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The effect of surface treatment on the mechanical properties of Poly(lactic acid)/Guineacorn husk particulate Bio-composites.

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Abstract
Guineacorn husk particulate filled poly(lactic acid) bio-composites were prepared by compounding with a single screw extruder and then injection moulded. The Guineacorn husk particulate (GHP) filler was treated with a combination of alkali and silane treatments (ALKSIL) and the content was varied from 0 – 40% at 10% intervals. The effect of the surface treatment on the mechanical properties of the biocomposites was investigated. The results showed that the tensile and flexural strength properties of the bio-composites produced from treated filler were greatly improved by 10% and 43% respectively as compared to the bio-composites produced from untreated filler at 40% GHP content and these properties decreased with increase in filler content. On the other hand, tensile and flexural moduli properties increased with filler loading with those of the treated filler bio-composites being respectively 12% and 17% higher than the untreated filler bio-composites. Scanning electron microscopy (SEM) of tensile fractured samples showed some filler pull out and also good bonding between the filler and matrix upon surface treatment.

Keywords: Guineacorn husk particulate; Bio-composites; Poly(lactic acid); surface treatment; Filler.

1. Introduction
The use of plastics for wide range of applications such as packaging, transportation, consumer products etc. cannot be overemphasized. These plastics are made from petroleum resources which are considered to be limited and finite. The increase in the use of plastics over the years has resulted in an increase in plastic wastes since they are non-degradable and their litter especially in the oceans and seas pose a major threat to birds, fish and other animals [1].
The rising concern on the environment on the dangers posed by the utilization of these commodity plastics led to the increased interest in developing polymers and composites from renewable resources. These bio-based plastics are sustainable, largely biodegradable, they will reduce our dependency on the finite fossil fuels and are reported to be CO_2 neutral since they decrease the amount of CO_2 released in the atmosphere. Other benefits obtainable from these bio-based plastics apart from less greenhouse emission and biodegradability are that the base materials are renewable and sustainable [2-4].

A promising bio-based plastic is poly(lactic acid)(PLA), a linear aliphatic polyester which is synthesized by ring-opening polymerization of lactide and lactic acid obtained from the fermentation of corn, potato, sugar cane etc. [1, 2, 4-6]. PLA can be similarly processed as polyolefins (PP,PVC,PS,PE) and other thermoplastics. It has attractive features such as clarity, good mechanical properties, flavour and aroma barrier capability, good heat sealability but brittle and more expensive than the commodity plastics. These properties can be modified through the use of lignocellulosic or agro-waste materials that would reduce the cost without sacrificing biodegradability and by using impact modifiers such as Polyethylene glycol (PEG), Biomax strong, citrate, triacetine etc. to improve the impact and elongation properties [2, 5, 7-10].

Lignocellulosic or agro-waste materials as fillers in fiber or particulate form in biobased polymers such as PLA to form bio-composites have several advantages such as low density, low cost, renewability, environment friendly, low energy consumption, low abrasiveness, abundance and most importantly, biodegradability [2, 3, 11-14]. The various kinds of lignocellulosic materials that have been used as reinforcement in biopolymers include kenaf fiber and powder [15, 16], cotton and ramie fibers [17], rice husk flour [18], wood flour [19], bamboo flour [12], coir [20], spruce husk, olive husk and paper flours [21] and a host of others.

Guineacorn husk is an agricultural waste material which is obtained from guineacorn (Sorghum bicolor) plants after the harvest season mostly in the Northern part of Nigeria. Most of the husk is left on the farmland to rot or is burnt which is a source of environmental pollution while a minute quantity is used as feed for animals especially in the rural areas. Therefore, this study is aimed at using this huge amount of waste which is generated yearly and mostly unutilized to produce agro-waste-filled bio-composites to give it an industrial application as well as generate wealth.

As with most lignocellulosic materials which have polar hydroxyl groups on their surface, the husks too are not left out. As a result, lignocellulosic materials in hydrophobic matrices exhibit poor mechanical properties due to poor interfacial adhesion between the fillers and the polymers. The adhesion has been reported to be improved by surface modifications such as treatments by silane, alkali, esterification, peroxide, permanganate [22].

