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Effect of alkali treatment on the mechanical properties of Poly (lactic acid) / Guineacorn husk particulate bio-composites

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Abstract

The paper focuses on the influence of alkali treatment on the mechanical properties of biocomposites made from poly(lactic acid) (PLA) and guineacorn husks particulates (GHP) with respect to that of the untreated (untrd) biocomposites. The composites were prepared using a single screw extruder and an injection moulding machine with particulate compositions varying from 0-40% at 10% interval. It was observed that the tensile strength of the bio-composites decreased with increase in filler content with a maximum value of 31.24MPa at 10% filler content. The tensile modulus recorded an increase with increase in filler content with a maximum value of 2505MPa at 40% filler content while the maximum hardness stood at 72.9HRR at 30% filler content. The alkali treated bio-composites exhibited better properties as compared to those of the untreated ones.

Keywords

Poly (lactic acid); Guineacorn husks; Tensile strength; Bio-composites; Pasticizer; Alkali; Filler; Acetic acid

Introduction

Traditional fiber reinforced composites are composed of carbon fibers, glass fibers, which are incorporated into thermosets or thermoplastic polymers. They have been used for a variety of applications including those used in consumer products for casing, packaging, etc. With increasing number of applications due to increasing number of world population, disposal of composites after their intended life has become a problem as substantial costs are incurred and recycling most polymer composites is proving difficult [1, 2].

The growing environmental awareness and new rules and regulations are pushing the industries to develop materials that are more ecologically friendly [3].This has led to the development of biocomposites which have performance that is comparable with those of the conventional polymers and can be degraded at the end of their intended use [4]. Biocomposites employ the use of renewable materials such as biopolymers as matrices and plant lignocellulosic materials as fillers or reinforcements. They can be used in non-durable applications (a few years), products intended for a short term use (a few times) or for indoor applications [2, 5].

Poly (lactic acid) (PLA) is a versatile and hydrophobic polymer made from agricultural-based feed stocks which are fermented to lactic acid and then polymerized. It is fully biodegradable in the soil, compost or water and the degradation products are reported to be non-toxic to the environment. However, it is known to be stiff and brittle, and it is therefore necessary to use plasticizers to improve the elongation and impact properties [2, 3, 5, 6]. A number of plasticizers including glycerol, biomax strong [7], triactine, tributyl citrate [6], poly (ethylene glycol) (PEG) [8], citrate esters, partial fatty acid ester and ethylene oxide [9] have been used as impact modifiers for PLA. Essentially, the plasticizers were used to lower the glass transition temperature, increase ductility and improve the processibility of PLA [10]. Some typical applications for bio- polymers such as PLA include plastic bags for household bio- waste, barriers for sanitary products and diapers, planting cups, disposable cups and plates etc [3]. PLA can be melt-processed with standard processing equipment such as extrusion and injection moulding at temperatures below those at which natural fibers start to degrade. These open possibilities of producing bio-composites from lignocellulosic materials and PLA as the use of renewable and biodegradable fillers is desirable to provide cost-competitive polymer composites [1, 5]. The motive is that the constituent materials would reduce volumes of waste deposit while undergoing degradation in a landfill [4].

Lignocellulosic materials have many advantages compared to synthetic fibres, for example low weight/density, low cost, renewable, they do not cause skin irritations, reduced wear in processing equipment and they are recyclable and biodegradable. The most important of these properties is their ecological friendliness as they are produced from renewable resources [3, 11]. Despite several merits, lignocellulosic materials also possess few drawbacks such as poor wettability, incompatibility with some polymeric matrices and high moisture absorption. To tackle the problem of compatibility, specific treatments have been suggested such as surface modification through alkali treatment and treatment with coupling agents, which in turn will enhance the overall performance of the composites [12].

Nigeria is a country blessed with a lot of agricultural produce including guineacorn (Sorghum bicolor). It is one of the most extensively grown cereals in the country especially in the Northern parts of the country. In Nigeria, guineacorn is the third cereal in terms of volume of production after maize and millet [13, 14] with more than 4.5 million tonnes harvested in 2010 representing 25% of the total cereal production [15]. Huge amount of wastes are generated from this crop yearly and only a minute quantity are consumed by animals while the rest are burnt on the farmlands which constitutes air pollution. The husks are the covering for the guineacorn seeds and are obtained after the seeds have been removed either through manual or mechanical means.

In light of the above, wastes from this important crop is investigated in this study as possible filler in poly (lactic acid) (PLA) to form biocomposites. The PLA in this study was blended with Biomax strong (PLABM) which serves as an impact modifier.

