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Effect of Particle size and Alkali-Laccase on the Properties of Pterocarpus Angolensis (Mukwa) Wood Flour

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Abstract

The desire for advanced performing renewable materials and friendly to the environment has grown worldwide. Lignocellulosic materials have demonstrated great potential as reinforcing agents in the manufacturing of composite materials. Achieving such materials also depends on the optimization of parameters not limited to particle size, temperature, duration of treatment, manufacturing technique and the type of modification. Laccase enzyme, a biological modification deemed friendly to the environment with the aid of alkali pre-treatment was adopted for removal of hemicellulose and lignin that binds the cellulose fibres together. In this paper, particle sizes between; +100-200 µm, +200-300 µm, +300-425 µm, and +425-710 µm were immersed in 5wt% sodium hydroxide (NaOH) concentration followed by laccase modification. The enzyme activity, temperature and soaking duration were kept constant. The effects resulting from the modifications on the above particle sizes of waste mukwa were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and weight loss assessment. Significant improvements were observed on the untreated fibres. The morphology of modified fibres showed small differences while the crystallinity index revealed noticeable differences between the particle sizes. The surface modifications reduced the weight of the overall particles as impurities were extracted and influenced some functional groups; hydroxyl (-OH), lignin, cellulose, and hemicellulose. An improvement was also observed on the thermal stability of the treated fibres. The modifications were more effective on particle size +100-200 µm followed by +200-300 µm while the coarse particles did not show much improvement.

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Keywords: Alkali; hemicellulose; laccase; lignin; Pterocarpus angolensis

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Generation of wood waste from saw-mills/wood workers has become one of the major concerns as the waste is predestined for landfills that in turn become health hazardous to the society and environment. Researchers have adopted wood waste as reinforcing fillers in the manufacturing of wood plastic composites (WPCs) [1]. This comes from the fact that wood flour is of low cost, renewable and readily available [1]. Moreover, the addition of wood improves the flexural strength, working properties, stiffness, elastic modulus and thermal stability of the WPCs [2,3]. However, wood possesses disadvantageous attributes such as high content of hydroxyl (OH) group, low bulk density, low thermal resistance, the presence of impurities and proneness to biological degradation. Such attributes negatively influence the compatibility between wood flour and hydrophobic plastic, thereby decreasing the mechanical properties of the composite [1,2,4]. Various treatments such as alkaline, enzymes, and silane coupling agents have been used to improve the wood-plastic compatibility [3,5]. Different studies have been conducted on the effect of wood particle size distribution for the properties of WPCs [1,6]. Their studies showed the importance of considering particle size/distribution on optimizing the functional properties of WPCs. Therefore, the aim of this work was to investigate the effect of particle size and alkali-laccase treatment on the morphological, crystallinity and thermal stability of mukwa wood flour in preparing it for manufacturing of eco-friendly WPCs.

2. Experimental procedure

2.1. Materials

Waste mukwa wood flour was collected from a local furniture manufacturing company Terry Cooney in Gaborone. Laccase enzyme, sodium acetone buffer were provided by Biology department in Botswana Int' Uni. of Sci. and Tech (BIUST) and sodium hydroxide pellets of 99% concentration were supplied by Rochelle Chemicals, South Africa.

2.2. Mukwa flour treatment

Appropriate amounts of mukwa wood flour were sieved into ceramic containers labeled A (+100-200 µm), B (+200-300 µm), C (+300-425 µm) and D (+425-710 µm). All samples were weighed prior to oven drying at 115°C for 24hrs to reduce moisture contents. The flours were then weighed and transferred into labelled beakers followed by addition of same amounts of aqueous 5wt%NaOH in each. The flours were soaked for 2.5h at room temperature. Filtration of alkalised mukwa was done and the flours were thoroughly rinsed with water to remove excess NaOH before drying them at 100°C for 24hrs [7]. Laccase enzyme was then introduced to the alkalised and raw flours in the presence of sodium acetone buffer ph 4.5; the enzyme activity and temperature were kept constant. The flours were incubated in a water bath at 37°C and speed of 180 rpm for 24hrs. They were then thoroughly washed with water until about ph 8 was achieved followed by oven drying at 60°C for 48hrs [8]. A weight loss/gain measurement was taken before and after every treatment was done. Equations 1 and 2 were used for calculation of weight changes following the treatments;

$$\text{Weightloss}(\%)\text{Laccase} = \left[\frac{W_0 - W_1}{W_0}\right] \times 100 \quad (1)$$

$$\text{Weightloss}(\%)_{\text{5wt\%NaOH + Laccase}} = \left[\frac{W_X - W_Y}{W_X}\right] \times 100 \quad (2)$$

Where W_0 was the initial dry weight of mukwa wood flour before laccase, W_1 the residual dry weight of mukwa wood flour after laccase treatment while W_x is the dry weight after 5wt%NaOH treatment and W_y is the final dry weight of mukwa after 5wt%NaOH+laccase treatment [9].