In this article, the effect of a combination of alkali and silane treatments on the mechanical properties of PLA/Guineacorn husks particulate (GHP) filler bio-composite was investigated. In order to improve the impact properties, Biomax strong was blended with PLA.

2. **Experimental**

2.1. *Particulate filler preparation*

The guineacorn husk was thoroughly washed with detergent to remove all forms of dirt including stones and sand. It was then dried in the sun after which it was oven dried at 105°C for 6hrs. The dried husks were then ground using a laboratory mini-crusher with a sieve of 0.5mm size attached to its outlet. The ground particulates were soaked in hot water for 24hrs to remove any volatile matter and afterwards, they were dried in the laboratory for three days before any treatment was carried out. The dried particulates was termed untreated (UNTRD)

2.2 *Treatment*

The particulate filler was given a combination of alkali and silane (ALKSIL) treatment. For the alkali treatment, the particulates were soaked in 5% w/w NaOH concentration for 24hrs at room temperature [24]. The particulate filler was then rinsed repeatedly with distilled water containing little quantity of acetic acid until no trace of NaOH was left which was confirmed by determining the pH of the remaining water. It was then dried in air for two days and then oven dried at 80^{o}C for 24hrs. The alkalized particles were treated with 3-Aminotripropylethoxysilane (APS) first, by hydrolysing 5% APS in alcohol (methanol) - water mixture (60-40) and a little quantity of acetic acid was added to adjust the pH of the solution to 4.5. The particles were soaked in

the solution for three hrs after which it was repeatedly washed with distilled water and then dried in the air for three days then it was oven dried at 80^{o}C for 24hrs.

2.3 *Compounding and Extrusion Process*

Compounding was performed using Brabender single screw extruder with temperature profile of 160/175/175/165^{o}C from hopper to die at screw speed of 40rpm. The filler content was varied from 0 to 40% at 10% interval while the Biomax strong was 5% by PLA fraction. Pure PLA and 5% Biomax (PLABM) served as the control in this study. The composites were extruded and collected in a water tank with continuous flow of water. The extruded strands were pelletized using a type 881207 granulator. The pelletized materials were heated in an oven at 50^{o}C to remove moisture before storing in a desiccator prior to injection moulding. All the materials used were properly dried before compounding.

2.4 *Injection Moulding*

A BOY 22M injection moulding machine was used to produce tensile test specimens according to ASTMD638, flexural test bars according to ASTM D790 and Impact specimens according to ASTM D256. The temperature profile used was145/180/180/165^{o}C, mould temperature was 30^{o}C with 30 seconds cooling time. All specimens were conditioned in a Binder KBF240 humidity chamber at 23^{o}C and 50% Relative humidity for 40hrs before testing.

2.5 *Mechanical Testing*

Tensile and flexural tests were conducted according to ASTMD638 and ASTM D790 respectively with an Instron 5982 machine. The cross head speed used was 2mm/s for tensile test and 5mm/s for flexural test. Izod impact test was conducted on unnotched specimens according to ASTM D256 with a Zwick impact testing machine. A 7.5J hammer was used for the samples. Five samples were used for the tensile and flexural tests while three samples were used for the impact test and the average values were recorded. The hardness test was conducted with a Mitutoyo Universal Hardness testing machine. The surfaces of injection moulded specimens were smooth enough so there was no surface preparation before carrying out the test. The test type was Rockwell hardness with R scale (HRR), the indenter used was ¼ inch steel ball with minor and major loads of 10 and 60Kgf respectively. The indentation was made on five points and the average values were recorded. All the tests were carried out at room temperature.

2.6 *Morphological studies using scanning electron microscope (SEM)*

Tensile fractured surface was studied with JOEL-JSM 5600 series Scanning Electron Microscope (SEM). The specimens were sputter coated with a thin layer of gold to avoid electrostatic charging during sample examination.