Material and method

Guineacorn husks particulates (GHP) was obtained from Zaria after the harvest period, PLA of grade 3051D and Dupont Biomax 100 strong were purchased from Nature works USA, Sodium Hydroxide (NaOH) pellets and Acetic acid were obtained from The Netherlands and Sigma-Aldrich respectively.

Particulate filler preparation

The husks were thoroughly washed with detergent to remove all forms dirt including stones and sand. They were 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 attached to its outlet. The ground husks were then soaked in hot water for 24hrs to remove any volatile matter and afterwards, they were dried in the open air before alkali treatment. The dried particulate filler was termed untreated (UNTRD) filler.

For the alkali (ALK) treatment, the particulate filler was soaked in 5% w/w NaOH concentration for 24hrs at room temperature. The filler was then rinsed repeatedly with distilled water containing little quantity of acetic acid until no trace of NaOH was confirmed. The NaOH modified filler was then dried in air for 2days then oven dried at 105°C for 24hrs.

Compounding and Extrusion Process

Compounding was performed using a Brabender single screw extruder with temperature profile of 160/175/175/165°C from hopper to die and screw speed of 40rpm. The fillers were varied from 10 to 40% at 10% interval with Pure PLA blended with 5% Biomax strong as matrix and termed PLABM. The extrudates were passed through a water tank with continuous flow of water. They were then pelletized using a type 881207 granulator. The pelletized materials were heated in an oven at 50°C to remove moisture before storing in a desiccator prior to injection moulding.

Injection Moulding

A BOY 22M injection moulding machine was used to produce tensile bars (dumbbell shapes) according to ASTM D638, flexural bars according to ASTM D790 and impact samples according to ASTM D256. The temperature profile used was145/180/180/165°C, injection pressure of 50 bars, mould temperature was 30°C and 30 seconds holding time.

All injection moulded specimens were conditioned in a Binder KBF240 humidity chamber at 23°C and 50% Relative humidity for 40hrs before testing.

Mechanical Testing

Tensile and flexural tests were conducted according to ASTM D638 and 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.

Morphological studies using scanning electron microscope (SEM)

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

Results

Figure 1 is the results for tensile strength of poly(lactic acid) filled guineacorn husks particulate biocomposites. Figure 2 shows the results for tensile modulus of PLABM/GHP biocomposites. The elongation at break of the biocomposite against filler content is presented in Figure 3. The variation of flexural strength of the biocomposite against filler content is presented in Figure 4. Figure 5 is the result of flexural modulus against filler content for PLABM/GHP biocomposite. Figure 6 is the impact strength result of PLABM/GHP biocomposite. The result for hardness of PLABM/GHP biocomposite is presented in Figure 7. Morphological observations of tensile fractured surfaces using scanning electron microscope is presented in Figure 8.