2.3. Flour characterization

The morphological changes of chromium coated untreated and treated mukwa flours were examined using scanning electron microscopy, model JSM-7100F. The thermal stability of untreated and treated mukwa wood flour was measured using LECO 701 thermogravimetric analyser at a heating rate of 10ºC/min, under a nitrogen atmosphere in the temperature range of 25-700ºC. The Bruker D8 advance X-ray diffractometer, with generator operated at 40kV and 40mA was used to assess the crystallinity of treated and raw mukwa flours. The samples were scanned in the 2θ range of 5-55°. The Segal empirical method by Segal, et al. [10] was used to determine the crystallinity index (CrI) as follows;

$$\text{Crl}(\%) = \left[\frac{I_{002} - I_{am}}{I_{002}}\right] \times 100 \quad (3)$$

Where I_{002} is the crystallographic counter reading and I_{am} is the amorphous phase counter reading at 2θ in the samples.

3. Results.

3.1. Weight loss analysis

Percentage weight loss analysis was done after every treatment on mukwa wood flours of various particle size and the results are presented in Table 1. Thermal treatment is known for aiding cellulose hydrolysis of fibres without extracting any non-cellulosic components such as hemicellulose, lignin and pectin [11,12]. A decrease in weight loss has been observed from particle size of +100-200 to +425-710 µm suggesting that thermal treatment was more effective on particle +100-200 µm. It is thought that finer particles will lose moisture rapidly in comparison to bigger particles as they have smaller surface areas. Laccase treatment reduced the overall weight of the flours with particle size +100-200 µm producing the most reduction followed by +200-300, +300-425 and +425-710 µm respectively. Laccase degrades lignin and phenolic thereby exposing more hydroxyl groups [13].

Table 1: Percentage weight loss analysis of thermal, alkali and laccase treated mukwa wood flour

Weight loss (%)	+100-200 µm	+200-300 µm	+300-425 µm	+425-710 µm
Thermal	10.23	9.35	9.05	8.06
Laccase	11.30	7.50	3.90	7.40
5wt%NaOH+Laccase	7.20	6.90	5.80	0.80

Alkali treatment extracts a portion of non-cellulosic components [14]. The 5wt%NaOH+laccase was more effective on particle size +100-200 µm followed by +200-300 µm as they produced better weight losses of 7.20% and 6.90% respectively. The 5wt%NaOH+laccase treatment was not that effective on the coarse particle size of +425-710 µm as it produced the least weight loss of 0.8%. Alkali pre-treatment has demonstrated to be effective as further weight losses were recorded. From the previous study [8], laccase treatment produced significant weight loss with an alkali-laccase recording weight gains with the assumptions that the samples did not dry enough hence the 48 hours dying on this experiment. The weight losses due to laccase and alkali-laccase treatments are deemed to be extractives that add to the overall weight of the flours.

3.2. SEM analysis of mukwa wood flours

Fig.1 shows morphological changes as a result of laccase and 5wt%NaOH+laccase treatments on particle sizes +100-200, +200-300, +300-425 and 425-710 µm. All the untreated flour images (Fig.1A-D) reveal oily and waxy structures on the surface of the fibres. The laccase treated flours (Fig.1E-H) rather show a smoother profile in comparison to untreated and 5wt%NaOH+laccase. The laccase images have little-protruding structures on the surface, suggesting that laccase treatment extracted some of the non-cellulosic materials binding the fibres together. Laccase treatment is known for exposing fibre surfaces by extracting some of the fats, lignin, protein, and hemicellulose [15].

Some differences can be seen on across laccase treated flours. Fig.1G and H of particle size +300-425 and +425-710 µm show presence of surface impurities at a higher degree in comparison to +100-200 and +200-300. This suggests that laccase treatment was more successful on cleaning finer particles. Better fibre surface cleaning was achieved by the 5wt%NaOH+laccase presented in Fig.1I-L. The images show rough profiles, with the roughness coming from the NaOH pre-treatment. Alkali treatment is known for making fibre surfaces as rough as cellulose-binding materials are extracted [7]. However, micro-cracks and some porosity on particle size +200-300 and +300-425 µm (Fig.1I and L) can be seen, this might be due to alkali treatment hence negatively influencing the quality and functional properties of the fibres.