3. **Results and discussion**

3.1. *Tensile strength*

The results for the tensile strength (Figure 1) showed a decrease in tensile strength with increase in filler loading. The tensile strengths of the treated bio-composites are higher than those for the untreated ones. The better tensile strength exhibited by the ALKSIL treated biocomposites over those of the UNTRD could be as a result of better adhesion between the matrix and filler due to the ALKSIL treatment. It was reported that the tensile strength of particle-filled polymer composites depends on the interfacial adhesion between the matrix and filler which will facilitate the transfer of stress to the filler during deformation [23]. Also, alkali treatment resulted in an improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking [24-26]

hence, promoting resin-filler interpenetration at the interface. Gomes *et al.*, [27] also reported improvement in the tensile strength of cornstarch-based resin/Curaua fibre bio-composites when the fibres were given combined treatment of alkali and silane treatment.

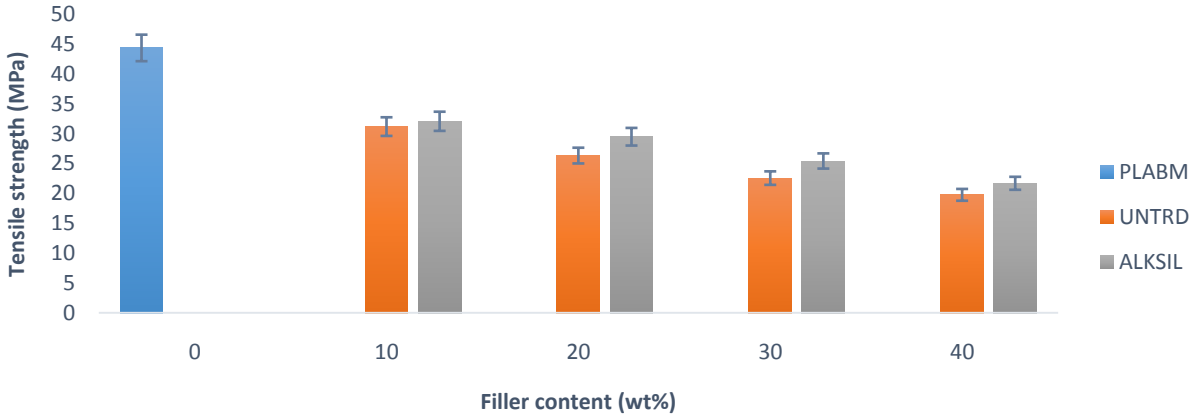

Figure 1: Tensile strength of Poly(lactic acid)/guineacorn husks particulate biocomposites against filler content

3.2. *Tensile modulus*

The result of tensile modulus of the bio-composites is represented in Figure 2. It was observed that the tensile modulus increased with filler loading and those of the ALKSIL treated were higher than those of the UNTRD. At 40% GHP, the tensile modulus for the ALKSIL treated bio-composites was higher than that of the UNTRD by 12% and that of the matrix by 44% while the tensile modulus of the UNTRD biocomposites was higher than that of the matrix by 29%. The general increase in tensile modulus with filler loading is commonly attributed to the inherent rigidity of fillers which exhibit higher stiffness than the polymer matrix [28-30]. From the results obtained, it could be inferred that increase in tensile modulus of composites with GHP loading is an indication that lignocellulosic fillers have the ability to impart greater stiffness on the matrix and since increase in filler content resulted in increase in tensile modulus, it means tensile modulus is dependent on the filler content rather than the matrix [31, 32]. The result is in agreement with the report of Salmah *et al.*,[29] that reported improvement in tensile modulus of PLA/coconut shell powder bio-composites for both treated and untreated powders with those treated being higher than those of the untreated.

