Mechanical, physical and biodegradability performances of treated and untreated groundnut shell powder recycled polypropylene composites

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Abstract

In this study, groundnut shell powder (GSP) was used for the reinforcement of recycled polypropylene (recycled PP). The GSP consisting of two-particle sizes viz. (0–250 μm and 250–420 μm) was partly treated with sodium hydroxide at room temperature and the GSP both treated and untreated were compressed and compounded with recycled PP to produce GSP-recycled PP composites. For comparison, recycled PP was equally produced as a control sample. The effects of GSP addition and sodium hydroxide treatment on recycled PP were investigated through the mechanical testing of the developed composites. The mechanical properties (tensile strength, hardness, and toughness) of the composites were evaluated and the tensile strength of both treated and untreated GSP-recycled PP composites is higher than the recycled PP and the treated GSP of particle size 0–250 μm having the highest tensile strength at 25 wt% GSP in recycled PP matrix. The hardness of the recycled PP increases with increasing content of GSP while the toughness decreases with increasing concentration of GSP in the recycled PP matrix. The water uptake of the GSP-recycled PP composites was equally studied, and the results revealed that the treated GSP-recycled PP composites has lower rate of water absorption as compared to untreated GSP-recycled PP composites. Thermal stability and crystallinity of the composites and monolithic recycled PP were investigated, and it was discovered that the thermal stability and crystallinity of the polymer were enhanced with GSP addition. Morphological characterization of the selected samples through a scanning electron microscope (SEM) and x-ray diffraction (XRD) were equally done to validate the mechanical performance of the composites. Finally, biodegradability study on the composites and the control sample was conducted and it was found out that, the addition of GSP in both forms promotes the biodegradation of the recycled PP polymer. Such biodegradable GSP-recycled PP polymer composite materials are highly valuable for manufacturing food takeaway packages and some of the interior parts of the automobiles.

1. Introduction

Natural fiber reinforced polymer composites have attracted the attention of scientists and researchers as an alternative material in automobile and aerospace applications because of their low cost and low specific gravity [1]. The need for environmental sustainability and the issue of recycling of plastic have spurred the researchers to concentrate more efforts on the development of biodegradable plastic polymer products. Lignocellulosic fibers have comparative advantages over synthetic fibers in that the lignocellulosic fibers have low-cost, low specific gravity, renewability, biodegradability, abundance, low equipment abrasiveness, high specific strength and stiffness [2–5]. The major drawback of using natural fibers as a filler in the thermoplastics polymer are their poor compatibility with the polymer matrix due to its hydrophilicity and thermal instability [5, 6]. Lignocellulosic
fibers have hydroxyl group in their fiber network structure that tends to repel hydrophobic character of the polymer matrix. Besides, lignocellulosic fibers have strong affinity for moisture absorption and this has negative effects on the dimensional stability of the resulting natural fiber/polymer composites [7]. To improve lignocellulosic fibers interaction with the polymer matrix, surface modifications of the natural fibers are necessary. Physical and chemical modifications of natural fibers have been reported in literature [8–10]. Surface modifications do not only improve the compatibility between the filler and the matrix but also promote effective dispersion of the natural filler into the polymer matrix and consequently enhanced the mechanical properties. Physical methods of fiber treatment also known as friendly methods include the use of plasma, fungi, bacteria and enzyme which are highly efficient and environmental friendly however, high cost and long treatment time are the demerits of the methods that hinders their commercial success [11]. Chemical modification of lignocellulosic fibers involve the use of surface treatment agents such as silane, sodium hydroxide, isocyanate, permanganate, maleic anhydride and peroxide [7, 12]. Although the use of hazardous chemicals could pose serious threat to our environment but the ease of processing with short treatment time couple with the ability to be implemented at industrial scale have made chemical treatment more popular [11]. Among all the chemical methods of fiber treatment, sodium hydroxide is the widely use due to their effective and availability, Sodium hydroxide treatment of empty palm fruit bunch fiber both at room and elevated temperatures has been reported while in another study, sodium hydroxide at different concentrations was used for the treatment of bamboo fibers and the crystallinity of the bamboo fiber was found to increase with the concentration of NaOH and treatment time. The increased crystallinity of the fiber was attributed delignification of bamboo that generated microfibril with greater crystallinity. Alkali treatment (sodium hydroxide treatment) causes the removal of the hemicellulose and lignin from the natural fibers because of breaking of bundles of complex fiber network into microfibrils. This decrease the fiber diameter and increase fiber surface roughness [15]. Alkali treatment is also very effective in the removal of the waxy layer of fatty acids from the surface of fibers that result in the production of a rough surface topography [16]. Chemically modified fiber polymer matrix composites have been reported to have improved mechanical properties due to better filler-matrix interaction and also reduced water absorption tendency [17].

