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Mechanical and Water Barrier Properties of Inhomogeneous Clay Nano-Particles Reinforced Thermoplastic Starch

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Abstract: *This research investigated the development of biodegradable bioplastic as a possible replacement for petroleum-based plastics, which constitute a serious environmental hazard. These hazards include but are not limited to flooding resulting from blocked sewage and danger to aquatic life in marine environments. Solution casting method was used to blend inhomogeneous kaolinite clay nano-particles with distilled water, starch, dilute acetic and nitric acids to produce different compositions of thermoplastic starch (TPS)/Clay composites with clay reinforcements ranging from 2.5 to 10 wt.%. The composites were characterized using X-ray diffraction (XRD), and the mechanical and water absorption properties were determined. The result revealed a 9-fold improvement in the tensile strength (0.72 MPa), flexural strength increased 5-fold (3.34 MPa), and hardness increased 2-fold (23.56 HVN) as well as a reduction in water absorption by 3-fold (6.63%) when compared to the control. Furthermore, the 10 wt.% clay content composite showed the highest mechanical properties. The significant improvement in the listed properties was attributed to a reduction in crystallinity and the formation of new chemical bonds between the thermoplastic starch and the nano-clay. It was observed that the properties of the composites can be further enhanced if a synchronized machine blender (such as an extruder) is employed.*

Keywords: *Biodegradable, Thermoplastic Starch, Inhomogeneous, Aluminosilicate Clay, Nanoparticles.*

1. INTRODUCTION

Petroleum-based plastics have become a significant contributor to the pollution of our environment due to their non-biodegradable nature as well as the highly polluting extraction process of crude oil, which is the primary raw material for producing these types of plastics [1]. These challenges have led to a growing interest in using more eco-friendly plastics, such as plant-based polymers like starch. Starch is a biodegradable, bio-based polysaccharide consisting of linear amylose and branched amylopectin polymers. Both polymers consist of chains composed of α-D-glucopyranose residues connected by α-1, 4-glycosidic bonds, while the chains are connected to each other by α-1, 6-glycosidic bonds, which creates branches in the starch polymer [2]. Most plants synthesize starch via photosynthesis and is thus an abundantly available, renewable, and cheap biopolymer [3]. However, naturally occurring starch is limited in its applications due to its poor mechanical properties and hydrophilicity [4]. To overcome these issues, starch is further processed by mixing with plasticizers such as glycerol, citric acid, urea, sorbitol, or glycerine, which reduces the internal hydrogen bonds between the starch polymer chain while increasing free volume and molecular mobility [5-7]. This is done in the presence of elevated temperatures and shear forces to improve the polymer's plasticity and thermoplastic properties of the polymer thus yielding the thermoplastic polymer called thermoplastic starch or TPS.

Thermoplastic starch, though an improvement to starch polymer, also has its own physical and mechanical property deficiencies, such as sensitivity to ambient moisture and low strength at low temperatures [8, 9]. To reduce these flaws, TPS is often blended with other synthetic polymers like polylactic acid, polystyrene, and polypropylene [10, 1, 11], which lowers its biodegradability and increases its cost.

Another method of improving TPS involves blending TPS with nanocomposites which are multiphase solid materials where one of the phases has one, two, or three dimensions less than 100 nm. The nanocomposites we are referring to in this case are finely ground aluminosilicates which are minerals composed of aluminium, silicon, and oxygen, plus countercations. They have a structure in which silicate tetrahedrons and aluminium hydroxide octahedrons are arranged in layers to form sheet-like structures (phyllosilicates) or in a 3-dimensional lattice (tectosilicates) [12]. The presence of hydroxyl groups in both the TPS and the nano-clay particles and their matching surface polarities enables them to blend [4, 13].