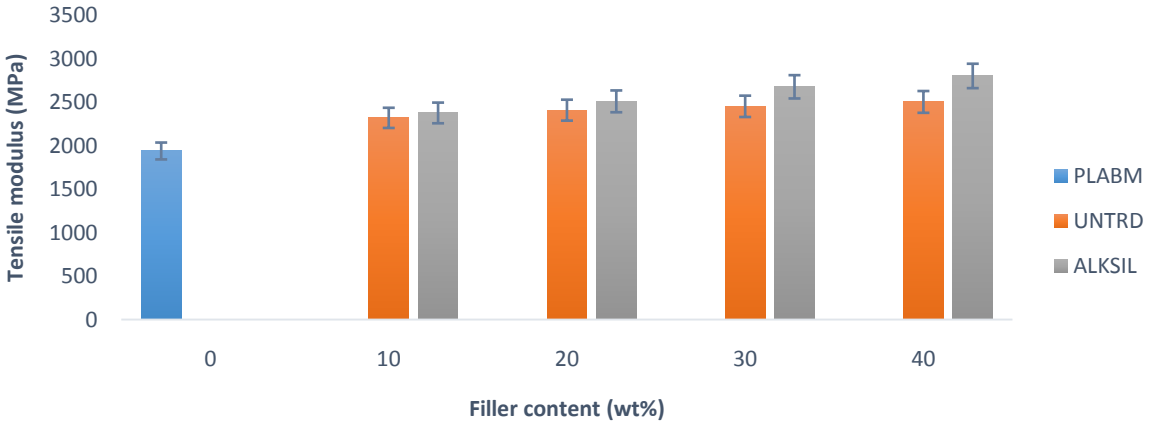

Figure 2: Tensile modulus of Poly(lactic acid)/guineacorn husks particulate biocomposites against filler content

The results for the elongation at break of the bio-composites are shown in Figure 3. From the results, the EB decreased with increase in filler content and those of the ALKSIL treated were higher than those of the UNTRD only at 10 and 20% GHP contents. The reduction in EB with filler loading has been reported elsewhere [33-35]. The reduction could be attributed to the fact that fillers cause polymer matrices to lose their elastic properties due to stiffening effect which leads to restriction of polymer chain mobility. Also, with increase in filler content, the matrix reduces in quantity which consequently reduces the effect of the matrix as compared to that of the filler which then leads to an increase in modulus of composites but reduction of EB [30, 31, 35, 36].

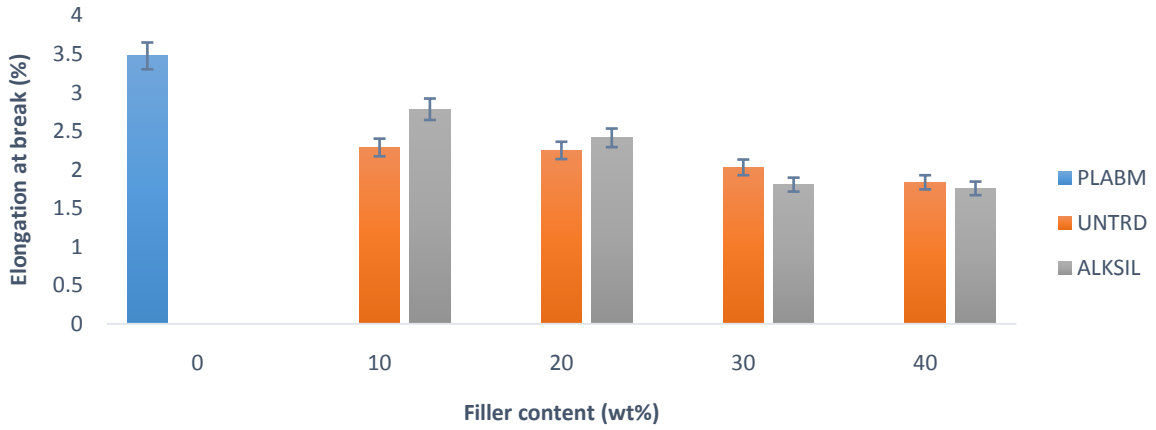

Figure 3: Elongation at break for Poly(lactic acid)/guineacorn husks particulate biocomposites against filler content

3.4. *Flexural strength*

The results for the flexural strengths are as shown in Figure 4. It was observed that the flexural strengths of the bio-composites decrease with increase in filler loading from 10-40%. Also, the matrix (PLABM) had a flexural strength of 52.105MPa which is greater than the strengths of some of the reinforced bio-composites but non-the less, the flexural strength of the ALKSIL treated bio-composite at 10 and 20% were higher than that of the matrix.

