to the band, cross-mixed and allowed to mix for 3 mins, then glycerine (plasticiser) was added to the band. The composite sheets were labelled accordingly. The composite samples obtained from the mixing were placed in metal moulds and then onto the compression moulding machine for shaping at a temperature of 150 °C and pressure of 25 bar for 5 minutes with a dimension of 120mm x 100mm x 3.2mm, followed by cutting and preparation for further testing according to the ASTM standards for testing.

Table 1: Formulation and composition of LDPE/PLA/Clay composites

Sample	Low-Density Polyethylene (LDPE) (g)	Polylactic Acid (g)	Nano clay (g)	Glycerin (ml)
A	100	-	-	-
B	90	5	5	5
C	80	5	10	5
D	70	5	15	5
E	60	5	20	5
F	50	5	25	5

Methods

Determination of mechanical properties

Tensile test

The tensile strength test was carried out using the Monsanto Tensometer (model No: W6466) according to ASTM D-638. Dumbbell-shaped samples with gauge dimensions 50 mm x 10 mm x 3.2 mm were subjected to a tensile force and tensile properties such as tensile strength, Strain, and modulus for each sample.

Flexural test

The flexural strength test on the blends was carried out in accordance with ASTM D-790. The specimen measuring 100 mm x 25 mm x 3.2mm was placed on a support span horizontally at 80 mm gauge length, and a steady load was applied to the centre by the loading nose, producing three-point bending until the sample specimen failed. The maximum load (N) and the corresponding deflection (mm) were recorded as the sample specimen failed. The flexural strength and flexural modulus were calculated

Impact test

The impact test was carried out according to the standard specified ASTM D-156; the specimen was cut to a specimen dimension of 64mm x 12.7mm x 3.2mm, and 45° notch was inserted at the middle of the test specimens from all the produced blend samples. The impact energy test was carried out using the Izod Impact Tester (Resil impactor testing machine). The specimen was clamped vertically (IZOD) on the jaw of the machine, and a hammer of weight 1500 N was released from an inclined angle of 240°. The impact energy for the corresponding tested specimen was taken and recorded. Impact strength was calculated and recorded accordingly.

Hardness test

The hardness tests were carried out in accordance with ASTM D2240 using a Vickers Microhardness Tester. The sample was placed on the mounting stage, and the indenter was lowered until it came in contact with the sample at uniform pressure. The reading indicating resistance to indentation was displayed on the machine screen and recorded accordingly. This was repeated three (3) times at different positions on the sample, and the average hardness was taken using the equation:

$$Average\ hardness = \frac{1st + 2nd + 3rd}{3}$$

Water Absorption Test

The water absorption test was carried out on the composites. The samples were immersed in a container filled with water and then allowed to stay for 24 h, after which they were removed from the water, a dry towel was used to dry the samples and reweighed to note the final mass. This was carried out for 75 days at an interval of one week. The result obtained was used to calculate the percentage water absorption. Using the equation:

$$Water\ absorption\ (\%) = \frac{W_f - W_i}{W_i} \times 100$$

where:

W_f = Final weight of sample

W_i= Initial weight of sample before immersion in water

RESULTS AND DISCUSSION

Tensile results

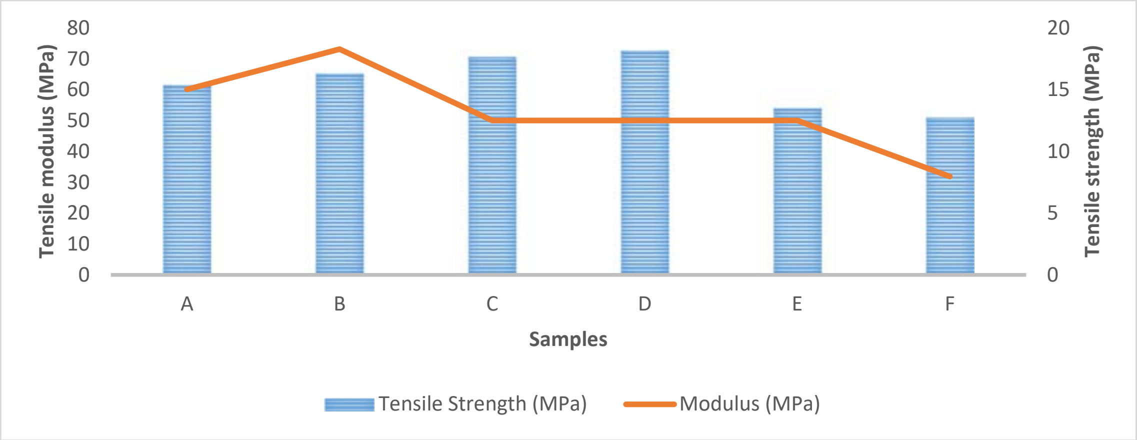

Figure 1: Result of the effect of natural fillers on the tensile strength and modulus of polyethylene composite

Figure 1 shows that the control sample A had a tensile strength of 15.38MPa. Sample B had a tensile strength of 16.31 MPa. Sample C has the tensile strength of 17.66 MPa. Sample D has the highest tensile strength of 18.20 MPa.