Polypropylene (PP) is one of the most widely used plastics due to its economy (affordable), recyclability and higher thermal stability [6]. Recycled polypropylene (rPP) generally have lower properties than the pure or virgin PP. The properties of rPP usually deteriorates because of degradation and cycling. Thus the result of the processed recycled materials are usually discouraging and their use for the production of useful material is dwindling [15]. However, environmental legislation has restricted them from outright dump in soil and other open places as such, recycling of plastics is a better option and this has created interest in the preparation of valuable composites, hence encourage recycling of materials. Besides, some interesting results have been achieved from previous works and the results are quite impressive with properties comparable to virgin or pure pp-based composites [2, 13]. Processing of rPP-based composite is crucial for achieving better physical and mechanical properties. The use of melt mixing and solution mixing followed by extrusion have been reported to be effective in the preparation and fabrications of polymer composites [18]. The effect of processing variables such as mixing time, temperature and speed on the mechanical properties of pp-natural fiber composites have equally been investigated [19]. Long mixing time, high temperature can result in the thermal degradation of the natural fiber while high rotor speed result in the breakage of the fibers. Again, at shorter time and low rotor speed, poor dispersion of the fiber into PP matrix could occur and if low temperature is chosen, incomplete melting of the pp might result thereby leading to poor mechanical performance of the composites. Thus, to obtain superior mechanical and physical properties, optimization of the variables is significant.

Groundnuts (Arachis Hypogea) is among the prominent crops grown in Nigeria with estimated capacity of 23,390,000 million tons as at year 2002 [20]. Also, in 2011, Nigeria was estimated (2,962,760 tons) to be the third largest producer of groundnuts in the world after China (16,114,231 tons) and India (6,933,000 tons) [21]. However, the policy of the current administration of Federal republic of Nigeria is expected to have increased the estimated output (2,962,760 tons) owing to the keen interest of the government on economic diversifications. Groundnut shell is a waste product obtained after harvesting groundnut seed from its pod. Traditionally, groundnut shells are mostly used for making household fire especially in some part of Nigeria which constitute environmental hazard. Commercial success of groundnut shells have not been reported although Kanayo et al [22] used ash form of groundnut shell in conjunction with silicon carbide as reinforcement agent in the development of Al-Mg-Si hybrid composites and significant improvement in corrosion resistant and mechanical properties was reported. Also, in our previous work [23], groundnut shell powder was used in both treated and untreated form to reinforced recycled polyethylene and the result showed improvement in mechanical properties with evidence of biodegradations. Plant fibers commonly used for the reinforcement of polymer matrix to produce biodegradable polymer composites includes kenaf, jute, flax, sisal, coir, and bamboo [14, 24–28]. Valorization of groundnut shells through its incorporation into polymer matrix will not only add to the list of available lignocellulosic plant fiber fillers but also enhance environmental sanitation thereby
promoting healthy ecosystem. Biodegradability improvement of polypropylene is an interesting area of research that has taken attention of researchers worldwide as a continuous effort towards green and healthy ecosystem [18, 29]. Addition of natural fibers such as groundnut shell powder is expected to contribute significantly to the biological degradation of polypropylene with better physical properties. Oliver-Ortega et al [27] did comparative study on the mechanical performances of polyamide 11 and polypropylene containing stoneground wood fibers at various concentrations. PP-based composites showed higher mechanical performance at low stoneground wood content than the polyamide 11-based composites counterpart. Furthermore, Sunilkumar et al [30] studied biodegradability of low-density polyethylene fill with chitosan composites using Aspergillus nigar. The growth of the Aspergillus nigar colony was found to increase with increasing chitosan content through weight loss study. In addition, the rate of biodegradation is faster in the treated samples (32%) than the untreated counterpart. This was attributed to the fact that treatment promote wettability of the composite film thereby making them more susceptible to fungi attack. Although, contradicting results have been recently reported by Youssef et al [24] after their investigation on the biodegradable performance of wood plastic composites containing treated and untreated fibers in soil environment. The treated fibers composites showed slightly decrease in biodegradability and this reduction in biodegradability of the treated fiber composites in soil according to the authors was because of removal of undesirable lignocellulosic fibers constituent which made the fiber more compatible with the polymer matrix. Thus, the extent of biodegradation of the biocomposite materials depends on the microorganism population as well as their environment.

