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CASSAVA LEAVES AS PACKAGING MATERIALS

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New packaging materials made from cassava leaves (CLs) were successfully prepared having desirable sheet properties. The CLs were treated with various concentrations of NaOH solution (mercerization), prior to the sheet making process. Several characterization methods were applied to elucidate the performance of the mercerized CLs. The results show that the tear index of 15% mercerized CLs is comparable to that of available paper or plastic sheets, having low moisture uptake, good wetting time, smooth sheet formation and non-toxicity. It is expected that the use of CLs as packaging material could reduce the dependency on paper and plastic based packaging.

Keywords: cassava leaves, tapioca, packaging, mercerization, moisture absorption

INTRODUCTION

Cassava (*Manihot esculenta* Crantz) is the most agronomically important of the cyanogenic crops, particularly as food source. Cassava is a very rustic crop that grows well under marginal conditions, where few other crops could survive. A large proportion of cassava varieties is drought tolerant, can be produced on degraded soils, and is resistant to the most important diseases and pests.¹ Due to its versatile nature, it is frequently referred to as the “drought, war and famine crop” to much of the developing world. The most important commercial product of cassava is the storage root, which is full of starch. Roots of cassava are edible and are used as the main source of carbohydrate food, particularly in Africa. Besides food, the processing of roots could produce starch and flour that are useful in industrial fermentation for biotechnology,² as edible films and coatings³ and as biodegradable polymeric material.⁴ The importance of cassava leaves (CLs) is comparable to that of the roots. In African countries, CLs stand top in the list of leaf consumption, having become the basic vegetable and being highly valued.⁵ In Asian countries on the other hand, the leaves can be regarded as waste or by-product of the harvested roots.

One factor that makes cassava different from other tuberous plants is that, in a raw state, it

contains toxic compounds. Cyanogenic glucosides (decomposing to liberate hydrogen cyanide (HCN)) are present in all parts of the cassava plant. CLs contain 5 to 20 times greater HCN than the roots.⁶ Interestingly, CLs exhibit a hydrophobic waxy surface, which could form a water-repellent component, preventing the formation of a water film. The quantities of wax have been determined for several species of cassava and were found to range between 10-30 $\mu\text{g}/\text{cm}^2$.⁷ However, there is still lack of studies on the moisture sensitivity of CLs. With the advent of technological approaches, focus has shifted to widening the application of CLs to newer uses with the aim of adding value, one of the most interesting applications being as food packaging material. For a long time, the common food packaging materials have been dominated by the use of petroleum based plastics. However, increased use of synthetic packaging has led to serious ecological problems owing to its total non-biodegradability. Although its complete replacement is nearly impossible to achieve, specific applications, like food packaging, made from agricultural resources could be a perspective. Paper based products have been one of the earliest food packaging materials. The pulp and paper industry is one of the world's largest

contributors to the greenhouse gases by producing vast amounts of pollutants and landfill waste.⁸ The main advantages of paper as a packaging material are its low cost, wide availability, lightweight, printability, environmental friendliness and mechanical strength. Its most serious shortcoming is its sensitivity to moisture. The permeability to moisture and fat can be reduced by coating with wax.⁹

Therefore, we aim to investigate the potential usage of CLs as packaging material. It will be motivating to utilize its waxy component as it could provide a natural non-wettable characteristic to the processed sheets. It is envisioned that by utilizing CLs we could reduce the by-products of harvesting the cassava plant. The CLs will be chemically treated using a conventional mercerization process (treatment with NaOH solution) at various solution concentrations. It will be shown that the CLs are appropriate for forming packaging sheets with desirable properties at a certain NaOH concentration.

