The Water Absorption and Thermal Properties of Green Pterocarpus Angolensis (*Mukwa*)-Polylactide Composites

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The water absorption, chemical resistance and biological properties are contributing factors to the overall performance of bio-composites, especially for outdoor applications. The functional properties of bio-composites are dependent on the interfacial bonding mechanism, which is controlled by the surface modification and processing parameters of natural fibers. Therefore, this study aims to investigate the potential of enhancing the mukwa/polylactide (mukwa/PLA) interface through an economic and ecological surface modification of recycled mukwa wood fibers via alkali-laccase modification. The fabricated bio-composites intended for making durable farm poles for semi-arid conditions of Southern Africa were characterised via water absorption, chemical resistance, thickness swelling, hardness and thermal properties. Less thickness swelling and water absorption were found on the alkali-laccase/PLA composites. The less-dense (1.09 g/cm^3) alkali-laccase treated composites showed better chemical resistance. Much swelling of the composites was observed on the 40% nitric acid (HNO_3), while 60%NaOH shrunk the composites and PLA by <3.5%. The laccase/PLA bio-composite showed a maximum thermal stability of 733 ˚C. The activation energy (Ea) optimised on the laccase/PLA composite with the highest of 104 kJ mol^{-1}. Maximum crystallinity of 45.8% was achieved on the untreated/PLA composites. The alkali-laccase modification maximised the hardness of composites with 35.45 HV on alkali-laccase/PLA.

Keywords: alkaline; activation energy; laccase; Mukwa; thickness swelling; water absorption

Introduction

Recycling natural fibers from renewable sources like agricultural biomass waste has prompted legislative laws that conserve the environment (do Nascimento, et al. 2021). The primary advantage of natural fibers is availability at low cost, less energy consumption during manufacturing and exacting, less wear during processing, low density, and possess acceptable specific properties (Afroza Khatun, et al. 2019). Natural fibers are also sustainable, biodegradable, supreme in their eco-friendliness, and non-hazardous (Rangappa, Siengchin and Dhakal 2020, Setswalo, Molaletsa, et al. 2021). The functional properties of wood polymer composites (WPC) benefit from reinforcing polymers with wood fibers, as fibers improve the

strength of composites. Hence a need to develop instrumental factors of natural fiber-reinforced composites, such as the surface adhesion characteristics of the fibers, thermal stability, and the dispersion of the fibers in the thermoplastic composites (Afroza Khatun, et al. 2019). The interaction of cellulosic fibers with polymeric materials is affected by numerous hydroxyl groups (-0H) responsible for strong hydrogen interactions between chains. Also, the incompatibility of hydrophilic lignocellulosic fiber with the hydrophobic polymeric matrix is primarily caused by the polar structure of cellulose (Odalanowska, Skrzypczak and Borysiak 2021). WPCs have strong affinity to moisture and their overall performance of WPCs is negatively influenced by the hydrophilic nature of wood (Adhikary, Pang and Staiger 2008, Butylina, Martikka and Kärki 2010). The properties of natural fibers depend on their ageing, chemical composition, density, internal structure, cell dimensions, microfibrils angle, and defects (Binoj, et al. 2016). Such challenges have been addressed through coupling agents and surface modification of natural fibers. They enhance the interaction of fibers with matrices by altering the structure of natural fibers, separating non-cellulosic material from cellulose-rich fractions (Arumugam, Arumugam and Muthusamy 2020).