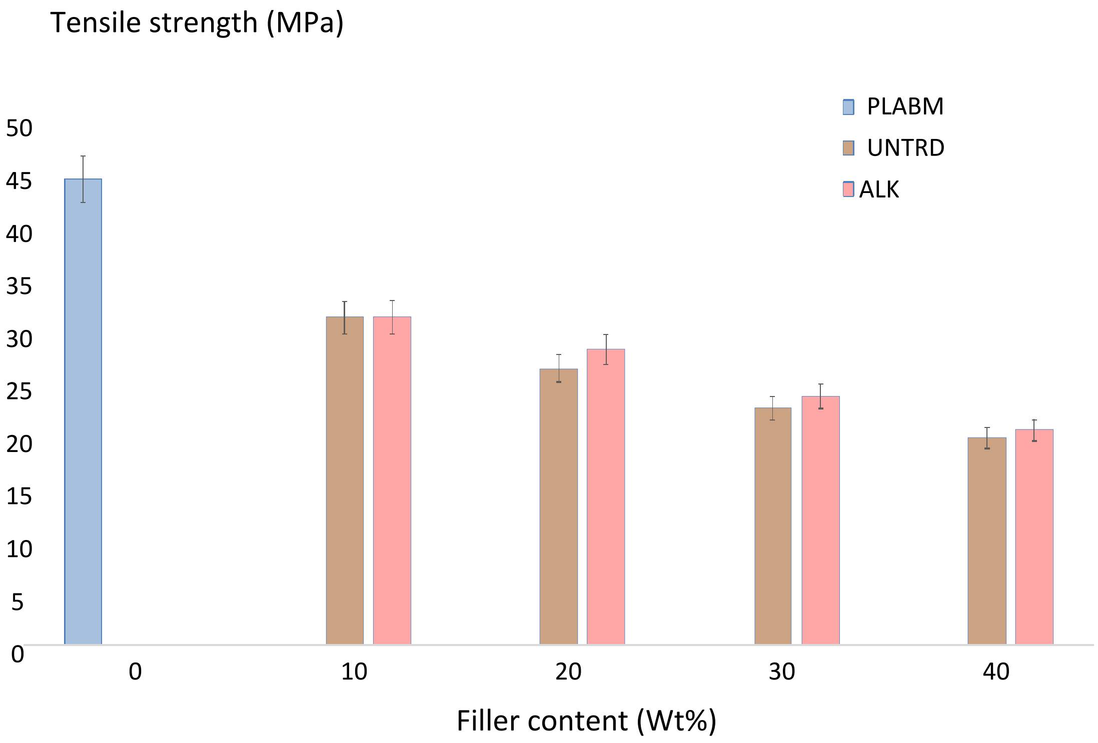

Figure 1. Tensile strength of PLABM/GHP biocomposites against filler content

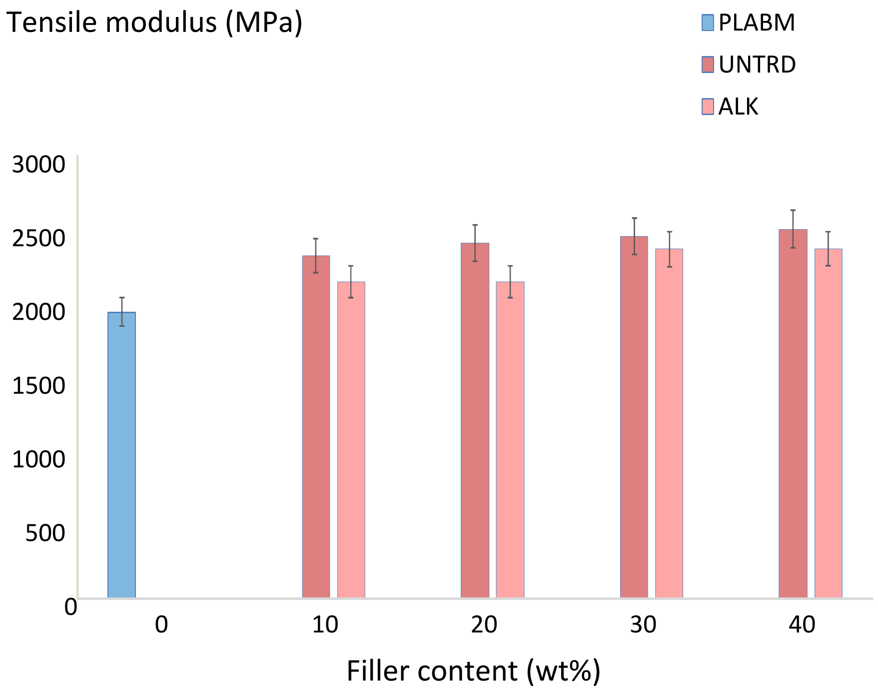

Figure 2. Tensile modulus of PLABM/GHP biocomposites against filler content

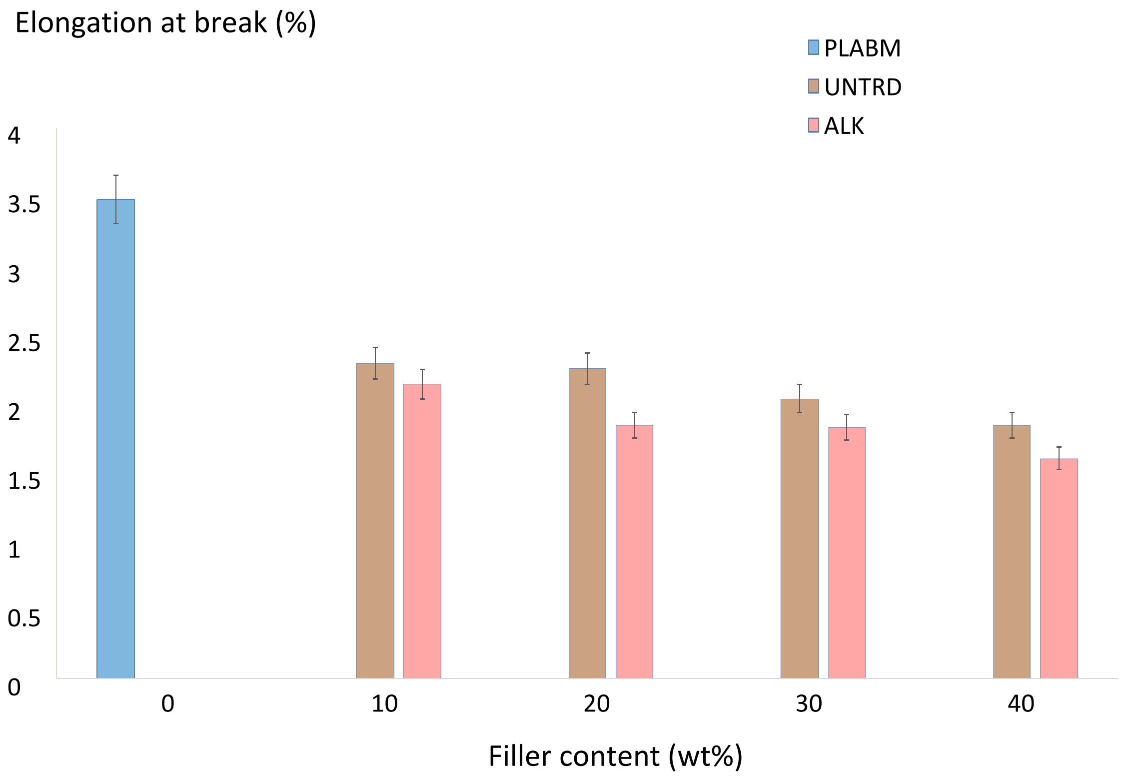

Figure 3. Elongation at break for PLABM/GHP biocomposites vs filler content

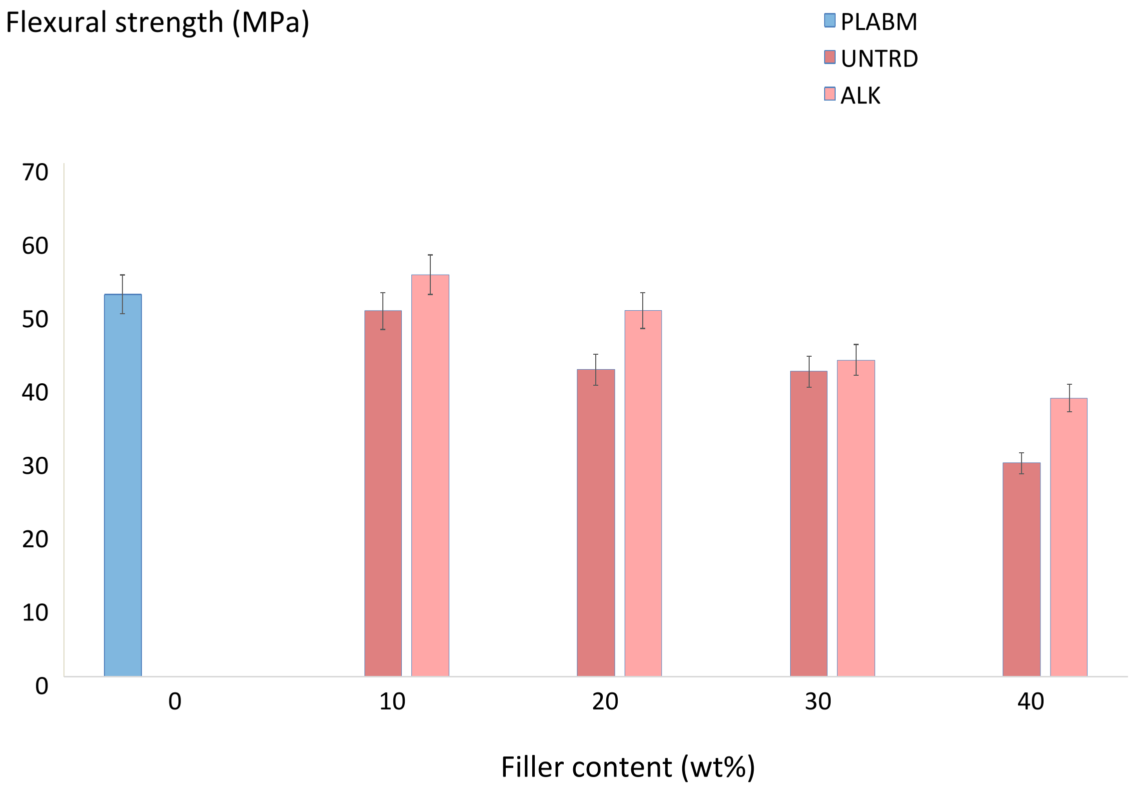

Figure 4. Flexural strength of PLABM/GHP biocomposites against filler content

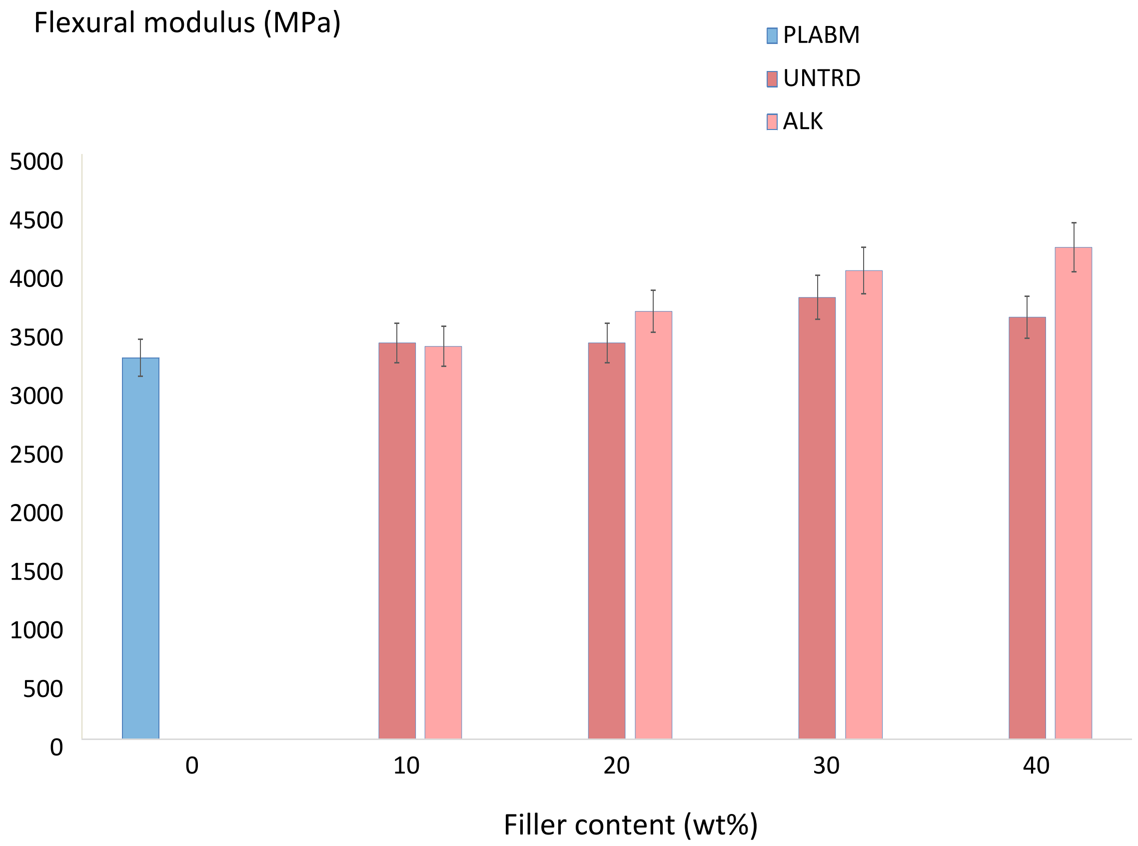

Figure 5. Flexural modulus of PLABM/GHP biocomposites against filler content

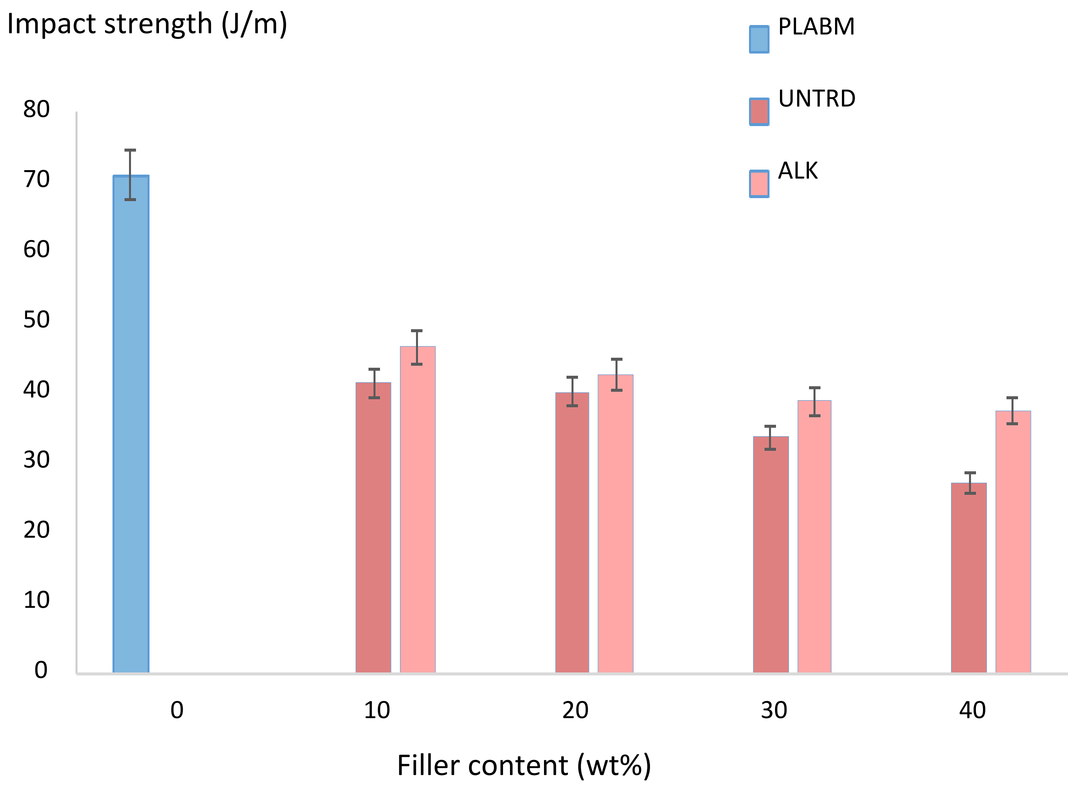