Various studies have been carried out on this relatively new type of TPS composite, Hasanul et al. [9] used a solution casting method to reinforce TPS with small amounts (2 to 10 wt.%) of montmorillonite, hectorite, and kaolinite clays separately and obtained mechanically improved composites with the most optimal properties obtained from the 10 wt.% montmorillonite composites with improved tensile strength of 44 KPa and toughness of 106 KJ/m^{3,} as well as a drop in water absorption to 55%. Ren et al. [14] achieved a more promising result, they used a Haake batch mixer to blend 3 to 7 wt.% of halloysite clay with TPS and obtained an overall best result from the 7 wt.% halloysite reinforced composite with a tensile strength of 10.87 MPa and water absorption of 7.5%. In the case of Fekete et al. [15], an improved composite with a tensile strength of 19 MPa and water vapour penetration of 7.5x10^{-15} (g/msPa) was obtained after blending 15 m/m% montmorillonite clay with TPS using a sonicator ,solution casting and a climate chamber. Similar improvements were achieved by Alikarami et al. [16], Zhang et al. [17] and Kwasniewska et al. [8]. Although the studies mentioned above led to improvements in the mechanical properties of the TPS, the methods came with some challenges, such as compatibility and processability issues, mainly due to uneven dispersity of the nanocomposites within the TPS matrix. Other researchers in this field, like Calambas et al. [19], Aouadi et al. [20], Behera et al. [21] and Wang et al. [22] introduced other polymers like polyvinyl alcohol, polystyrene, polyethylene, and polyester into the TPS/clay mix, which improved their compatibility and thus their mechanical and barrier properties but which ultimately reduced their biodegradability as well as increased the cost and complexity of their production.

In this study, rather than use pure or modified clay as has been widely used, readily available inhomogeneous (impure) clay, as well as a simple and relatively affordable solution casting methodology to develop Thermoplastic Starch/clay composites, were used. The objective, therefore, is to determine afterward if the inclusion of this type of clay particles could also improve the mechanical properties and reduce the water absorption of the composites.

2. MATERIALS AND METHODS

2.1 Materials

The raw clay was sourced from Oregun Clay Company, Ikeja, Lagos state, Nigeria. Irish potatoes were bought from a local market in the Ojo local government area of Lagos state, and mostly defective potatoes and potato peels were used in the starch extraction process. Glycerol, white vinegar (acetic acid), and nitric acid were purchased from Uche Scientific Co. Ltd, Bariga, Lagos state.

2.2 Milling of Clay

The raw clay was milled for 24 hours to a nanometer particle size range using a Planetary Ball Mill (model JC-QM-2). The milling sequence is presented in Figure 1 a, b, and c.

(a) Unmilled Clay (b) Ball Mill (c) Milled Clay

Figure 1: Sequence of clay milling process

2.3 Extraction of Starch from Potatoes

The potatoes were washed thoroughly with potable water, grated, mixed with water, and blended. After that, the blended mixture was strained through a 60 mesh (0.25 mm aperture) sieve, and the remnant in the sieve after straining was discarded. At the same time, the strained solution was collected in a transparent plastic container and allowed to settle for 1 hour.

The settled solution (now divided into 2 layers) was decanted carefully to remove the water, leaving the starch that had settled at the bottom of the container. The starch was mixed with distilled water, left to settle for another 30 minutes, and then decanted again to remove the separated water.

The leftover starch in the container was then oven-dried. The starch extracted is white and powdery when dried and ground, as shown in Figure 2 c.

2.4 Preparation of Thermoplastic Starch (TPS)

The preparation process is a modified version of that used in [23] involving simple solution-casting. A mixture of one-part (1 tablespoon or 15 ml) starch and seven-part (7 tablespoon or 105 ml) of distilled water was mixed in a beaker. Then, two teaspoons or 10 ml of glycerol were added to the mixture, 10 ml of vinegar (acetic acid) was added, and the whole mixture was stirred thoroughly. The solution was then heated using a Hotplate (Stuart UC152) at 250°C while continuously stirred.

(a) Potatoes Peels (b) Extraction Tools (c) Extracted Starch

Figure 2: Sequence of starch extraction process

When the viscosity of the mixture started increasing, 1.25 ml of the 0.5 molar HNO_3 solution was added to the mixture to assist the vinegar in the chemical breakdown of the polymer chains in starch to enable the glycerol to gelatinize the starch and also increase the fluidity of the bioplastic for easy casting into moulds of known dimensions. The mixture was continuously stirred until the mixture became transparent, which occurred in about 10 minutes.

The mixture was then poured into the mould and allowed to cool to room temperature until it was scorched and solidified. These plain TPS bioplastics served as our control samples. Table 1 shows the mixing ratio used to produce the plain TPS.