Modifications such as alkaline (Bartos, et al. 2020), enzymes (Brodowsky, et al. 2020), silane (Wang, et al. 2020), acetylation (Oladele, et al. 2020, Zaman and Khan 2021), hydrogen peroxide (Mohd Sabri, et al. 2020), have been used. Alkaline modification disrupts hydrogen bonding in the network structure of fibers and increases their surface roughness (Faruk, et al. 2012, Kabir, et al. 2012). These increase the quantity of -OH groups on the fiber surface, yielding better wetting capabilities, the thermal stability of the wood fibers, and interaction with polymeric materials (Zierdt, et al. 2015). Enzymes are biocatalysts that accelerate biochemical reactions and degrade lignin, pectin, and hemicellulose, improving fiber aspect ratio (Karaduman, Gokcan and Onal 2012). Various enzymes are available for specific extraction, for instance, cellulose destroys amorphous cellulose and β-1,4-glucosidic bonds in crystalline. Xylanases (hemicellulases) degrade the hemicellulosic components. Pectinases hydrolyse pectin, and laccase is known for degrading lignin (Seghini, et al. 2020). Sreekumar et al. (2009) examined the effects of benzoylation, sodium hydroxide, silane, and permanganate treatment on the moisture uptake of polyester-sisal fibers. They reported improvements in the water absorption properties following surface modifications. Additionally, better performance was on fibers treated with 5wt.% NaOH. Zalinawati et al. (2020) reported reduced thickness swelling and water absorption on alkali-treated Buri palm fiber epoxy composites than the untreated composites. Composites exposed to moisture decreased the tensile properties due to the degradation of the fiber-matrix interface. Alkaline treatment improved the chemical composition, mechanical properties, crystallinity, and surface morphology of natural fibers (Cai, Takagi, et al. 2016, Singh, Singh and Dhawan 2020). The water absorption of the composites decreased while the thermal stability improved owing to

the removal of lignin, hemicellulose, surface oils, and waxes due to alkaline treatment (Mohan, Reddy and Gowda 2015, Oushabi, et al. 2017).

Ramadevi et al. (2012) also reported reduced moisture absorption after alkalization of single cellulosic abaca fiber. Improved resistance to water of the Alfa fiber polylactic acid composites has been reported, owing to the enzymes for their ability to remove hydrophilic materials (Werchefani, Lacoste and Belguith, et al. 2020a). George et al. (2016) investigated the effect of enzymes on the thermal behavior and water absorption of flax and hemp polypropylene composites. Enzymes reduced the fibers by 25% (wt.), the surface polarity of fibers, improving the water resistance and thermal stability without compromising the mechanical properties of the hemp and flax polypropylene composites. Enzymes improved the chemical resistance of abaca fibers reinforced PP composites to the acid and base, reducing the moisture absorption of the composites by 20-45% (Bledzki, et al. 2010). Traditionally, the barks of mukwa have been used as medicine for nose bleeding, heavy menstruation and diarrhoea treatment (Fern and Fern 1989). The applications were extended to treating stomach, abdominal pains, headaches, diarrhoea, blood in the urine, sores, schistosomiasis, nettle rash, mouth ulcers, and skin problems. Additionally, furniture and musical instruments were made (Fern and Fern 1989, Geldenhuys 2013, Becking 2018). Despite mukwa wood showing numerous applications, limited study has been reported on mukwa wood as a source of raw material in the production of indigenous mukwa polymer composites. Attempts on preparing mukwa wood fibers for possible reinforcement in the manufacturing of bio-composites have been made (Setswalo, Namoshe, et al. 2017, Setswalo, Oladijo, et al. 2019). The resulting mukwa/PLA bio-composites displayed competitive mechanical properties (Setswalo, Oladijo, et al. 2022). It is noted that high solid mukwa waste in the form of wood chips, sawdust and flour is generated in the wood processing industrial such as in construction and making furniture. The generated waste is usually destined to landfills, and or burnt. It is therefore necessary to combat land mismanagement, and particle pollution caused by mukwa remains through generation of economic green composites friendly to the ecosystem.

Related studies have focussed on developing WPCs considering one or two of the fiber processing parameters (Huang, et al. 2022). Meanwhile, few studies have investigated the effect of alkali-laccase modification with limited work considering a holistic approach incorporating a combination of processing parameters; particle size, soaking duration, alkaline concentration and temperature. It has been suggested that the above parameters influence the functional properties of natural fiber polymeric composites (Setswalo, Molaletsa, et al. 2021). Therefore, this study looked into enhancing the bonding quality between mukwa and PLA through eco-friendly surface modifications, with the view of improving the bio-composite's water absorption, thickness swelling, thermal stability, hardness and resistance to decay. The materials synthesis benefited from a sustainable process since waste usage was justified. The prospects of developing eco-

friendly mukwa/PLA bio-composites that are lightweight, retaining good chemical, stiffness and water resistance for making farm poles applicable to semi-arid and humid conditions of Southern Africa are investigated.