Figure 6. Impact strength of PLABM/GHP biocomposites against filler content

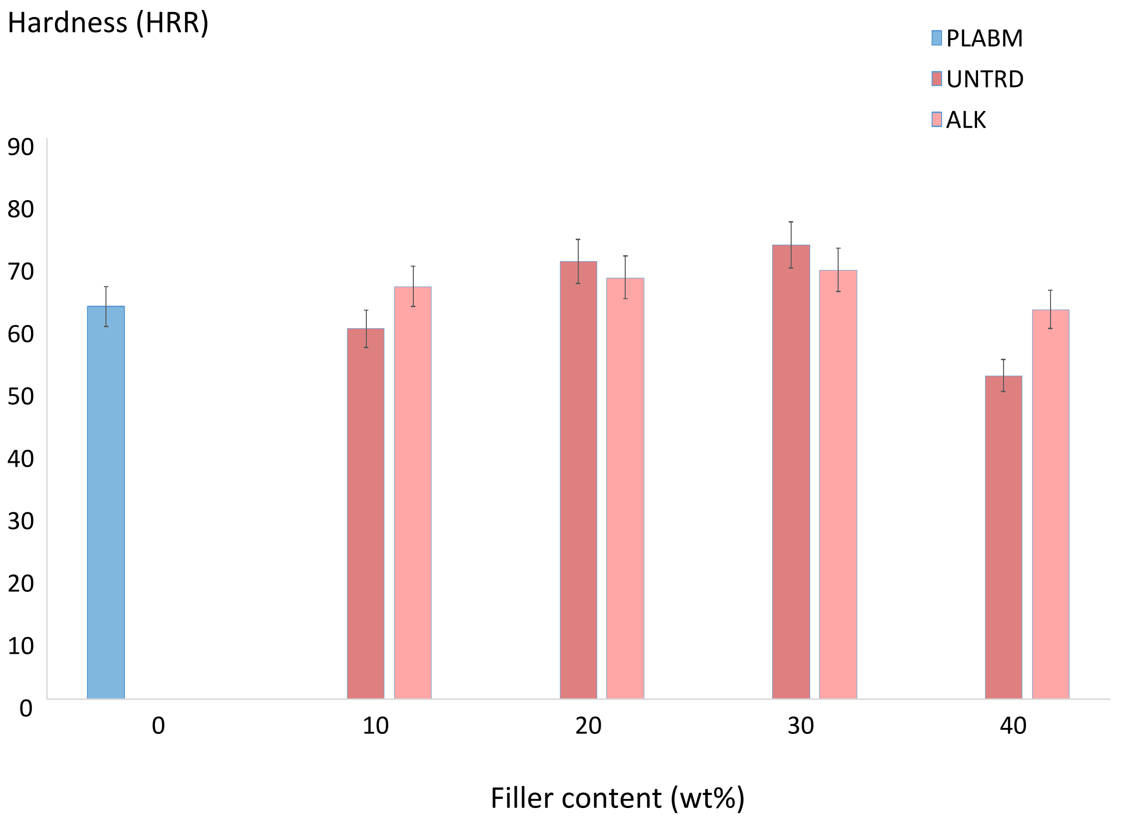

Figure 7. Rockwell hardness of PLABM/GHP composites against filler content

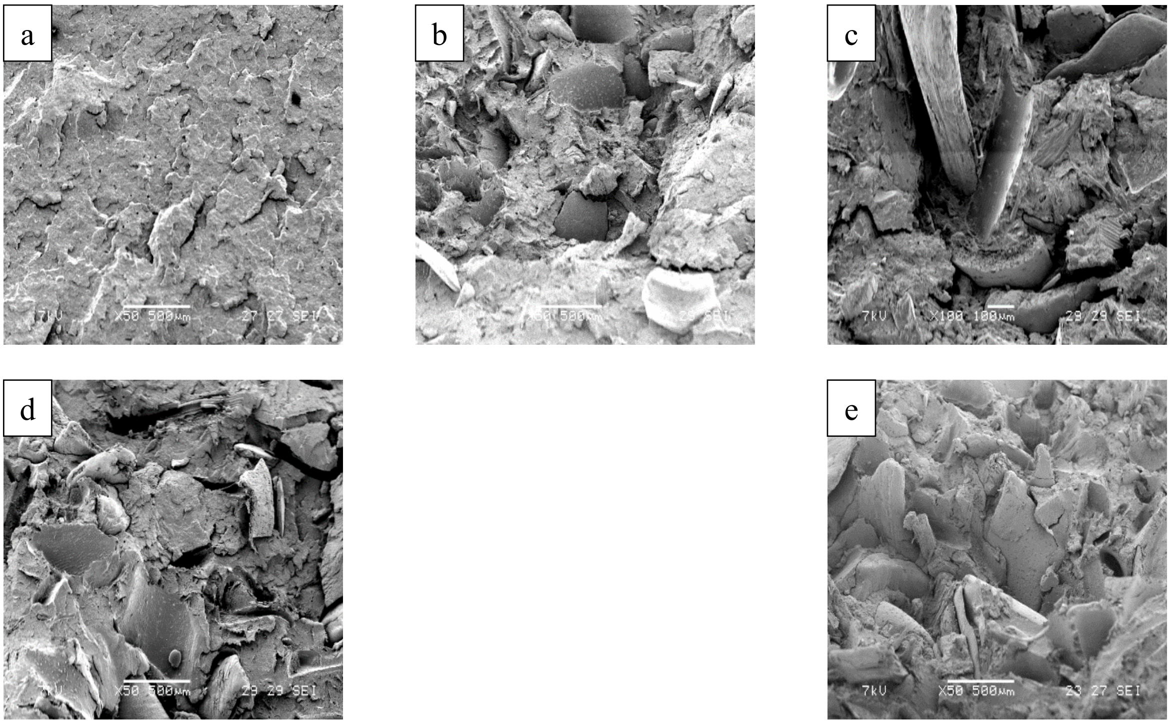

Figure 8. Tensile fractured surfaces for PLABM and PLABM/GHP biocomposites (a) unreinforced matrix (b) 10% untreated GHP content (c) 40%GHP untreated (d) 10% alkali-treated biocomposite (e) 40% alkali-treated biocomposite

Discussion

The tensile strengths results of the produced biocomposites are shown in Figure 1. It was observed that the unreinforced matrix (PLABM) with a tensile