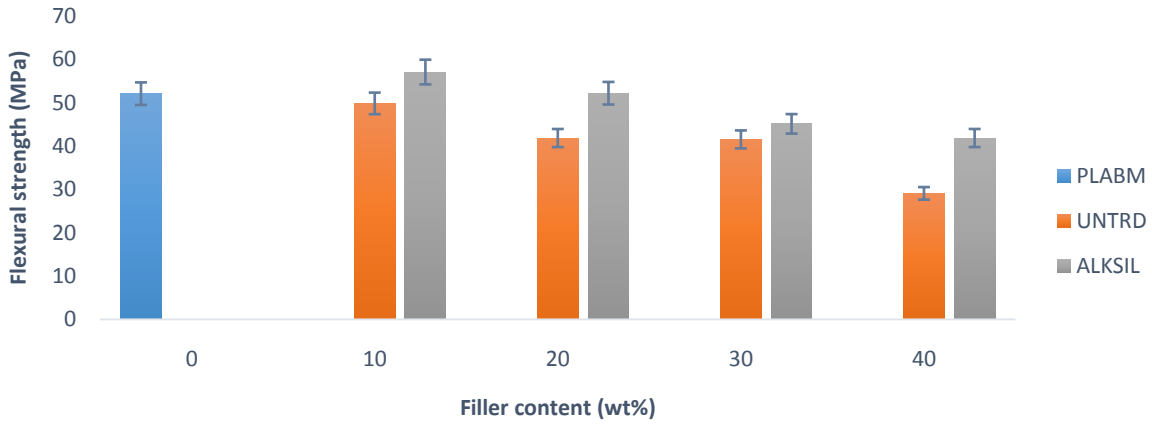

Figure 4: Flexural strength of Poly(lactic acid)/guineacorn husks particulate biocomposites against filler content.

Comparing the flexural strengths of the treated bio-composites as against the untreated ones, it was observed that those for ALKSIL treated were higher than those for the untreated ones. At 20% filler loading, the ALKSIL treated bio-composite with a value of 52.2MPa improved by 24.73% over the UNTRD ones. Kim *et al.*, [37] reported a decrease in the flexural strength of PLA/pineapple and cassava flours composites with increase in flour

contents and addition of coupling agent, the flexural strength for the 30% filler improved as a result of better transmission of load to the flours which was possible because of the improved interaction between the flours and PLA. The reduction of flexural strength with filler content could be attributed to the controlled mobility of matrix by the filler particles [38]. In some other studies [39-41], flexural strengths were observed to increase with addition of fillers and even improved further with various treatments on the respective fillers used.

3.5. *Flexural modulus*

As presented in Figure 5, the flexural modulus increased with increase in filler loading. The flexural modulus for the reinforced bio-composites is higher than that of the unreinforced matrix while those for the treated bio-composites were higher than the UNRTD ones. The increase in flexural modulus with filler addition is attributed to the stiffer nature of filler with respect to the matrix. This also indicates better adhesion between the filler and matrix as surface treatment was applied. The increase in flexural modulus with increase in filler addition and with further treatment is in agreement with other studies [39, 40].

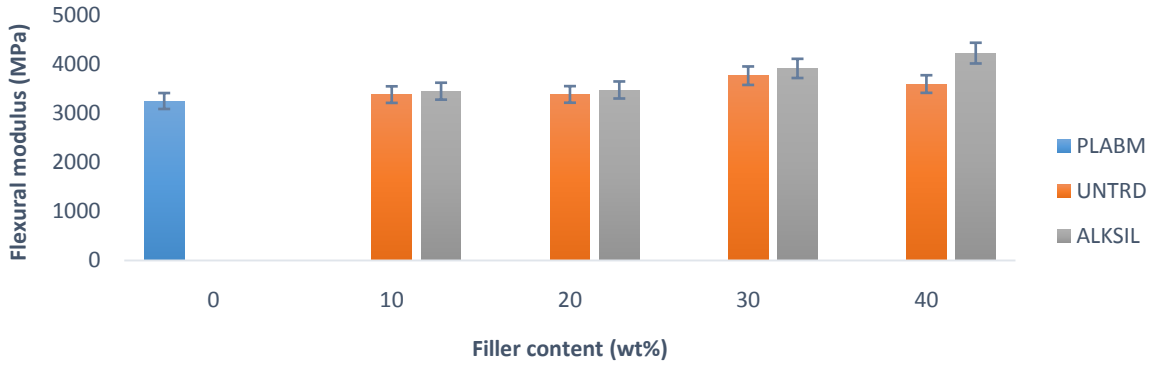

Figure 5: Flexural modulus of Poly(lactic acid)/guineacorn husks particulate biocomposites against filler content