Materials and methods

Materials and chemicals

Waste mukwa wood fibers were collected from Terry Cooney, a company that manufactures furniture in Botswana. The sodium hydroxide (NaOH) pellets of 99.9% concentration, toluene, hydrogen peroxide (H_2O_2,), acetone, hydrochloric acid (HCL, 37.5%), nitric acid (HNO_3, 99.9%), sulphuric acid (H_2SO_4, 97%), acetic acid (CH_3COOH, 98%), sodium chloride (NaCl, 95%min), and hydrofluoric acid (HF, 99.98%) were purchased from were procured from local chemical companies (Westhood Agency and Africa Sales). The olive oil (eatable grade) was bought from local retail shops. The laccase enzyme was obtained from the Biological department laboratory in BIUST. The PLA 3052D biopolymer was supplied by NatureWorks LLC (Asia Pacific Ltd, Thailand) having a density of 1.24 g/cm^3, relative viscosity (3.3), melting flow rate of 14g/10min (210 °C, 2.16 kg), yield strength (62 MPa), glass transition temperature (55-60 ºC), and melting temperature of 145-160 ºC as provided by the supplier.

Surface modification of mukwa wood fibers

The recommended particle size/distribution of mukwa wood fibers was obtained through sieve analysis (Setswalo, Oladijo, et al. 2019). Prior to alkalisation in aqueous 5wt% NaOH, at 30 °C for 2.5 hrs, the mukwa wood fibers were oven dried to reduce moisture content. The treated mukwa wood fibers were then washed to remove excess NaOH and oven-dried at 100 °C for 24 hrs. The untreated and alkalised mukwa wood fibers were then subjected to laccase enzyme and incubated for 24 hrs at 150 rpm under a temperature of 37 °C. Before oven drying at 60 °C, the treated mukwa wood fibers were thoroughly washed with water, constantly checking pH until it reached 7 (Setswalo, Namoshe, et al. 2017, Setswalo, Oladijo, et al. 2019, Setswalo, Oladijo, et al. 2022).

Manufacturing of mukwa/PLA composites

The untreated and treated mukwa/PLA composites were manufactured using compression molding. To remove moisture, the mukwa wood fibers and PLA pellets were oven-dried at 60 °C overnight. A co-rotating twin-screw extruder (Xinda, PSHJ 35-40 L/D, China) compounded the untreated and treated mukwa wood fibers together with the PLA, maintaining fiber to PLA ratio of 35:65 by weight (wt.%) fraction. Operating temperatures for the barrel zones were at 145, 140, 150, 155, 160, and 165 °C, and the die zone at 170 °C at a rotating speed of 150 rpm. Before preparing the specimens, the composites were dried overnight in an air oven at 60 °C. The samples

dimensioned 200 x 200 x 8.5 mm (length, width, and thickness) were formed by a compression molding machine (Carver, CMG 30H-12 ASTM model B, USA) at compressive pressure of 2500 psi and a temperature of 180 °C for 20/20/10 min (preheat/heat/cool) respectively (Setswalo, Oladijo, et al. 2022).

Characterisation of mukwa wood fibers

Bulk density

The bulk density of the untreated, alkali, laccase, and alkali-laccase treated mukwa/PLA composites was determined using equation 1 (Afroza Khatun, et al. 2019). The bulk density for each sample was conducted five times, with an average recorded.

$$D = \left[\frac{\text{weight of the composite}}{\text{Length}\times\text{Width}\times\text{Height}}\right] \quad (1)$$

Absorption properties

The poor water resistance of natural fiber-reinforced polymeric composites (NFRPC) affects their absorption properties which correlates with the durability of materials (Halligan 1970, Zalinawati, et al. 2020). The untreated and treated mukwa/PLA composites of rectangular dimensions (50 x 12.4 x t mm^3) were cut for water absorption and thickness swelling testing according to the ASTM D570 standard. Ten samples of each composite composition were immersed in distilled water for durations of 1, 7, 14, 21, and 28 days at room temperature. An analytical balance measured the dry and wet weight of the composites accurately. Immersed composites were wiped using a clean piece of dry fabric to remove the water on the surface of the composites before weighing. Equation 2 was then used to calculate percentage weight gain at any time interval, signifying the water absorbed by the composites (Ngaowthong, et al. 2019, Chandra, et al. 2021).

$$\text{Water absorption (\%)} = \frac{\text{Wet weight}-\text{Conditioned weight}}{\text{Conditioned weight}} \times 100 \quad (2)$$