Development of biodegradable pp–natural fiber–based composite is a center of attraction to many researchers and manufacturers however, the use of groundnut shell powder in the reinforcement of recycled polypropylene has not been explored. In this current work, groundnut shell powder (treated and untreated) of different particle sizes and at different concentrations was used to reinforce recycled polypropylene to improve the mechanical and physical properties of recycled PP polymer. Biodegradability studies on the prepared GSP–recycled polymer composite was investigated using fungi (Aspergillus nigar).

2. Materials and method

The groundnut shells were sourced from the subsistence farmers in Lafia, Nasarawa state, Nigeria while the sodium hydroxide pellets and litmus papers were purchased from Finlab, Palmgrove, Lagos Nigeria. Recycled polypropylene rPP (density = 0.91 g cm$^{-3}$, MFI = 5.58 g/10 min) was purchased from local company in Ojota Lagos Mainland, Southwest, Nigeria.

2.1. Preparation of groundnut shell powder

The groundnut shells (GS) were washed with water and dried in the natural sun for three days. The dried groundnut shells were grind in a pulverized machine in Bariga Market, Mainland Lagos, Nigeria and thereafter sieved into two particle sizes (0–250 μm and 250–420 μm) to obtained groundnut shell powder (GSP).

2.2. Surface modification of GSP using sodium hydroxide

The groundnut shell powder was divided into two parts and equally in accordance to their particle sizes. One part left untreated while the other part was treated with sodium hydroxide. The treatment was done following the procedure as reported in the paper [31]

The sodium hydroxide treatment of the GSP was done by adding one gram of GSP into 10% 10 mL sodium hydroxide (NaOH) solutions and continuously stirred for 4 h. Thereafter, the solution was poured into the sieve; rinsed and washed with distilled water until it turns neutral (PH of 7). The powder was filtered and dried in a vacuum at 80 °C for 12 h to obtained treated groundnut shell powders.

2.3. Preparation of GSP–recycled polypropylene composite

The production of GSP–recycled polypropylene composites was done by initial mixing and subsequent consolidation into composites. The two roll mills were switched on and the fastening of the nip of the rolls was ensured prior to the feeding of the recycled polypropylene. Feeding of the recycled polypropylene was done in between the nips of the rolls which could melt so as to reduce the molecular weight of the plastic. When the plastic had melted and band around the front roll of the mill between the nip of the rollers formed, the filler (GSP) was introduced gradually into the nip of the rolls and then cross mixing of the GSP and recycled polypropylene was carried out to ensure homogenous and uniform distribution of the filler in the recycled PP matrix. Adjustment of the nips of the roller was done to a desired thickness and thereafter the compounded material was sheeted out before transferring it for further processing.
The hardening of the compounded material was performed on hot press with electrically heated platens. The temperature of the platens was fixed at 140 ± 5 °C and when this temperature was reached, the molds were preheated until the platen temperature was attained. The material was cut into sizes to take the shape of the mold and then placed in between the platens at a pressure of 3 tons for the duration of 10 min. Finally, the hardened sample was removed from the mold after it has cooled. This procedure was repeated to produce the GSP-recycled polypropylene composites of varying GSP contents (5% to 30% wt GSP). Both treated GSP-recycled polypropylene and untreated GSP-recycled polypropylene composites were produced in this process and a total of 25 samples (12 treated GSP-recycled polypropylene composites, 12 untreated GSP-recycled polypropylene composites and 1 recycled polypropylene as control sample) were prepared. The sample designation as presented in the paper are stated in table 1 below.

2.4. Mechanical testing

2.4.1. Tensile testing

The mechanical tensile testing of the samples was performed using instron tensile testing machine (load cell of 50 KN) model 3367 in accordance to ASTM D638 standard. The prepared sample in the shape of dumbbell was placed in the tensile testing machine and the tensile strength was evaluated. Three measurements were made for each sample and the average value was evaluated and reported as the tensile strength of the sample.

2.4.2. Impact testing

The impact strength of the samples was evaluated using TQ impact machine model TQ-TE15 and the test was carried out in accordance to the ASTM D5628 standard. A prepared notched specimen was placed into the machine with a pendulum of known weight. The pendulum was raised to a known height and then allowed to fall and breaks the specimen and finally rose to a measured height. The difference in height of the pendulum before and after is the measure of the impact energy of the specimen. Two measurements were made on each sample and the average value was calculated as the impact energy of the sample.

2.4.3. Hardness testing

The mechanical hardness of the samples was performed using hardness machine (shore Durometer) model E-Durometer shore digi S1-D in accordance to the ASTM D2240 standard. A load of 453 g was applied and indenter of sharp angle of 30° was used during the test. Ten (10) measurements were made on each sample at various locations and the mean value was recorded as the hardness of the sample.