3.6. *Hardness*

The Rockwell hardness values of the bio-composites are as shown in Figure 6. The results showed that, in general, the hardness increased with filler loading up to 30%GHP and decreased afterwards. Except at 10 and 40%GHP contents, the hardness for the UNTRD bio-composites were higher than those of the treated ones. At 30% filler addition, the ALKSIL treated bio-composite was 4.5% better than that of the UNTRD. An increase in the hardness values upon surface treatment was probably due to good dispersion of fillers in the matrix which subsequently minimized voids leading to the strengthening of the bond between the filler and matrix [39].

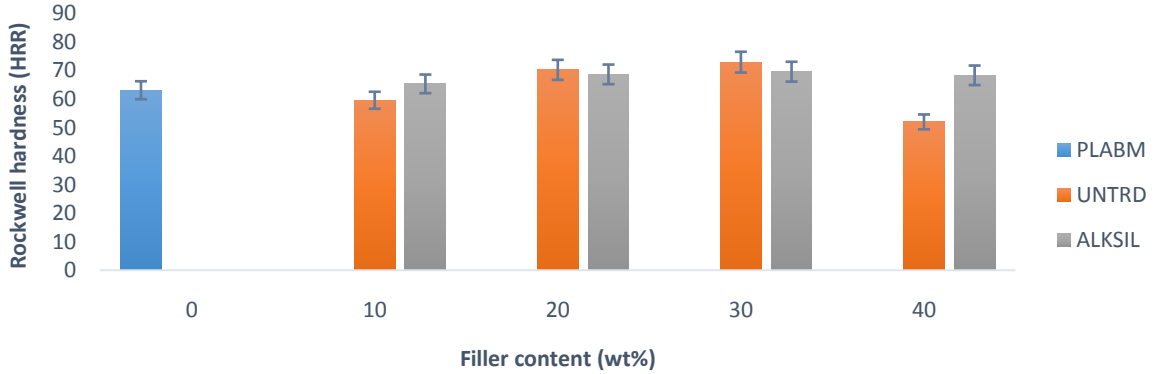

Figure 6: Rockwell hardness of Poly(lactic acid)/guineacorn husks particulate composites against filler content

3.7. *Izod impact strength*

The unnotched impact strength results in Figure 7 shows that the unreinforced matrix had the highest impact strength with a value of 71.1 J/m and there was a progressive decrease with increase in filler content. The ALKSIL bio-composites had better impact strength as compared to the UNTRD samples. A decrease in the impact strength of bio-composites with filler content has been reported [13, 32, 42]. The ability of uncoiling of polymer chains under load thereby absorbing energy in the process would be reduced by addition of fillers which makes the resulting composites stiffer [32]. It is noteworthy to mention that unnotched impact strength of composites is controlled by fracture initiation which in turn is controlled by stress concentration present at defects in the system and it is also affected by energy consumed due to flexural plastic deformation before crack initiation [13, 42].