As the amount of filler content increased in samples E and F, a decrease in tensile strength was seen in sample E (13.50 MPa) and sample F had the lowest tensile strength of 12.75 MPa. Sample A tensile modulus was 60.07 MPa. From sample B to F, the sample tensile modulus decreased as the amount of filler content increased. Sample F become more brittle compared to sample B. This is because more clay is in the sample, hence making it harder and brittle. The nanosheet surface is hydrophobic owing to Si–O covalent linkages. The hydrophilicity of nanoclays can be achieved using exchangeable hydrophilic cations. Nanoclay particles can absorb water, and stacked silicate layers may swell. Incorporation of clay nanoparticles in polymers reveals improved mechanical, thermal, electrical, flame-resistant, and gas barrier properties (Calambas, 2021). The introduction of nano clay into bio-based food packaging materials decreases the elongation at break value of the films, and thus, overall elasticity of the nano composite is reduced by the inclusion of the nanomaterial. This is because nanoclay's stiffening and reinforcing properties create a network of polymeric phases and reduce the mobility of polymer chains, as observed by the studies of Radfar (2021).

Flexural test results

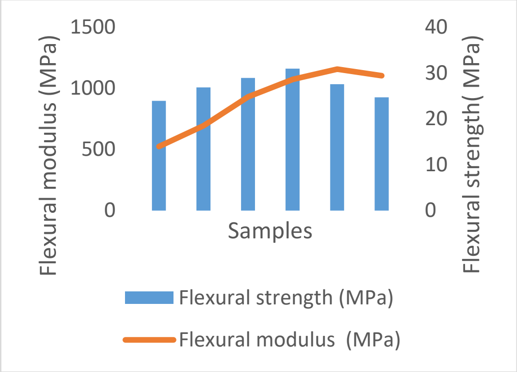

Figure 2: Result of the effect of natural fillers on the flexural strength and modulus of polyethylene composite

Figure 2 shows that sample A had a flexural strength of 23.92MPa, and a general increase was seen in the flexural behaviour (strength) up to sample D (30.94MPa). Sample E showed a decrease in flexural strength, 27.36 MPa followed by Sample F, which had a value of 24.67 MPa. The flexural modulus for sample A was 523.776 MPa, and the modulus kept increasing for sample B (692.76), C (929.67), D (1071.99) and E (1156.06). Hence, the addition of nanoclay and polylactic acid increased the flexural modulus.

Impact test

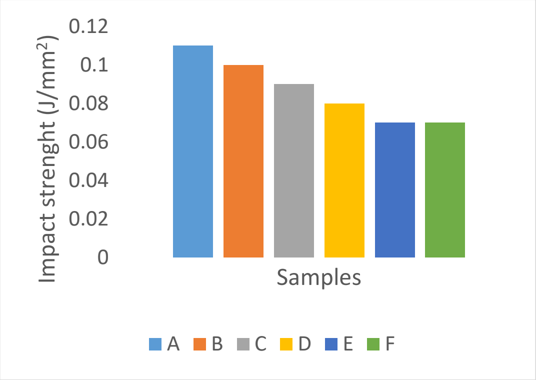

Figure 3: Result of the effect of natural fillers on the impact strength of polyethylene composite

Results showed a decrease in impact strength as seen from sample A to sample F. The results revealed that as the amount of nanoclay and polylactic acid content increased, it decreased the impact strength, which could be attributed to the brittle nature of nanoclay and polylactic acid. The presence of LDPE particles between PLA chains also increased the mobility of PLA chains, allowing them to deform easily (Radfar, 2020). Although the enhanced mobility of PLA chains might have a positive effect on PLA/LDPE blends in terms of impact strength properties, it has led to a reduction in the rigidity of the blends (Lu, 2005).

Hardness test

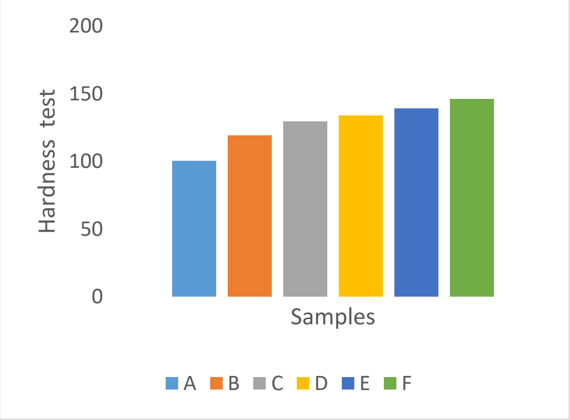

Figure 4: Result of the effect of natural fillers on the hardness of polyethylene composite

Results showed an increase in the hardness of the composite. Sample A has an average hardness of 106.3, while sample F has an average hardness of 145.9. This can be attributed to the good interfacial bonding between the PE / nanoclay / Polylactic acid using glycerine as a compatibiliser. The primary purpose of incorporating a nanoparticle (reinforcement agent) into a biopolymer matrix is to improve the mechanical properties of the packaging material (Emadian, 2017).