2.5. Physical test

2.5.1. Water absorption

The water absorption of the samples was determined based on ASTM D-570. The samples were sectioned, cleaned, dried at 80 °C for 4 h to give constant weight and then weighed prior to their immersion in distilled water at room temperature. After 24 h of their immersion in distilled water, the samples were removed, and the surface wiped off before weighed. The difference between the initial weight (w₀) and the final weight (wₙ) after immersion in distilled water is recorded. The procedure was repeated for every 24 h for 30 days and the percentage water absorption (w%) was determined based on the equation [7]

\[ w\% = \left( \frac{w_n - w_0}{w_0} \right) \times 100. \]
2.5.2. Differential scanning calorimetry
The DSC characterization of the samples was done with the DSC machine model Mettler–DSC822. The heating rate of 10 °C/min and the temperature range of 50 °C to 220 °C was employed through-out the experiment. The sample was weighed (5 mg) and then placed in aluminum crucible. The cover lip was placed on top of the crucible and mechanically pressed for about 3 s. Perforation was gently made on the cover lip with the aid of safety pin and the sample was finally placed on the DSC machine for the analysis. The degree of crystallinity ($X_c$) of the R and the composite samples was evaluated by the equation (2) [3].

$$X_c = \left( \frac{\Delta H}{\Delta H_{m} \times W} \right) \times 100.$$

Where $\Delta H_m$ is the heat of fusion of the sample, $\Delta H_{m}$ is the heat of fusion of 100% crystalline PP taken as 138 J g$^{-1}$ [3] and W is the mass fraction of the matrix.

2.5.3. Biodegradability studies
Biodegradability experimentation of the samples was conducted by inoculating the GSP-recycled polypropylene composites with Aspergillus niger on a potato dextrose agar media and then incubated at room temperature (25 °C) for a period of 21 days as reported in the papers [23, 30]. The samples were cut to sizes and placed with face on the surface of mineral salts agar in a petri dish without any carbon source. The samples were examined every day for the evidence of the colony growth. The percentage weight of the samples was determined to validate the extent obdegradation of the samples as a result of the fungi growth on them.

2.6. Characterization
2.6.1. X-ray diffraction
The x-ray diffraction of model 8 advanced Brucker, Germany was used to characterize the GSP-recycled polypropylene composites. A step size of 0.02°/s, voltage of 30 Kev, current of 30 mA and copper target was employed. Cu-Kα radiation was generated from the x-ray source with Ni filter to reduce the undesirable radiations before hitting the samples. Tilting of the stage was done at angle 20 ranging from 3° to 60°.

2.6.2. Scanning electron microscope
Scanning electron microscopy of the samples were carried out to investigate the morphology of the GSP-recycled polypropylene composites. Prior to the SEM imaging, the samples were coated with gold to avoid sample charging during SEM imaging. The coated samples were inserted into the gold coat machine chamber and then flush to create vacuum at a pressure of 0.25 mbar. The coating was done at a current of 40 mA for 25–30 s. The SEM imaging was done using a JEOL SEM model JSM6610LV scanning electron microscope operated at 20 Kev.

3. Result and discussion
3.1. Water absorption
The result of the water uptake of the prepared GSP-recycled polypropylene composites is presented in Figure 1. Five samples including control sample (recycled PP) were presented as shown. The rate of water absorption is very high is the first two days of the experiment for all composites and the control sample (recycled polypropylene). The untreated GSP-recycled polypropylene composites (25U420) has higher moisture uptake as compared to the treated counterpart (25T420). Similarly, the moisture uptake of untreated GSP-recycled polypropylene composite (25U250) is higher than the treated GSP-recycled composite (25T250) but the trend changed after about 17 days of the experiment in which the rate of water absorption of the untreated is lower than the treated GSP-recycled composites of the same particle size. It is also interesting to know that after 24 days of the experiment, there was no meaningful change in the moisture absorption of the composites as shown in the Figure 1. The increasing rate of water absorption with addition of GSP is due to its hydrophilic nature (presence of amorphous cellulose and hemicellulose) [9]. Treated GSP-recycled polypropylene composites showed relatively lower moisture uptake because of the sodium hydroxide treatment which removed some of the components (hemicellulose) of GSP that lowers its hydrophilicity. The moisture absorption of GSP in the recycle polypropylene is detrimental to the mechanical performance of the composites. Good interfacial adhesion can reduce moisture penetration into the composites and this can be achieved by fiber modifications [32]. It is also important to know that larger particles of GSP absorbed more moisture than the relatively small particles of GSP. This is because, the larger particles GSP has large aspect ratio which provide favorable path for the water transport thereby facilitating the ingress of moisture. Again, for 25T250 samples, the moisture uptake at the beginning was very low, however, the initial absorption might have significant effect of the interfacial
adhesion bond which created micro gaps between the GSP and recycled PP matrix. This promotes significant uptake of moisture after about 17 days of commencement of the experiment. Saturation level was attained at about 25 days and thereafter, there was no significant uptakes of moisture as shown in Figure 1. The accessibility of moisture to the GSP/recycled polypropylene interface from the environment can cause the swelling of the fiber thus create shear stress at the interface that promote the delamination of the GSP fiber from recycled PP leading to low mechanical tensile strength of the composites. However, treatment of GSP prior to their introduction into the recycled PP has substantially reduced the moisture uptake of the composites as shown in Figure 1. The penetration of moisture into the composite is conduct by three major mechanisms [33]. The first mechanism involves diffusion of water molecules into the micro pores between the polymer chain. This is the mechanism responsible for the water uptake of pure recycled polypropylene. The second mechanism is the transportation of water by capillary into the gaps and flaws at the interface between the GSP fiber and recycled PP matrix and finally the third mechanism is the moisture transport due to the presence of micro-cracks that exist in the recycled PP matrix caused by incomplete compounding during composite preparations.