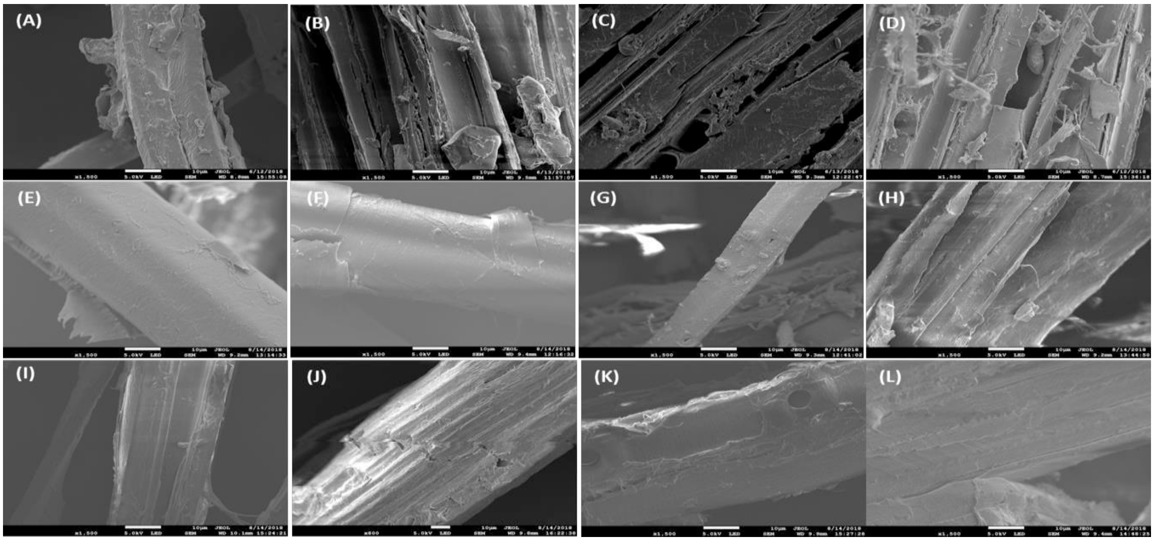

Fig. 1. SEM images of untreated (A-D), laccase (E-H) and alkali-laccase (I-L) treated mukwa wood flour of particle sizes +100-200, +200-300, +300-425 and +425-710 µm

3.3. XRD analysis of mukwa wood flours

The effect of laccase and 5wt%NaOH+laccase treatments on the crystallinity of particle sizes, +100-200 µm, +200-300 µm, +300-425 µm, and +425-710 µm were examined with results presented in Table 2. An amorphous peak about 2θ 16.1_{o} and crystalline cellulose peak at 22.2_{o} were used for calculation of crystallinity index using Eq 3. An overall increase in CrI (%) has been observed on surface treatments of laccase and alkali-laccase. Both laccase and 5wt%NaOH+laccase treatments performed better on particle size +100-200, +200-300, +300-425, +425-710 µm respectively. Setswalo et al, [7] reported an increase in crystallinity following alkali-laccase treatment. Alkali treatment realigns cellulose molecules as amorphous lignin and hemicellulose are lost thereby increasing crystallinity index [16,17]. Increase in crystallinity of cellulose has been reported to increase the tensile and Young's modulus of fibres [18]. Alkali pre-treatment has shown to be vital as crystallinity index increased following the hybrid treatment.

Table 2. The crystallinity index of untreated, laccase and 5wt%NaOH+laccase on various particle sizes

Crystallinity Index (%)	Particle Size (µm)			
	+100-200	+200-300	+300-425	+425-710
untreated	31.15	37.11	37.11	30.34
Laccase	52.63	44.68	40.71	43.63
5wt%NaOH+Laccase	54.97	48.61	47.49	46.61

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3.4 Thermogravimetric analysis of mukwa wood flours