Table 1: Composition of the thermoplastic starch (TPS) Solution

Component	**Quantity(ml)**
Starch	15
Water	105
Glycerol	10
Acetic acid	10
Nitric acid	1.25

2.5 Preparation of the TPS/Clay Composite

A mixture of 15ml starch,105ml distilled water,10ml each of glycerol and vinegar was mixed in a beaker, then a specific amount (in weight percent) of nano clay powder was added to the mixture, also, 1.25ml of the 0.5 molar solution of the nitric acid was added to the mixture during heating. The resulting mixture was stirred continuously as it was heated at 300°C till the mixture became viscous and sticky (gluey), all of this took about 15 minutes.

The mixture was then poured into the moulds to dry and solidify at room temperature for at least two weeks. Four different sets of samples of this TPS/Clay Composite were produced, with concentrations of clay of 2.5 wt. %, 5 wt. %, 7.5 wt. % and 10 wt. % respectively. Table 2 shows the weight percentage composition of the nano clay powder and TPS solution used in preparing the five sets of bioplastic samples and Figure 3 shows the production sequence of the bioplastic samples.

Table 2: Clay and thermoplastic starch solution percentage composition

Clay reinforcement addition (wt.%)	**TPS solution (wt.%)**
0	100
2.5	97.5
5	95
7.5	92.5
10	90

(a) Heating and mixing of solution (b) Casted samples in Moulds (c) Dried Plain TPS and TPS/Clay Composites

Figure 3: Sequence of bioplastics production process

2.6 Sample Characterizations

The following tests procedures were carried out on the prepared bioplastics to determine their mechanical, barrier and structural properties.

i. **Tensile Properties:** Tensile properties were measured using a Universal Testing Machine (Instron machine series 6800), test samples had dimensions of 25 mm by 6 mm by 2 mm. Four samples each were tested for the plain TPS and the four different TPS/clay composite produced respectively and the average, as well as the standard deviations, were calculated.

ii. **Flexural Properties:** The flexural properties were measured using a Universal Testing Machine (Instron machine series 3369), a 3-point test method was used, and test samples had dimensions of 65 mm x 25 mm x 3 mm. Four samples each were tested for all the sample compositions and the average as well as standard deviations was calculated.

iii. **Hardness:** The hardness values of the samples were measured using a Matsuzawa MMT-X Vickers microhardness tester (Matsuzawa MMT-X), three micro indentations each were measured per sample, and the averages and standard deviations were calculated.

iv. **Water Absorption Test:** The water absorption tests were carried out using a modified version used by [24], where dried 2 cm^2 strips of each of the five different samples produced were immersed in five different containers having 200 ml of distilled water for 24 hours, after which they were removed and weighed. Then, the water absorption was calculated using Equation (1)

$$\text{Water Absorption (\%)} = \frac{(Wf-Wi)100}{Wi} \quad (1)$$

Where, Wi = weight of the sample before immersion in water

Wf = weight of the sample after immersion in water

v. **X-ray Diffraction (XRD) Analysis:** X-ray diffraction (XRD) analysis was carried out on the nano-clay powder as well as the developed bioplastics using an X-ray diffractometer (Rigaku Miniflex 600) (40 kV, 50 mA) at a scanning rate of 0.5°/min.

3. RESULTS AND DISCUSSIONS

3.1 Macrostructure Inspection

While drying the cast samples at room temperature and under direct sunlight, it was observed that the plain TPS bioplastic was prone to cracking and tearing much more than the clay composites both at thicknesses below or greater than 2 mm.

The thoroughly dried plain TPS was much more transparent at thicknesses < 2 mm and became more translucent as the thickness increased, while all the clay composites were opaque at thicknesses above 2 mm, but the 2.5 wt.% and the 5 wt.% clay composites were slightly translucent at thicknesses < 2 mm.

It was also observed that both the thoroughly dried plain TPS and the clay bioplastics composites had varying degrees of affinity for ambient moisture, as evidenced by the deposition of water droplets on their surfaces when exposed to cool and damp environments, thus requiring all the samples to be put inside sealed plastic containers (the plain TPS sample had the highest affinity while the 10 wt.% clay composites had the lowest).

It should be noted that the dimensional and structural stability of the samples did not seem to be affected by the water droplets, signifying that not much moisture absorption was going on, which meant the samples probably had good water barrier properties. The dried samples were reduced in size and thickness by about 40% on average compared to the just-cast (wet) samples.