Water absorption

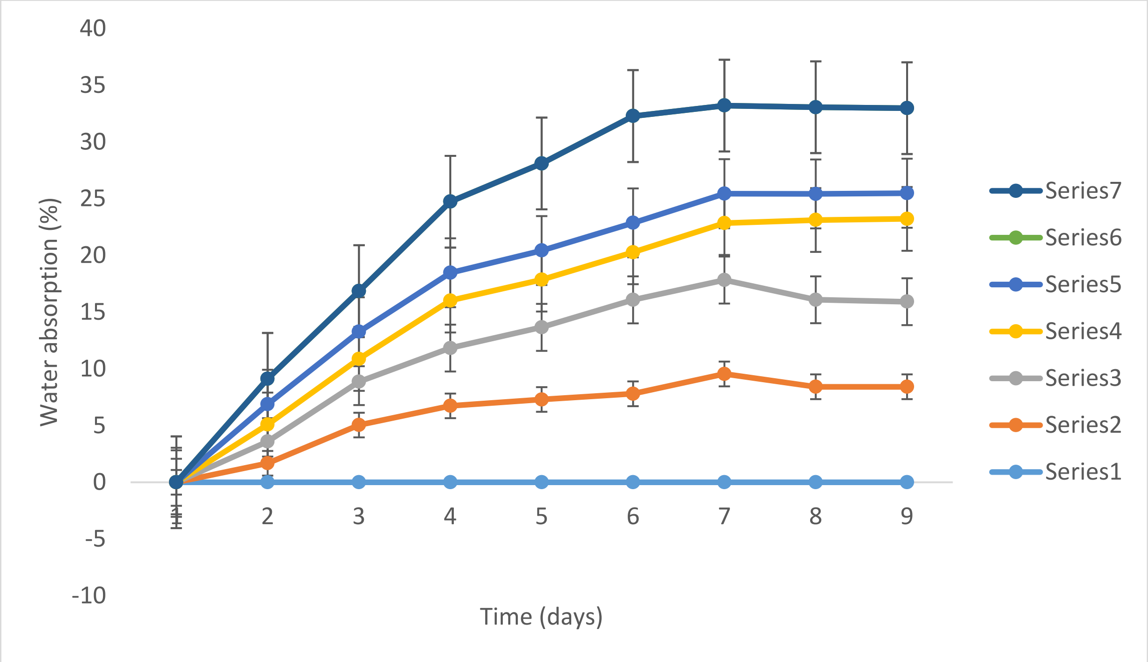

Figure 5: Result of the effect of natural fillers on the water absorption properties of polyethylene composite

Results showed that all samples absorbed water every week due to the hydrophilic Polylactic acid and clay. Samples B, C, and D showed maximum water absorption up to forty-two days (7 weeks) and a decline in the water absorption rate. Sample E, which contains 25% nano clay, kept absorbing water even after 75 days, as studied by other scholars. The water absorption capacity of nanoclays depends on the number of exchangeable cations in the interlayer.

PLA, a biodegradable and compostable polymer, was used to evaluate the biodegradable nature of nanoclay. The results of the biodegradation experiments demonstrate that the biodegradation phase of nanoclay-containing films began earlier than that of pure PLA films (Chadha, 2022). The incorporation of clay nanoparticles into polymers reveals improved mechanical, thermal, electrical, flame-resistant, and gas barrier properties (Abulyazied, 2021). The high surface area and nanometric size of the clays enable them to form an efficient interaction for transmitting tensile stress, and nanoclays reduce the rate of biodegradation of the packaging materials. Nevertheless, most importantly, when considering the limited studies performed, the migration levels of nanoclay are very low, while it is non-toxic. A higher concentration of nanoclay film (1.5%) results in the production of aggregates, which degrade the mechanical characteristics.

CONCLUSION

A bio-composite of low-density polyethylene, polylactic acid, nanoclay, and glycerine was developed to enhance physico-chemical and degradation properties for food packaging. Sample D (70% LDPE, 5% PLA, 15% nanoclay, 5% glycerine) showed the highest tensile and flexural strength due to strong interfacial cohesion and PLA's superior properties. Hardness and water absorption increased with nanoclay, while impact strength decreased. Nanoclay and PLA enhanced biodegradation, with nanoclay degrading more rapidly. The composite suits applications like toys and tabletops, but further research is needed for cost-effective, non-toxic food packaging.

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