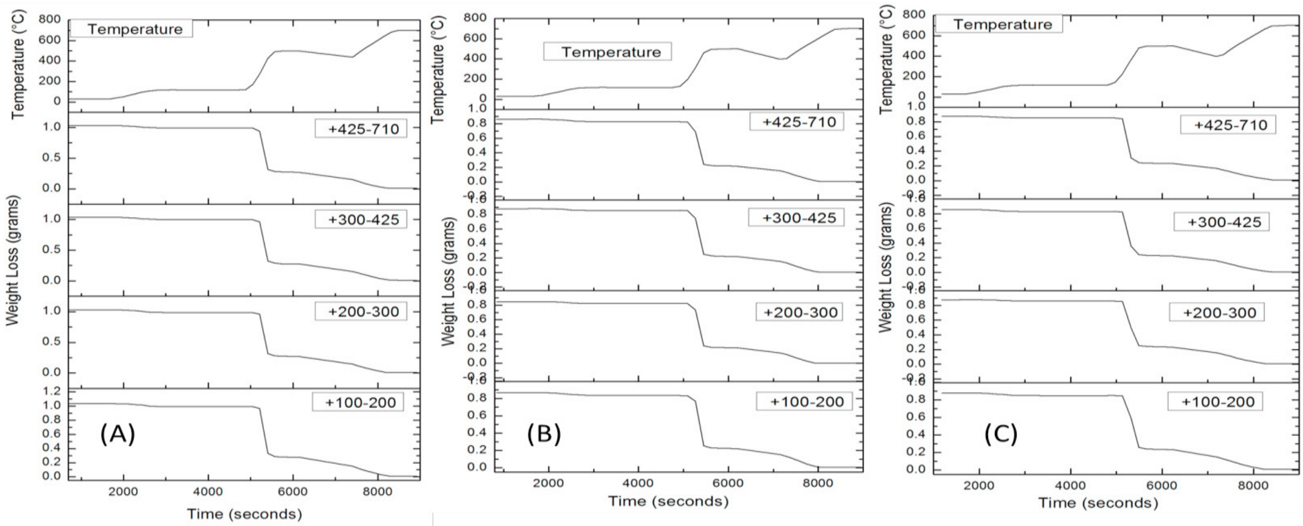

Fig. 2. Thermograms of (A) untreated, (B) laccase treated and (C) 5wt%NaOH+laccase treated mukwa wood flours at various particle sizes

Fig. 2 shows thermograms of untreated, laccase and 5wt%NaOH+laccase treated mukwa wood flours. They all reveal a two-staged decomposition process of weight losses above temperatures of 120oC. The first degradation stage for all untreated flours occurred at a temperature range of 145-380^{o}C. However, for the laccase treated flours decomposition occurred at 190-450, 200-450, 150-440 and 145-440^{o}C for particle sizes +100-200, +200-300, +300425 and +425-710 µm respectively. The 5wt%NaOH+laccase treatment produced better thermal stability on particle sizes +100-200 and +200-300 µm, this was revealed by higher decomposition temperatures of 210-460^{o}C and 200-450^{o}C for the first decomposition stage while the final stage produced 500-650^{o}C and 490-640^{o}C respectively. These weight losses are attributed to thermal depolymerization of some of hemicellulose and lignin [19].

When comparing the best results of particle size +100-200 µm of the current study with the previously studied particle size -100 µm [8], it can be seen that more weight was lost on particle size +100-200 µm on both the laccase and 5wt%NaOH+laccase treatments. An improvement of 5.19% and 14.17% on laccase and 5wt%NaOH+laccase respectively have been reported on the current study. Moreover, significant improvements on the crystallinity index have been produced on the current study with laccase and 5wt%NaOH+laccase recording increases of 13.13% and 17.97% respectively. Though not much can be said about the morphological changes, the current study shows more surface roughness on 5wt%NaOH+laccase which could proof beneficial for the mechanical interlocking with plastic. In essence, both the laccase and 5wt%NaOH+laccase treatments were more effective on particle size +100-200 µm than particle size -100 µm.

4. Conclusions

This study was investigating the effect of particle sizes (+100-200, +200-300, +300-425 and +425-710 µm), laccase and alkali-laccase on mukwa wood flour. The treatments were more effective on finer particle sizes +100-200 µm and +200-300 µm as they produced better weight losses, surface morphology and crystallinity index. The treatments were successful in cleaning mukwa wood flour with laccase treatment producing smooth fibre surfaces while alkali-laccase showed rougher surfaces. The crystallinity index of particle size +100-200 µm was better in comparison to other particle sizes with alkali-laccase displaying the best value of 54.97%. Moreover, alkali+laccase treatment produced better thermal stability on particle size +100-200 µm. From this experiment results, it has been deduced that a hybrid treatment of alkali-laccase is better than a using laccase only.

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