3.2 Tensile Properties

The tensile properties of the pristine TPS plastic and the TPS/Clay composites with different clay contents are given in Figures 4 and 5. It can be seen that the tensile properties of all the composites (except elongation at break) are better than that of the plain TPS (control) sample, although at varying degrees with TPS/Clay (90/10 wt.%) composite having the highest tensile strength of 0.72 MPa and TPS/Clay (92.5/7.5 wt.%) composite the lowest of 0.19 MPa. This improvement could be attributed to the insertion of the nano-clay particles among the TPS matrix, thereby forming chemical bonds due to polar interactions between the polymer and the clay ions [17]. Also, the layered and plate-like microstructure of the clay enables them to easily slide above each other, which improves the tensile strength [15].

The elongation at break of the control (plain TPS) was more than that of all the composites, possibly due to the higher influence of glycerol on the control sample than on the composites [24]. Also, it is believed that there are insufficient interactions and bonding between the TPS and the clay due to the inhomogeneous nature of the clay and the simple solution casting methodology adopted.

3.3 Flexural Properties

The flexural properties of the pristine TPS and the TPS/clay nanocomposites of different clay contents are given in Figure 6. Like the tensile properties, the flexural properties of all the composites were better than those of the pristine TPS, with the 10 wt.% clay composites having the highest flexural strength of 3.34 MPa.

This could be attributed to the plasticizing effect of the clay in the TPS matrix [19]. The flexural modulus of the 10 wt.% clay composite was the highest, indicating the highest resistance to bending of all the samples (pristine TPS inclusive). This could be a result of it having the highest percentage of clay or due to the form of dispersion of clay in the TPS matrix, which is through exfoliation [14].

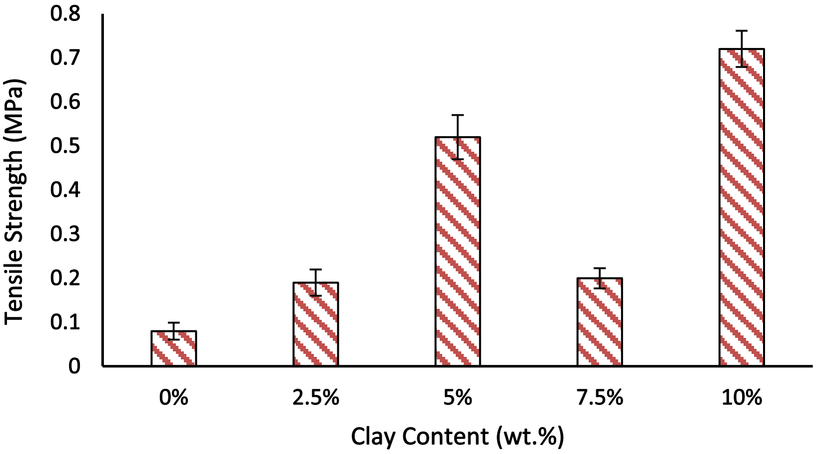

Figure 4: Graph showing the tensile strengths of TPS/clay nanocomposites.

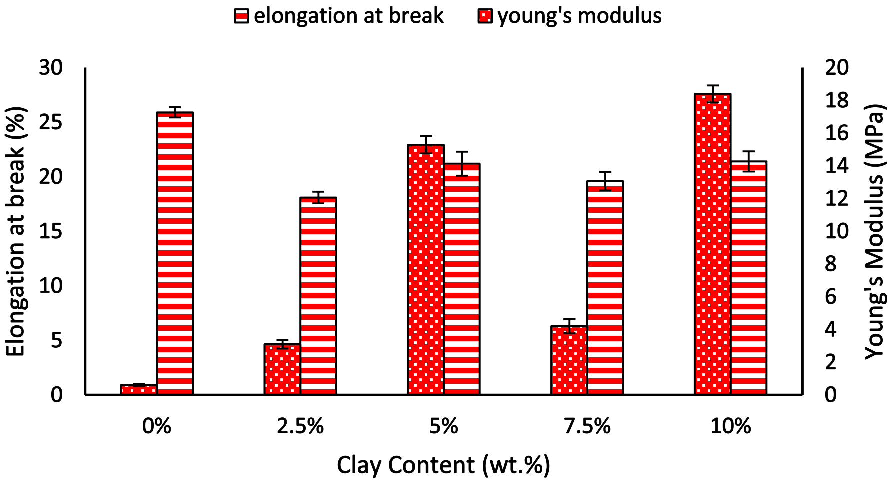

Figure 5: A plot of elongation at break and young's modulus of TPS/clay nanocomposites