The changes in thicknesses of the composites were measured using a micrometer screw gauge, and equation 3 was used for computation of thickness swelling. The standard deviations and averages for the tested samples were computed for statistical purposes. With T_0 and T_1 being the thicknesses of the composites before and after soaking, respectively (Zalinawati, et al. 2020).

$$\text{Thickness swelling (\%)} = [T_1 - T_0/T_0] \times 100 \quad (3)$$

Chemical resistance

The chemical resistance of untreated, treated mukwa/PLA composites, and PLA was studied according to the ASTM D543-95 standard. Five samples were conditioned, then weighed, and immersed in the respective chemical reagents for 7 days at room temperature. After 7 days, the samples were removed and washed with distilled water and then pressed between clean filter papers to dry them. The samples were then weighed, and equation 4 was used to determine the percent weight gain or loss. The optical microscope (Leica DM2700 M equipped with MC170 HD camera) was used to observe the mukwa/PLA composites that had drastic changes following the chemical reagents.

$$\text{Weight gain or loss (\%)} = \frac{\text{Final weight} - \text{Original weight}}{\text{Original weight}} \times 100 \quad (4)$$

Thermal stability

The thermal stability of the polylactide, untreated, and treated mukwa/PLA composites were examined using Mettler Toledo TGA 3+ analyser. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere and a 20 ml/min feeding rate. Broido's equation (equation 5) was used to compute the kinetic activation energy (Ea) of the untreated and treated mukwa/PLA composites. Where Y is the normalised weight (W_t/W_0), W_t is the weight of the composite at any time (t), W_0 is the initial weight of the composites, and R is the universal gas constant (8.314 J/mol K). In contrast, T and k are temperatures in kelvin, and the Boltzmann constant (1.3806 x10^{-23} J/K), respectively (Jebadurai, et al. 2019). Plotting In [In(1/Y)] vs 1/T should yield a line such that the activation energy values can be derived from the slope (-Ea/R).

$$\ln\left[\ln\left[\frac{1}{Y}\right]\right] = -\left(\frac{E}{R}\right)\left[\left(\frac{1}{T}\right) + k\right] \quad (5)$$

The thermal transitions of the untreated and treated mukwa/PLA composites were determined by a differential scanning calorimetry (DSC 3+) analyser Mettler Toledo. About 5-10 mg of each composite were heat scanned from 25 to 400 °C under a nitrogen atmosphere flow rate of 20 ml/min. A heating rate of 10 °C/min was kept constant throughout the analysis. The samples were heated, cooled, and reheated under the same conditions. Equation 6 was used for calculating the crystallinity index (X_c) of the composites (Lourençon, et al. 2020). The melting enthalpy (ΔH_f^0) of 100% crystalline polylactide is 93.7 J/g, with W being the weight fraction of PLA in the composite, and ΔH_f is the heat of crystallisation (Manich, et al. 2010, Lourençon, et al. 2020).

$$X_c = \left(\Delta H_f / \Delta H_f^0\right) \times (100/W) \quad (6)$$

Hardness testing

The hardness of the untreated and treated biocomposites were tested using a Vickers hardness (Innovatest Europe BV, Netherlands) tester. Five samples of each composite of dimensions (50 x 50 x 8.5) mm^3 were prepared and tested according to the ASTM E-384 standard, and the standard deviation (SD) was calculated. A major load of HV 0.3 intender was applied on the bio-composites for 10s (dwelling time) (Nukala, Kong, et al. 2022a). The indentations were analysed using an optical microscope equipped with an HD camera at a magnification of X20.

Results and discussion

Bulk density

The effect of surface modification on the bulk density of the composites is shown in Figure 1. The PLA was denser (1.24 g/cm^3), followed by the untreated/PLA composites with 1.19 g/cm^3. These could be attributed to amorphous materials adding weight to the untreated/PLA composites. The hybrid treatment of alkali-laccase proved to be instrumental in reducing the bulk density of the composites to 1.10 g/cm^3, a reduction of 7.6%, 6%, and 4.3% on the untreated/PLA, laccase/PLA, and alkali/PLA composites respectively. Such lightweight polymeric composites can be used where weight reductions and greener materials are a priority without compromising the properties of the components, such as in packaging and automobile interiors. Blending a polymer with natural fibers has been reported to reduce the bulk density (Afroza Khatun, et al. 2019).