3.2. Differential scanning calorimetry
Figure 2 shows the DSC characteristic of recycled PP and the selected composite samples. Two endothermic peaks were observed for both the control sample (rPP) and the composites indicating the melting temperature \( T_m = 110 \, ^\circ C \) for rPP while that of composites is \( 112 \, ^\circ C \) exception of the 25T420 which has slight variation (112.6 \( ^\circ C \)). The first endothermic peak occurred around 110 \( ^\circ C \) while the second endothermic peak exist at about 120 \( ^\circ C \). These peaks occurred due to the ordered or crystalline soft segment. Moreover, the endothermic peak of GSP/recycled PP composites shifted to the higher temperature and the melting enthalpy was larger compared to the monolithic rPP. In addition, the treated samples showed better thermal stability than the untreated GSP/recycled PP composites. The \( T_m \) for the rPP is 125 \( ^\circ C \) while the composites are 126 \( ^\circ C \). Thus, the melting point of the composites are slightly higher than the recycled PP and this is attributed to the incorporation of GSP in the recycled PP. The percentage crystallinity of the recycled PP and the composites are presented in table 2. The crystallinity of Rpp is 30.11% and this value increased by about 5.5% when GSP is added to it. Also, treated GSP-PP composite (25T420) has the highest crystallinity (31.89%). Thus, enhancement in crystallinity of Rpp is more significant when treated GSP is incorporated in the recycled polypropylene as equally reported in the papers [3, 13]. This is because natural fibers tend to act as good nucleating agents for the crystallization in the recycled polypropylene. Besides, smaller particles GSP has propensity to aggregates and these large aggregates enhanced the growth of the crystal as they entangle polymer chain thus favor crystallinity.

3.3. Mechanical properties
3.3.1. Tensile strength, tensile modulus, Impact energy and elongation at break
The mechanical tensile strength of natural fibers reinforced composite of polymeric matrix is very crucial as this has provided avenue to develop material of industrial and practical applications. The tensile strength of treated and untreated GSP of different particle sizes and concentrations in recycled PP are shown in Figure 3. The tensile...
The tensile strength of recycled PP increased with the addition of GSP. The tensile strength of the monolithic polymer (recycled PP) is 19.3 MPa and when 5 wt% untreated GSP is added to it, the tensile strength increased to 21.2 MPa. From Figure 3, it is obvious that the tensile strength of the recycled PP increases with increasing percentage loading of GSP until it reaches maximum (25 wt%) in all form of GSP-recycled PP composites. Further loading of GSP beyond 25 wt% result in decreasing the tensile strength of the composites. It is also important to know that composites containing treated GSP exhibited higher tensile strength than the untreated counterpart. The treated GSP (T250) composites has the highest tensile strength (29.9 MPa) at 25 wt% loading which was closely followed by untreated GSP (U250) with tensile strength (29.7 MPa) at the same loading.