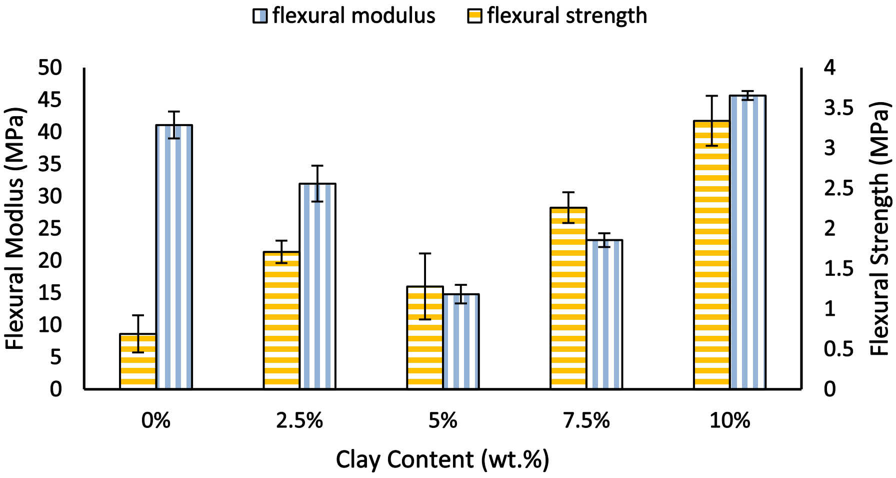

Figure 6: Chart of the flexural strength and the flexural modulus of TPS/clay nanocomposites

3.4 Hardness Properties

The hardness test results of the pristine TPS and the TPS/clay nanocomposites of different clay contents can be seen in Figure 7. Again, just like the tensile and flexural properties, the results of all the composites were better than those of the plain TPS, and the hardness value increased with increasing clay content. This could be attributed to the increased density of the composites as a result of adding the nano clay particles as well as the various hydrogen bonding and electrostatic attractions formed between the clay and the TPS matrix, as well as the layered structure of the phyllosilicate minerals of the clay which forms an effective barrier and reinforces the surface as well as the interior of the nanocomposites reducing any impact of the forces applied [17].

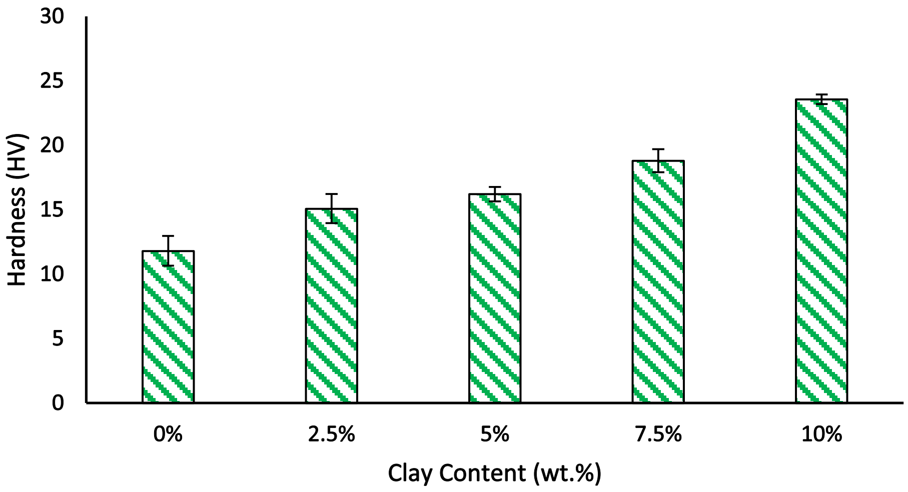

Figure 7: Hardness values of TPS/Clay nanocomposites

3.5 Water Absorption Properties

The weight increase of the samples (in percentages) after immersion in distilled water for 24 hours is shown in Figure 8. It is observed that the water absorption rate of all the TPS/Clay composites was less than that of the plain TPS sample (control), indicating that the inclusion of clay nanoparticles improved the barrier properties of the composites, although by various percentages with the 5 wt.% clay composite composites had the least water absorption of 6.67%, while the 7.5 wt.% and 10 wt.% clay composites had the highest of 13.33%. This could be due to the different levels of dispersion of the clay particles (by exfoliation only) in the TPS matrix. These results are higher than those in the literature [9, 19], although it must be said that the water absorption of the control sample was also relatively low when compared to those in the literature, probably due to its relatively high crystallinity [25].