Insert Figure 1 here

Water absorption

The water absorption behavior and moisture retention of NFRPCs influences and deteriorates their functional properties and lifespan (Werchefani, Lacoste and Elloumi, et al. 2020b). The relation between the water absorption of PLA, untreated, and treated mukwa/PLA composites, and the immersion duration is shown in Figure 2. For neat PLA, the water absorption was least across compared to the mukwa/PLA composites. These could be due to the absence of hydrophilic components present in mukwa wood fibers. The introduction of mukwa wood fibers into PLA increased the water absorption of PLA. Thus in agreement with the observation reported on Alfa fiber-PLA composites (Werchefani, Lacoste and Elloumi, et al. 2020b). The water absorption increased with prolonged immersion, with the maximum values of 5.48, 3.51, 3.77, 3.37, and 0.61% recorded on day 28 for the untreated, alkali, laccase, alkali-laccase, and PLA, respectively. The comparison between treatments in Figure 2 reveals poor water absorption properties on untreated mukwa/PLA composites. These could be attributed to relatively available hydroxyl (-OH) group reaction sites that encourage a hydrophilic character in the untreated mukwa. The rate

of absorption between day 1 and 7 corresponded to 1.57%, 1.14%, 1.08%, 0.96% and 0.27% for untreated/PLA, alkali/PLA, laccase/PLA, alkali-laccase/PLA and PLA, respectively.

Insert Figure 2 here

Significant differences were observed in treated composites, suggesting that surface treatments reduce the water absorption of composites (Xiao, Cheng and Zhong 2021) by inducing a hydrophobic character and exacting some hydroxyl groups and non-cellulosic (hemicellulose, extractives, and lignin) components. Hemicellulose is primarily responsible for moisture absorption (Mamun, et al. 2013). The laccase modification has been reported to impart a hydrophobic characteristic to jute fibers through oxidation of phenolic –OH groups and forming ethers by radical coupling (Dong, et al. 2018). The alkali-laccase treated mukwa/PLA composites showed superior water resistance than other composites (Figure 2). The extraction of hydrophilic components improves the water resistance of the composites, hence better water resistance on the treated composites than the untreated ones (Werchefani, Lacoste and Belguith, et al. 2020a). A water absorption study revealed increased water absorption on untreated composites. Perhaps this water regains increases due to the abundant hydroxyl groups in untreated elephant grass fibers (Rajesh, Ratna Prasad and Gupta 2018).

Thickness swelling

In terms of thickness swelling (Figure 3), untreated composites swelled more, followed by alkali, laccase, alkali-laccase treated, and polylactide, respectively. The results of this study are in agreement with an observation on the recycled newspaper fiber (RNF) and poplar wood flour (PWF)-polypropylene composites (Ashori and Sheshmani 2010). The poor thickness swelling on untreated composites could be attributed to surface impurities, hemicellulose, and lignin in extensive contents. Also, hydrogen bonding was not promoted; instead, water molecules were attracted due to the presence of hydroxyl groups which could have played a significant role in the increased thickness swelling (Zalinawati, et al. 2020).

Insert Figure 3 here

The removal of extractive and non-cellulosic components promoted better interfacial adhesion between treated mukwa wood fibers and PLA matrix, leaving minimal voids for water molecules to penetrate. All the mukwa/PLA composites were thicker at day 28 recording the highest thickness swelling increases of 2.98%, 2.55%, 2.43%, 2.15% for untreated, alkali, laccase and alkali-laccase, respectively. Additionally, the untreated/PLA composites were observed to be 0.43%, 0.55% and 0.83% thicker than the alkali, laccase and alkali-laccase/PLA composites. However, the PLA was found saturated at day 21 with 1.54%. Despite polymeric materials being non-polar, they slightly absorb water, as indicated in Figure 3. Lignocellulosic materials in the composites are mainly responsible for absorbing moisture. It is due to many porous tubular structures in the fibers accelerating the diffusion of water through the capillary action (Mohd

Ayob, Ahmad and Mohd Khairuddin 2015). A study on the effect of 10% NaOH bamboo-polypropylene composites reported increases in thickness swelling (Jamaludin, et al. 2020). The gains could be characterised by propagating cracks, swelling, twisting, and collapsing fibers induced by the strong alkaline treatment (Cai, Takagi, et al. 2015).