strength of 45MPa had a higher strength than the reinforced biocomposites whether treated or untreated and a progressive decrease was exhibited with increase in GHP content. However, the alkali treated biocomposites possessed higher tensile strength than the untreated ones. Similar observation was reported by Finkenstadt *et al.*, [2] that noticed a decrease in tensile strength in PLA/Sugar Beep Pulp (SBP) composite from 69.5MPa for the pure PLA to 29.55MPa for 45% SBP content. Also, [16], [17] and [18] reported similar findings. Furthermore, [19] reported higher tensile strengths for acrylic acid treated biocomposites over those of the untreated ones. The reduction of tensile strength with filler loading could be due to the irregular shape of filler resulting in poor capability to support stress transmitted from the matrix [20]. Furthermore, the reduction of tensile strengths at higher filler concentration could be due to increasing probability of filler agglomeration which could lead to a situation where there is more filler-to-filler interaction than filler –to-matrix interaction leading to generation of voids at filler-matrix interface and stress transfer to the filler becomes inefficient leading to low strength values [21, 22].

From the results in Figure 2, it was observed that the tensile modulus increased with increase in GHP content and the tensile moduli of the untreated biocomposites were higher than those of the alkali-treated ones. At 40%GHP content, the tensile moduli were 2505 and 2371MPa for the untreated and alkali-treated biocomposites respectively while for the unreinforced matrix, the tensile modulus was 1941MPa, a value that was less than those with reinforced PLA at all the GHP contents. This result is consistent with Shumigin *et al.*, [23] who observed that the modulus of PLA increased from 1975MPa for neat PLA to 2187MPa for reinforced PLA.