EXPERIMENTAL

Freshly picked Malaysian grown CLs were cleaned by running tap water and then stored at a temperature of 4 °C in a refrigerator, prior to use. The CLs were mercerized by soaking in a caustic soda (NaOH) solution of various concentrations (2, 8, 10, 15, 20, 25 and 30%). The soaking process lasted for 24 h under ambient conditions. Then, the treated CLs were rinsed thoroughly to obtain a pH of 7. Then the leaves were wet blended at 10⁴rpm for 30 s in a mechanical blender. The pulp was formed into sheets by hand and conditioned at 60°C for 2 h in an oven. HCN analysis was done according to the picrate method. 2 g of a cut CL sheet was placed in a test tube and moistened by adding a few drops of distilled water, followed by a few drops of chloroform. A sodium picrate strip (prepared by dipping a Whatmann filter paper strip into 1% picric acid and 10% sodium carbonate solution) was inserted in the test tube in hanging position without touching the sides or the sample. The tube was tightly closed and kept at room temperature for 6 h. Then the dried picrate paper strip was removed, chopped and inserted in a test tube containing 10 mL distilled water. The samples were thoroughly mixed and centrifuged at 5000 rpm for 10 min. The solution was examined for its absorbance using a Hach DR/2010 spectrophotometer at 520 nm. The tear test was performed to evaluate the tearing properties of the processed sheets, since it is the most common and important testing used in evaluating paper or sheet properties. The test was conducted using the Elmendorf Tear method (ASTM D-1922). Sample

sheets were cut according to the standard required dimensions and dried at 60 °C for 24 h before testing. At least five replicates were done for each CL type. The tear index was calculated as follows:

$$\text{Tear index} = \frac{\text{average tearing force (mN)}}{\text{average grammage } \left(\frac{\text{g}}{\text{m}^2}\right)}$$

Whereby:

$$\begin{aligned} \text{Average tearing force, mN} \\ = \frac{16 \times 9.81 \times \text{average scale reading}}{\text{number of plies}} \end{aligned}$$

The moisture absorption test was done on triplicate CL samples of 2 × 2 cm, placed on top of a wire mesh in five different relative humidity (RH) environments conditioned in desiccators, in accordance with ASTM E-108 standards. The RH were controlled using saturated salt solutions of LiCl (11%), KCH₃CO₂ (25%), Mg(NO₃)₂ (53%), NaCl (75%), and K₂SO₄ (97%). The samples were weighed at intervals of 6h for 48 h. The equilibrium moisture content at each water activity was calculated on a dry basis. The percentage of moisture absorption M_t (%) was calculated using the relation: (W_w - W_d)/W_d × 100, where W_w and W_d are the weights of the sample before and after exposure in controlled RH, respectively. The water wetting test was performed on square CL sheets with the dimension of 1×1 cm. A drop of water was allowed to fall from a burette with an approximate height of 1.0 cm from the sample. The time required to wet a 1 cm distance was recorded with a stopwatch. At least three replications were done for each CL sheet. FTIR spectra were obtained from KBr discs of samples, using a 2000 Perkin Elmer spectrometer with a resolution of 4.0 cm⁻¹. Scanning electron microscope (SEM) images were obtained using Leo Supra 50VP.

RESULTS AND DISCUSSION

FTIR spectroscopy

The components of green leaves are mainly bound with lignocellulosic components. The two most significant peaks for the FTIR analysis are located at 3400 cm⁻¹ and 1700 cm⁻¹. The spectrum of the untreated CL sheet in Figure 1a shows the band at 3400 cm⁻¹, which represents the intermolecular and intramolecular H bond of free OH of cellulose.¹⁰ The pronounced peak at 1700 cm⁻¹ is the characteristic peak of carbonyl (C=O) stretching vibration from free carboxylic acid, esters and fatty acids, which represent the constitutive compounds of leaf wax.¹¹ The existence of this wax associated peak is a sign that the wax is still present in the CLs after they were processed into sheets. Like many other leaves, CLs (unprocessed) consist of cuticles. A cuticle is a thin continuous membrane consisting of a polymer matrix (cutin) and associated

solvent-soluble lipids (waxes), which is about 0.1-10 μm thick. The cuticle of a plant is useful to the plant in that it acts as a permeability barrier for water and other molecules. Hydrophobic waxes on CL surfaces form a water repellent surface and thereby prevent the formation of a water film.⁷ It can be seen that the mercerization at 2% NaOH (Figure 1b) resulted in higher detection of the OH band, compared to the untreated CL, which is due to the more exposed cellulose surfaces. The 1700 cm^{-1} peak seems to be slightly reduced after the treatment. The 15% mercerized CLs (Figure 1c) show that the OH band is increased, while the 1700 cm^{-1} peak is preserved, indicating that the mercerization opens up available cellulose without significant loss of the wax content. Meanwhile, Figure 1d shows that the C=O functional band has a very low intensity, which indicates that the sample (30% treated CL) contains no or very few wax compounds. This is also accompanied by the intense OH band. High mercerization treatment will eventually lead to the efficient elimination of wax and to damaging the leaf structure, which will reveal more OH groups.