Chemical resistance

Table 1 depicts the chemical resistance of the untreated and treated mukwa/PLA composites and significant differences for all chemical reagents were observed. The reaction of untreated and treated mukwa/PLA composites is more significant on toluene, 3% hydrogen peroxide, 60% sodium hydroxide, 40% Nitric acid, and 5% Acetic acid. From Table 1, the most significant weight gains on both the untreated and treated composites were on the composites immersed in 40% nitric acid. The composites swelled, became rougher, and changed colour (bleached), as depicted in Figure 4(a).

Insert Tale 1 here

The polymer showed good resistance to nitric acid when compared to the composites. The alkali-laccase treated composites produced better acid resistance than the laccase, alkali, and untreated composites (Table 1). Polylactide showed poor resistance to toluene as it recorded the highest weight gain (16.94%) compared to other chemical reagents. Separation and swelling were associated with PLA immersed in toluene, as shown in Figure 5(a), whilst macro-cracking and discolouration (following immersion in toluene) were seen on composites [Figure 5(b)].

Insert Figure 4 here

Insert Figure 5 here

Though the composites showed poor resistance to 3% H_2O_2 and 5% CH_3COOH, the influence of surface modification was evident as the treated mukwa/PLA composites revealed better resistance when compared to the untreated composites. The presence of polar and hydroxyl groups in untreated cellulosic fibers leads to high absorptions affecting the dimensional stability of the composites (Mittal and Chaudhary 2018). Blending the mukwa fibers with polylactide improved the composites' resistance to peroxide and acetic acid, as it yielded superior resistance of 0.29% on both occasions. The PLA showed a substantial reduction in weight of -15.5%, followed by the untreated mukwa/PLA composite with -5.87% under 60% NaOH (Table 1). The strong alkali treatment produced a very rough composite surface, as shown in Figure 4c. Strong alkali treatments are well known for producing rougher surfaces and reducing the size of fibers and the resulting composites (Cai, Takagi, et al. 2016). The composites and PLA generally showed good chemical resistance to the HCL, H_2SO_4, HF, acetone, and olive oil. The optical microscope structures in Figure 6 revealed excessive swelling of the mukwa/PLA composites under 40%

HNO_3, hence the high values recorded in Table 1. The macro-structure of untreated/PLA composite (Figure 6b) showed the presence of voids that chemical reagents could have used for easy penetration hence the poor resistance. The presence of voids in polymeric composites is considered a defect and promotes the absorbance of water and other reagents (Sahu and Gupta 2020). The 60% NaOH showed separation of PLA and mukwa wood fibers, and the toluene image revealed crystallisation of PLA and macro-cracks that were about 0.17 mm in size (Figure 6d).

Insert Figure 6 here

Figure 7 correlates the thickness swelling of the untreated (Figure 7a) and treated mukwa/PLA composites ((Figures 7b-d) with water absorption and the two extremes of chemical resistance of 60%NaOH (highest weight loss) and toluene (upper weight gains) ((Figure 7e) at an interval of 7 days. A statistical regression method was adopted, depicting the correlations in terms of R-squared (R^2) values. The water absorption of the composites increased relative to increase in the thicknesses of the bio-composites. Optimal R^2 of 0.9717 was found on alkali/PLA composites, with the PLA, Untreated, laccase and alkali-laccase corresponding to values of 0.9565, 0.9514, 0.9090 and 0.8850 respectively. The alkali-laccase/PLA bio-composites showed less rate of swelling and this may be due to the quality of interfacial bonding induced by the alkali-laccase modification. For weight gain vs thickness swelling (Figure 7f), the 60% NaOH showed better chemical resistance with increased thickness swelling up to 1.2% (alkali-laccase/PLA composites), where a decrease occurred. However, as thickness swelling increased for toluene, the weight gains reduced. In both scenarios, the optimal chemical resistance was at thickness swelling of 1.2%, produced by the hybrid treatment of alkali-laccase.