Table 2. Melting point, enthalpy and percentage crystallinity of rPP and composites.

| Sample | T_m1 (°C) | T_m2 (°C) | Enthalpy (J/g) | X_c (%) |
|--------|-----------|-----------|----------------|---------|
| U0     | 110       | 125       | 41.56          | 30.11   |
| 25U250 | 112       | 126       | 28.50          | 31.77   |
| 25T250 | 112       | 126       | 28.54          | 31.81   |
| 25U420 | 112       | 126       | 28.57          | 31.85   |
| 25T420 | 112.6     | 126.5     | 28.61          | 31.89   |

Figure 3. Tensile strength versus percentage loading of the GSP.
Furthermore, the tensile strength is equally sensitive with the particle size of GSP as the composites containing GSP of small particle size (0–250 $\mu$m) seems to have higher tensile strength than those with relatively large particle size. The result achieved is almost the same as that reported when treated and untreated abaca was used to reinforced PP and tensile strength of 31 MPa and 27 MPa were achieved for treated and untreated abaca-PP composites respectively [8]. The increased in tensile strength with percentage loading of natural fibers in PP have been reported in other papers [18, 34]. However, in other reports, decrease in tensile strength with increase percentage loading of natural fiber loading in PP have equally been reported [6, 29]. The increasing tensile strength of recycled PP with GSP loadings could be attributed to increased crystallinity with addition of GSP and when the concentration of GSP increased beyond 25 w%, compounding of GSP-recycled PP becomes difficult thereby creating microspores and voids consequently weaken the interphase between the GSP and recycled PP matrix. This reduced the tensile strength of the composites. Again, treatment of GSP with NaOH reduced its hydrophilicity thereby making it more compatible with recycled PP and consequently promote interfacial adhesion which favored the increment of tensile strength of the treated GSP-recycled PP composites as compared to untreated GSP-recycled PP counterparts.

The tensile modulus of GSP-recycled PP composites is presented in Figure 4. The tensile modulus also increased with the addition of GSP to recycled PP and the tensile modulus of pure recycled PP is 143 MPa. Again, the tensile modulus of treated GSP composites is superior to that of untreated GSP composites as shown in Figure 4. The improved tensile modulus of the treated GSP-recycled PP composites is due to better interfacial adhesion between recycled PP matrix and the GSP fiber. The impact strength of the composites is presented in the Figure 5. Recycled PP has the highest impact energy and the impact energy of the recycled PP decrease with incorporation of both treated and untreated GSP. The impact energy of recycled PP is 593 J m$^{-1}$ and this value decrease when 30 wt% treated and untreated GSP of particle size 250 $\mu$m were added and the impact energy were 319 J m$^{-1}$ and 313 J m$^{-1}$ respectively. It is important to know that the reduction in impact strength with the addition of GSP is more significant in the untreated GSP than the treated counterparts. The decrease in impact energy with GSP addition might be due to the formation of voids during processing of the composites. These voids act as stress concentration factor which aid in the propagation of cracks in the composites. In the case of treated GSP-recycled PP composites, the interfacial bonding is high due to compatibility of treated GSP and recycled PP matrix, hence minimize the number of void formations in the composites.

Figure 6 shows the elongation at yield of the composites with the GSP loadings. The percentage elongation decreases with GSP inclusions until 15 wt% GSP is reached in which further loading of did not show any significant changes in the elongation at yield of the recycled PP. The treated GPS-recycled PP composites show relatively low percentage elongation yield as compared to untreated GSP-recycled PP composites.

3.3.2. Hardness

The hardness of natural fiber-polymer composites depending mainly on the distribution of the natural fibers in the polymer matrix [17]. Figure 7 shows the hardness of recycled PP and the GSP-recycled PP composites. The addition of both treated and untreated GSP into recycled PP matrix slightly increase the hardness of the
composites however, treated GSP seems to have better mechanical hardness than the untreated GSP. This might be attributed to the sodium hydroxide treatment which aid the distribution of the GSP in the recycled PP matrix, producing stronger interfacial adhesion between the GSP and recycled PP matrix thereby reducing the number of voids in the composites during processing. Table 3 shows the mechanical properties of the composites and pure recycled polypropylene.

3.4. Characterization

3.4.1. X-ray diffraction

The x-ray diffraction pattern of recycled PP and GSP-recycled PP composites is presented in Figure 8. The XRD pattern displayed for recycled PP confirmed the presence of monoclinic \( \alpha \)-phase crystals and the index planes were (041) and (060) [13]. From the XRD pattern, the peak intensity of the recycled PP was found to decrease when untreated GSP was added while the peak intensity increased when treated GSP was included. Again, widening in the peak width was equally observed in the GSP-recycled PP composites. The decreasing intensity with addition of untreated GSP might because the untreated GSP fiber contain amorphous components such as...
Table 3. Results of mechanical tests on various GSP-rPP composite blends.