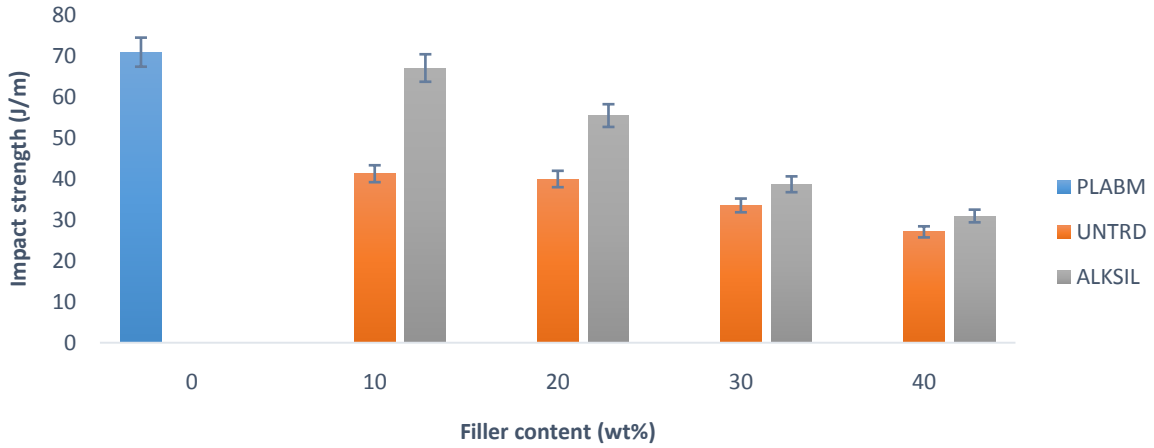

Figure 7: Impact strength of Poly(lactic acid)/guineacorn husks particulate biocomposites against filler content.

3.2. *SEM morphology*

Figure 8a-c shows the SEM morphology of tensile fractured surfaces of the bio-composites. 8a shows brittle fracture while 8b exhibited majorly filler pull-out which could be responsible for the poor mechanical properties. The final structure (8c) is that of the combination of alkaline and silane treatment. This shows a good dispersion of the filler in the matrix as there were less filler pull-out which probably explains the best properties obtained in the course of the study.

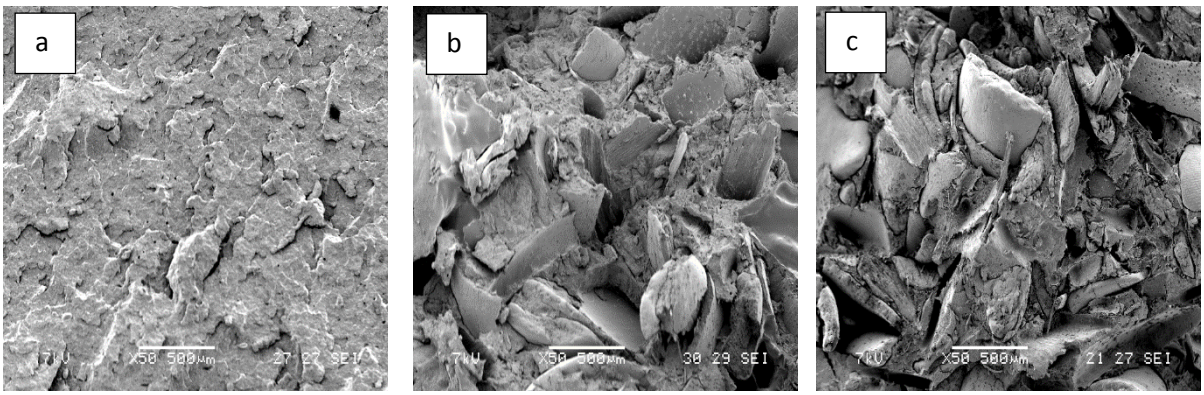

Figure 8: SEM micrographs for tensile fractured surfaces of PLABM/GHP Composites (a) Unreinforced PLABM (b) UNTRD at 40% GHP (c) ALKSIL-treated at 40% GHP

Conclusions

The present study was aimed at investigating the effect of a combination of alkali and silane treatments on the mechanical properties of PLA/GHP bio-composites. At the end of the study, the following conclusions were drawn:

1. There was a general decrease in tensile (32% for ALKSIL and 36% for UNTRD) and flexural (36% for ALKSIL and 71% for UNTRD) strengths from 10-40% of the biocomposites with increase in filler content.
2. There was improvement in the tensile (18% for ALKSIL and 8% for UNTRD) and flexural (22% for ALKSIL and 6% for UNTRD) moduli of the biocomposites with filler loading from 10-40%.
3. Combined treatment of alkali and silane showed a general improvement in mechanical properties over those of the untreated.
4. The SEM images showed filler pull outs which are more pronounced in the UNTRD sample.

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