Insert Figure 7 here

Thermogravimetric analysis (TGA)

The thermal stability of untreated and treated mukwa/PLA composites was relative to the weight loss and temperature ranging from 25 °C to 800 °C. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the samples are presented in Figure 8. The thermal analysis evaluates the physical, chemical, and structural changes occurring due to temperature changes (Monteiro, et al. 2012). Some differences in the thermal decomposition and weight loss are due to the chemo-mechanical treatment of the composites (Mohana Krishnudu, Sreeramulu and Venkateshwar Reddy 2020). The slight slope occurring on all composites at 60-70 °C is attributed to moisture loss. The moisture loss was verified by the small peaks occurring at around 60 °C on the DTA curves shown in Figure 8b. The untreated/PLA composites demonstrated better thermal stability in the first degradation stage, followed by the laccase/PLA, alkali-laccase/PLA, alkali/PLA, and PLA, respectively. The presence of lignin at a higher degree on the untreated/PLA could have improved thermal stability. Lignin presents a chemical anisotropy in its three-dimensional matrix and forms charcoal during thermal stress, indirectly enhancing

thermal stability (Lourençon, et al. 2020). Surface modification is well known for splitting fibers into finer filaments, promoting the interaction of fibers and matrix. In turn, this could be detrimental to the thermal properties of the resulting composites, as reported (Ray, et al. 2004, Lourençon, et al. 2020). A similar trend has been reported on untreated and alkali-treated composites (Mohana Krishnudu, Sreeramulu and Venkateshwar Reddy 2020). The dehydration of cellulose has thermal decomposition between 210-260 °C, followed by hemicellulose degradation (Monteiro, et al. 2012).

Insert Figure 8 here

The second peaks at 270, 305, 327, and 335 °C on the DTA curves for alkali/PLA, alkali-laccase/PLA, untreated/PLA, and laccase/PLA, respectively correspond to the depolymerisation of hemicellulose, pectin, dehydration of cellulose unit, and thermal cleavage of glycosidic, hydroxyl, and carbonyl bonds (Mohanty, Verma and Nayak 2006, Mohana Krishnudu, Sreeramulu and Venkateshwar Reddy 2020, Manimaran, et al. 2020). The third peak appearing on the DTA curves for the alkali and alkali-laccase treated composites has been observed at 320 and 340 °C, respectively. They could be attributed to the thermal decomposition of cellulose I (Jebadurai, et al. 2019). In this region, significant weight losses of about 83% were observed. The final decomposition stage attributed to α-cellulose was at temperatures around 550 °C, and the degradation process was steady (Manimaran, et al. 2020). Residuals of around 9.5, 8.3, 1.5, and 1% for alkali, alkali-laccase, laccase, and untreated mukwa/PLA composites were recorded.

The kinetic activation energies (Table 2) for polylactide, untreated, and treated mukwa/PLA from Broido's plot depicted in Figure 9 are from the linear plots. The temperature ranges of 250-400 °C, where the main thermal decomposition step occurs, were considered. The highest Ea of 165 kJ/mol was reported on the PLA, while alkali/PLA composite recorded the least Ea of 64.8 kJ/mol. These activation energies are within the specified range of 60- 170 kJ/mol for natural materials. Though some studies (Morgado and Frollini 2011) have reported an increase in Ea following mercerisation, significant Ea reductions have been reported in this study. It could be characterised by the incomplete transformation of Cellulose I to cellulose II. The hydrogen bonds in cellulose II are believed to be stronger than those in cellulose I. The more stable structure of cellulose II yielding from mercerisation produces higher Ea (Morgado and Frollini 2011).

Insert Figure 9 here

Differential scanning calorimetry (DSC)

The DSC curves of the samples are in Figure 10, with a broad endothermic peak in both the polymer and composites at around 60-78 °C. It corresponds with the heat vaporisation of absorbed water in the composites and polylactide (Bharath, et al. 2020). The addition of untreated and treated mukwa wood fillers into the PLA matrix shifted the peaks towards lower temperatures