| Material | GSP (wt%) | Strength (MPa) | Modulus (MPa) | Elongation at yield (%) | Toughness (J/m) | Hardness (Shore Scale D) |
|----------|-----------|---------------|--------------|-------------------------|-----------------|--------------------------|
| U 420    | 0         | 19.3 ± 0.55   | 143.5 ± 0.74 | 160.2 ± 11.49           | 593 ± 1.39      | 29.8 ± 1.68               |
|          | 5         | 21.2 ± 0.42   | 151.6 ± 8.78 | 135.2 ± 2.20            | 489 ± 14.74     | 32.8 ± 3.03               |
|          | 10        | 25.1 ± 0.42   | 162.0 ± 3.96 | 60.0 ± 0.33             | 449 ± 19.50     | 37.1 ± 2.96               |
|          | 15        | 26.8 ± 0.44   | 177.1 ± 6.03 | 23.4 ± 1.76             | 408 ± 1.47      | 41.4 ± 2.47               |
|          | 20        | 27.1 ± 0.75   | 193.5 ± 8.92 | 22.4 ± 1.79             | 367 ± 9.24      | 42.4 ± 2.10               |
|          | 25        | 28.2 ± 0.80   | 207.9 ± 11.62| 21.0 ± 3.27             | 318 ± 5.34      | 43.6 ± 2.44               |
|          | 30        | 26.8 ± 0.48   | 248.9 ± 7.91 | 19.1 ± 4.89             | 272 ± 12.47     | 44.9 ± 1.54               |
| T 420    | 5         | 21.4 ± 2.11   | 153.3 ± 4.32 | 100.1 ± 2.06            | 501 ± 13.66     | 33.8 ± 3.29               |
|          | 10        | 25.6 ± 3.11   | 166.7 ± 3.01 | 45.9 ± 8.46             | 451 ± 23.78     | 37.8 ± 4.14               |
|          | 15        | 27.3 ± 0.22   | 179.5 ± 4.21 | 13.7 ± 1.57             | 422 ± 4.49      | 41.6 ± 3.14               |
|          | 20        | 27.7 ± 0.06   | 199.1 ± 8.97 | 12.4 ± 0.52             | 400 ± 29.14     | 43.8 ± 3.96               |
|          | 25        | 28.8 ± 0.91   | 207.8 ± 7.48 | 12.1 ± 0.37             | 330 ± 28.82     | 45.6 ± 3.24               |
|          | 30        | 28.4 ± 1.57   | 258.6 ± 0.07 | 11.1 ± 0.83             | 280 ± 21.79     | 46.3 ± 2.76               |
| U 250    | 5         | 21.7 ± 0.83   | 156.3 ± 9.13 | 60.0 ± 3.69             | 534 ± 0.52      | 37.1 ± 2.56               |
|          | 10        | 25.6 ± 1.62   | 179.1 ± 1.30 | 28.3 ± 4.44             | 489 ± 2.15      | 41.2 ± 3.18               |
|          | 15        | 28.0 ± 1.36   | 199.3 ± 7.49 | 10.2 ± 2.07             | 455 ± 16.64     | 42.3 ± 3.10               |
|          | 20        | 28.8 ± 2.03   | 224.4 ± 10.67| 9.7 ± 1.80              | 407 ± 35.34     | 43.8 ± 3.25               |
|          | 25        | 29.7 ± 0.05   | 244.1 ± 0.53 | 9.6 ± 2.53              | 347 ± 14.19     | 46.0 ± 2.82               |
|          | 30        | 28.9 ± 1.49   | 292.3 ± 2.80 | 11.4 ± 2.67             | 313 ± 28.35     | 47.1 ± 1.84               |
| T 250    | 5         | 22.2 ± 0.76   | 162.7 ± 13.14| 31.6 ± 1.81             | 577 ± 24.88     | 39.1 ± 2.01               |
|          | 10        | 25.9 ± 0.95   | 184.6 ± 17.11| 18.3 ± 3.92             | 497 ± 17.78     | 41.9 ± 3.05               |
|          | 15        | 28.4 ± 0.67   | 203.5 ± 0.78 | 10.5 ± 0.36             | 460 ± 4.46      | 43.0 ± 3.92               |
|          | 20        | 29.1 ± 0.90   | 225.4 ± 1.24 | 9.6 ± 1.66              | 422 ± 0.68      | 44.0 ± 1.32               |
|          | 25        | 29.9 ± 0.27   | 232.9 ± 10.96| 9.4 ± 2.07              | 365 ± 15.58     | 46.9 ± 4.65               |
|          | 30        | 30.1 ± 0.53   | 300.3 ± 10.18| 9.2 ± 1.36              | 319 ± 6.25      | 47.5 ± 2.00               |

Figure 7. Hardness of the composites versus percentage loading of GSP.