Increase in tensile modulus as filler content increases could be due to the restriction of the macromolecules mobility and deformability imposed by the presence of particles and as modulus is a measure of a material's stiffness, increase in filler content makes the material become stiffer [20, 21, 23, 24].

Figure 3 is the result for elongation at break (EB) of the produced biocomposite. The unreinforced matrix exhibited the highest EB with a value of 3.5%. Furthermore, the untreated biocomposites possessed higher EB than the alkali-treated samples. The decrease in EB with particle loading could be due to the decrease in the mobility of polymer chain as more rigid filler is added to a softer matrix [20]. Similarly, Chun *et al.*, [25] reported a decrease in EB of PLA/Coconut Shell Particulates (CSP) composites with increase in CSP content due to reduction in PLA chain mobility resulting in a more rigid composite and MA treated composites had lower values than their untreated composites as well.

Flexural strength results of the biocomposites showed a progressive decrease as GHP content was increased as seen in Figure 4. The alkali-treated samples exhibited higher flexural strengths than their untreated counterparts at all contents of the filler. It was observed in the result that the alkali treated sample at 10%GHP content possessed a flexural strength that is higher than that of the unreinforced matrix. Huda *et al.*, [26] reported a decrease in the flexural strength of PLA/kenaf composites with kenaf fibre addition and surface treated fibre composites had higher flexural strength than the untreated ones. Koutsomitopoulou *et al.*, [27] also reported a decrease in flexural strength with filler loading. Thamae *et al.*, [28] reported that probably due to the compressive component of flexural strength which is not interface dependent, they observed an improvement in flexural strength of their studied composites with flour loading. However, at higher flour content, there was a decrease probably due to agglomeration of the particles. Ibrahim *et al.*, [29] who investigated the flexural strength of Polyester/OPA composites reported a decrease with OPA loading possibly due to poor surface adhesion between polyester and OPA and also due to limited quantity of the matrix with increase in filler, polyester resin was not able to completely wet on the surface of filler. This could also be a probable reason for the behaviour observed in this study.

The results for the flexural modulus showed an increase with GHP loading with those for the alkali-treated samples being higher than those of the untreated as shown in Figure 5. Flexural modulus has been defined as the ability of a material to maintain its dimensions before rupture [29]. Increase in modulus relates to the stiffness properties of the composites. Huda *et al.*, [26] reported an increase in flexural modulus with addition of wood fibres in PLA matrix. They reported also that PLA and PLA-based composites possessed higher flexural strengths and moduli than PP and PP-based composites.

The results for the impact strengths for the produced biocomposites are presented in Figure 6. From the results, it was observed that the unreinforced matrix possessed impact strength of 71J/m which was higher than those of the reinforced biocomposites. Furthermore, the impact strength of bio-composites containing treated fillers were higher than those of the untreated fillers possibly due to better dispersion of the fillers in the matrix as a result of the chemical treatment. Similar behaviour was reported by Ahmad *et al.*, [30] for Polyester/rice husk (RH) composites. They noted that impact energy is an indication of tolerance for sudden force where the composite is subjected to rapid crack propagation through the material. Fillers disturb matrix continuity and individual filler is a site of stress concentration, which can act as a micro-crack initiator [31]

Figure 7 indicates that the hardness of the biocomposites increased with increase in GHP content from 10 to 30% content for both the treated and untreated samples and then decreased afterwards. However, at 20 and 30% GHP contents, the untreated biocomposites exhibited higher hardness than the treated ones. Increase in hardness could be as a result of a more compact structure at the surface of the material which leads to greater resistance to penetration and consequently resulting in high hardness of the material [32]. Although Saini *et al.*, [33] reported increase in hardness with filler loading but, treatment with NaOH did not show any improvement at the end of their study.

The SEM of tensile fracture surfaces for PLABM/GHP biocomposites are shown in Figure 8a-e. The SEM images generally indicated brittle fractures which are more pronounced in the reinforced specimens (Figure 8b-e) than in the unreinforced specimen (Figure 8a). The images indicated filler pull out which were more pronounced in the untreated specimens (Figure 8b and c). The alkali-treated specimens showed cleaner images which indicate better adhesion between the filler and the matrix than the untreated specimens. This could be a reason for better tensile strength for the alkali-treated samples over the untreated samples.

Conclusions

From this study, the following conclusions were drawn:

÷ Tensile strength of the biocomposites decreased with increase in the GHP content

÷ The stiffness of the composites increased with increase in filler content as obtained from the results of tensile modulus.

÷ The impact strengths of the composites decreased progressively as filler content was increased

- The hardness of the biocomposites increased with increase in filler content.
- The alkali treated biocomposites exhibited better properties as compared to the untreated ones on a general note.

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