(Figure 10). Additionally, differences in the width of the peaks suggest a differentiation in the crystallisation process of the matrix (Odalanowska, Skrzypczak and Borysiak 2021). The crystallisation (T_c) and melting point (T_m) values for PLA, untreated, and treated mukwa/PLA composites, together with the calculated crystallinity index (X_c), have been presented in Table 2. The crystallisation of PLA is 119.84 °C and adding untreated and treated mukwa wood fibers into the matrix reduced the values by 0.5, 3.6, 7.2, and 27.5% for laccase, untreated, alkali-laccase, and alkali mukwa/PLA composites, respectively. A similar trend was observed in the T_m values. The endothermic peaks around 275-325 °C for alkali, alkali-laccase, and laccase treated mukwa/PLA composites are for the decomposition of polysaccharide cellulose content. Around that temperature range, an exothermic peak in the PLA was observed. An exothermic peak at around 350 °C only appears on the untreated mukwa/PLA composite and can be characterised by the thermal degradation of hemicellulose. The surface modifications are linked to removing fractions of the amorphous hemicellulose, pectin, and phenolic hydroxyl groups (Karaduman, Gokcan and Onal 2012, Dong, et al. 2018). A similar observation has been reported on moringa oleifera fibers (Bharath, et al. 2020). An endothermic peak around 360 °C for PLA has been observed. Table 2 shows the thermal analysis data and the crystallinity derived using equation 6.

Insert Figure 10 here

Insert Table 2 here

The crystal and nucleation growth are the two stages of polymer crystallisation. The PLA recorded the lowest Xc of 18.3%, followed by an alkali/PLA composite (Table 2). The crystallinity of alkali/PLA, alkali-laccase/PLA, laccase/PLA, and untreated/PLA increased by 8.4%, 18.8%, 22.8%, and 27.5% on the Xc of PLA. Surface modifications reduced the Xc of the composites and maybe due to the restricted diffusion and migration of PLA chains to the nucleus surface due to the tight bonding resulting from the surface modifications (Wang, et al. 2020). The Tc for laccase treated composites and PLA slightly increased compared to the untreated, suggesting an accelerated crystallisation rate.

Hardness testing

The hardness of bio-composites is a measure of usability (Ramesh, et al. 2022), and the hardness values of the untreated and treated mukwa/PLA bio-composites are revealed in Figure 11. The PLA showed the least average hardness of 20.71 HV, with bio-composites showing a continues increase following surface modifications. The reinforcing effect of mukwa wood fibers improved the toughness of mukwa-PLA interface, increasing the overall hardness of neat PLA. A similar trend has been observed on polymeric composites reinforced with lignocellulosic material (Nukala, Kong, et al. 2022, Nukala, Kong, et al. 2022a, Das, Sarmah and Bhattacharyya 2016). The alkali-laccase modification yielded an increase of 3.35 HV, 5.92 HV, and 14.74 HV on the laccase, alkali and untreated bio-composites, respectively. Addition of mukwa to PLA made

composites stiff, hard, rigid and restricted the movement of polymer chains (Kaymakci, Ayrilmis and Gulec 2013, Nukala, Kong, et al. 2022a).

Insert Figure 11 here

Conclusion

In this study, a holistic approach to fabrication of bio-composites through recycled mukwa wood fibers were prepared. The mukwa-PLA interface was enhanced through ecological surface modification to reduce the composite's absorption properties, and increase the chemical resistance and hardness. The water absorption was least on the PLA (0.54%), followed by alkali-laccase (2.507%), laccase (2.965%), alkali (3.097%), and untreated (4.198%) composites, respectively. The untreated mukwa/PLA composites immersed in 40% HNO_3 (8.19%) and toluene (6.61%) experienced excessive swelling while composites shrunk in NaOH (-5.87%). The composites showed good resistance to olive oil (0.05%), 10% HCL (1.18%), 30% H_2SO_4 (0.81%), and HF (0.23%). The PLA reached the lowest thickness swelling of (1.54%), followed by the alkali-laccase treated composites with 1.98%. The untreated composites (2.47%) swelled more than other composites due to extensive amorphous materials, the -OH group and many voids as revealed by the optical microscope. Upper activation energies were 165 kJ/mol, 104.2 kJ/mol and 101.1 kJ/mol for PLA, laccase/PLA and untreated/PLA, respectively. An optimal of 733 ˚C was observed on the laccase/PLA composites. The alkali-laccase/PLA had a stronger interface, producing better water and chemical resistance, reduced thickness swelling and density (1.09 g/cm^3). With the good chemical resistance, thermal, absorption properties, lightweight and optimal hardness of 35.45 HV, alkali-laccase/PLA bio-composites are potential alternative materials for making farm poles and other exterior applications.

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