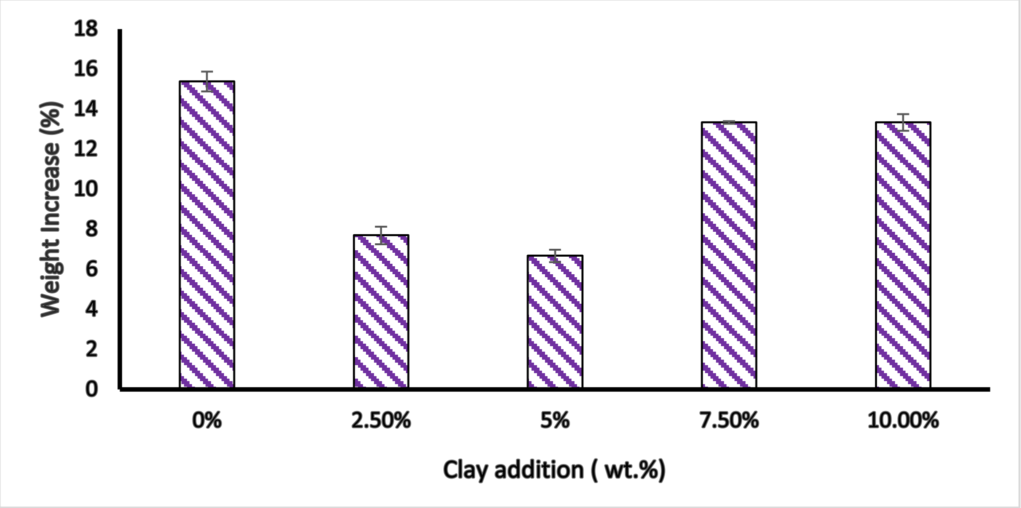

Figure 8: Percentage weight increase of the TPS/clay nanocomposites after 24 hours of immersion in water

3.6 XRD analyses of the clay powder, TPS, and TPS/clay nanocomposites

A chart showing the XRD chart patterns of the clay nanoparticles, starch powder, prepared plain TPS (control), and the prepared TPS/Clay nanocomposites (with different wt.% clay contents) can be seen in Figure 9. The plain TPS has a semicrystalline pattern with its highest peaks at angles of 38° followed by 22.5° and some other less intense crystalline peaks and broader amorphous peaks. This is possibly due to the use of dilute acids in breaking down the starch polymer branched chains, mostly in amorphous amylose polymer regions, which led to more closely packed polymers. Also, the use of a relatively large amount of water led to the formation of weak hydrogen bonds with the starch polymers that were broken on drying of the samples leading to the reformation of modified starch granules, thereby increasing the crystallinity and brittleness of the plain TPS [24]. The XRD patterns for the 2.5 wt.% and the 5 wt.% clay composites showed no crystalline peaks except low and broad amorphous peaks at diffraction angles within the 10° to 30° range. This could be attributed to random dispersion by exfoliation (separation into smaller bodies or platelets from larger bodies) of the TPS matrix's clay particles and the splitting of bonds of the starch polymers by the clay particles (bio cleaving) in the TPS matrix which reduced the crystallinity of the composites [21]. The XRD patterns for the 10 wt.% and 7.5 wt.% clay composites also had mostly amorphous peaks but also showed mild crystalline peaks characteristic of the highest crystalline peak of the clay powder at angles of 27.2° and 27.1° respectively, indicating that there was no bonding of the clay particles and the TPS materials by intercalation but only by exfoliation. It also indicated a slight phase separation of the clay and the TPS matrix probably due to the uneven dispersion of the clay in the TPS matrix leading to uneven bonding or interaction between the clay and the TPS materials [9, 19]. Chemical reactions or bonding (primarily by hydrogen and oxygen bond formation) took place between the clay nanoparticles and the plain TPS solution during mixing with the formation of new compounds or phases in the composites. These chemical bonding led to improved mechanical and barrier properties of the composites compared to the plain TPS plastic.