lignin, pectin, wax and hemicellulose while the only crystalline component is the cellulose. Thus, sodium hydroxide treatment removed the amorphous parts of the GSP, and this promote crystallinity in the composites containing treated GSP (25T420 and 25T250). Also, the increase in peak width could be due to the development of crystallite since GSP act as nucleating sites. Thus, the increasing mechanical properties can be attributed to increase crystallinity of the GSP-recycled PP composites as equally evident in the DSC results.
3.4.2. SEM analysis
The morphology of GSP/recycled PP composites was investigated by SEM on the fracture surface. Low magnification images of each of composition have been used to present the fiber distribution within the recycled PP matrix. Figure 9 shows the scanning electron images of recycled PP and the GSP-recycled PP composites. The SEM image of recycled PP is presented in Figure 9(a) which confirmed that there was no fiber inclusion. The images of untreated GSP-recycled PP composites are shown in Figures 9(b) and (c). Agglomeration of the GSP fibers were observed in the untreated GSP composites as indicated by the arrow. Also, pull-out of the GSP fibers were equally observed because of the weak interfacial bonding between the untreated GSP and the recycled PP matrix. However, in the case of treated GSP-recycled PP composites (Figures 9(d) and (e)) homogenous distribution of GSP throughout the recycled PP matrix is clearly observed and this result in better adhesion between the treated GSP and the recycled PP matrix. Besides, the agglomeration of the GSP was substantially reduced and this explained the improved mechanical performance of treated GSP composites over the untreated counterparts. This difference could be attributed to greater and favorable roughness of the treated GSP fiber with respect to the untreated ones. The presence of small pinholes on the GSP fiber surface (Figure 9(e)) may allow the ingestion of the molten polymers during compounding, which transforms after cooling in an effective mechanical anchorage, producing more effective adhesion.

3.5. Biodegradability of samples
The biodegradability of the polymer-based composite materials encompasses several stages. The first stage involves the attachment of the microorganisms at the surface of polymeric material and immediately followed by the growth of microorganisms with the aid of the carbon source contained in the polymer-based material. Subsequently, primary and ultimate degradation of the polymer occur where the main chain splits and that results in the formation of low molecular weight fragments. Figure 10 shows the growth of the fungi on the recycled-PPE composites. Before biodegradation, the pictures of the samples were taken and after five days, the evidence of the growth of fungi was observed on the samples containing GSP but there was no significant growth of the fungi on the surface of the control sample (rPP). The absence of the carbon source in addition to the microbial resistance of the rPP could be responsible for the absence of the fungi growth on it. Again, the effect of microbial attacked on the samples was investigated through weight loss measurement. Figure 11 shows the percentage weight loss of the samples after 21 days of the commencement of the experiment. The untreated GSP-recycled PP composites exhibited significant weight loss than the treated counterpart. Also, smaller particle size GSP-recycled PP composites showed higher weight loss than the large particles GSP-recycled PPE composites. This might be because small particle size GSP contain more cellulose than the large particle size which has more of lignin than cellulose. Again, sodium hydroxide treatment removed some components GSP that support the growth of the fungi; hence the decrease in weight loss of treated GSP-recycled PP composites.

4. Conclusion
The development of polypropylene composites with groundnut shell power as reinforcement requires control of the interface between and GSP and recycled PP matrix. Chemical treatment of GSP with sodium hydroxide has proven to be successful in the modification of GSP for better bonding with the hydrophobic matrix. Thus, the following conclusions can be drawn from this work:
The treated GSP-recycled PP composites showed low moisture absorption than the untreated GSP-recycled PP composites. The mechanical strength of the treated GSP-recycled PP is higher than the untreated GSP-recycled PP composites of the same particle sizes and the strength of all the composites is higher than the unreinforced recycled PP. The recycled PP composites containing 25 wt% GSP have the highest tensile strength.

Figure 9. SEM micrograph of the fractured samples (a) recycled PP (b) 25U250 (c) 25U420 (d) 25T250 and (e) 25T420.
The mechanical hardness of the composites increases with increased in weight percent of GSP. The addition of GSP to the recycled PP matrix increases its thermal stability as well as the crystallinity. The biodegradability study revealed that the addition of GSP either treated or untreated promotes the biodegradability of the recycled PP with untreated GSP exhibiting greater degree of biodegradation.

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**Authors contributions**

Mohammed Awwalu Usman analyzed the data and discussed the results, Ibrahim Momohjimoh organized the work and wrote the paper and Abdulhafiz Onimisi Usman performed the experiments.
Conflicts of interest

The authors declare no conflict of interest.

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