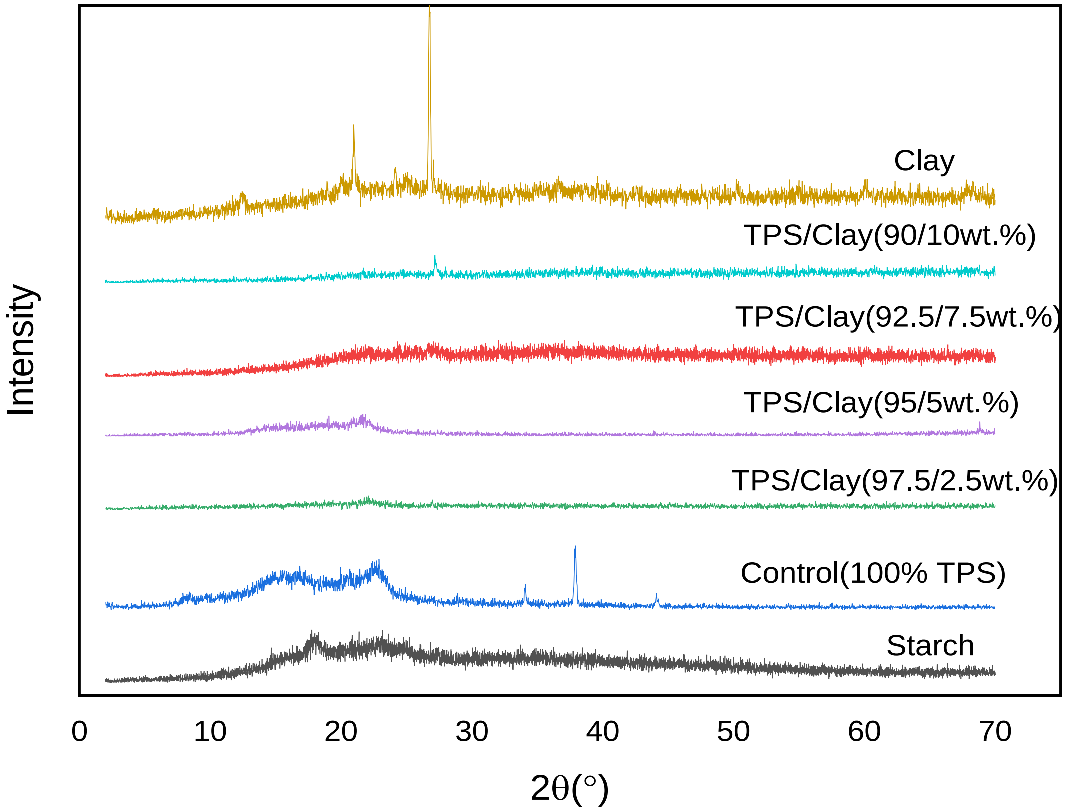

Figure 9: XRD patterns of the clay powder, starch powder, control sample, and all the composite samples

4. CONCLUSION

From this study, the following conclusions can be drawn:

It is possible to use inhomogeneous kaolinite clay nanoparticles to reinforce thermoplastic starch bioplastics using simple solution casting methodology and get an improved composite.

The tensile strength of the composite increased 9-fold (0.72 MPa), the Flexural strength of the composite increased 5-fold (3.34 MPa), the hardness values of the composites increased 2-fold (23 HV), and the water absorption of the composites reduced by over 2-fold (6.67%).

The XRD analysis revealed a reduction in crystallinity of all the composites suggesting a reduction in brittleness which accounted for their improved mechanical properties, although the analysis also revealed uneven dispersion of the clay in the TPS matrix and no bonding by intercalation possibly due to the methodology adopted.

The 10 wt.% clay composites had the most optimal properties of all the composites.

Further research still needs to be carried out on improving the mechanical and barrier properties of these composites even more as well as better and affordable mixing methodology for the clay nanoparticles and the TPS materials to make it viable for low income countries that don't have access to advanced equipment for TPS production.

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