HCN level

The release of HCN determines the toxicity level in the CLs. Though the present packaging was not designed to be edible, reports of the HCN level are vital to ensure it is within a safe level. The cyanide content of fresh CLs was described

to be in the range of 20-1860 ppm.¹² The HCN content of the raw unprocessed CLs (Table 1) was measured to be 223.83 ppm, which is in agreement with the environmental conditions of a tropical region, such as Malaysia. Higher HCN content had been reported for CLs grown in drought, harsh and disease prone environment (325-1179 ppm).¹³ The processed untreated CLs show that the HCN content reduced by as much as half, compared to raw CLs, which is explained by the ability of the leaves to rapidly lose cyanogens during the processing, due to its open structure and the presence of the hydroxynitrilelyase enzyme, which catalyses the hydrolysis of acetone cyanohydrins to HCN.¹⁴ Mercerization of CLs promotes a significant elimination of HCN starting with a 2% NaOH solution. The main reasons for the reduction of HCN are the exothermic reaction of NaOH dissolution and ionization of the hydroxyl group, followed by the wet blending (disruption of leaf structure with liberation of more enzymes) and washing during the sheet making and drying process. It has been described earlier that the HCN can be removed by stirring and boiling in water.¹⁵ It can be seen from Table 1 that the prepared CL sheets are free from HCN after being treated with NaOH solution. This signifies that the processed CL sheets are safe for packaging applications, particularly for food.

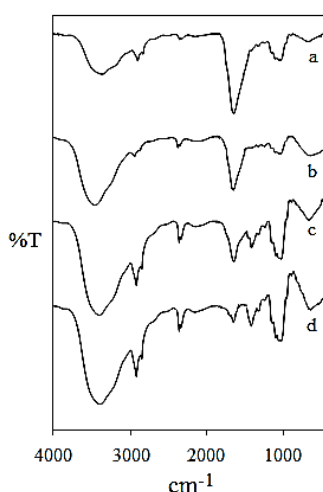


Figure 1: FTIR spectra of CL sheets ((a) untreated, and after (b) 2%, (c) 15% and (d) 30% NaOH treatment)

Tear index

Figure 2 depicts the tear index trend of the CL sheets mercerized with various concentrations of NaOH. The sheets of untreated CLs exhibit a tear

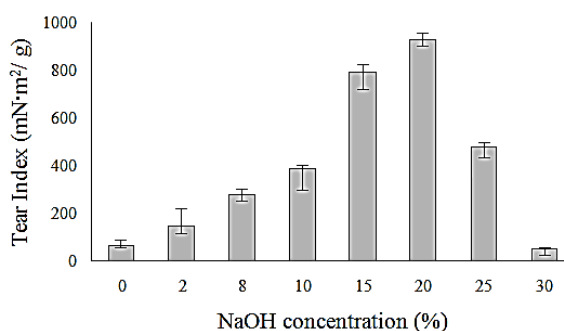


Figure 2: Tear index of CLs with increasing NaOH concentrations

index value of about 64 $\text{mN}\cdot\text{m}^2/\text{g}$. This poor resistance to crack propagation is due to the presence of many impurities, wax compounds, lignin, depolymerisation of cellulose and the

sheets' rough surface texture, which could introduce weak spots during the mechanical testing, as seen in the SEM image of Figure 3a. As waxes consist of very long-chain aliphatic mixtures with broad chain length distribution, it seems plausible that the processed CLs may be amorphous in large parts and exhibit properties of soft materials. The tear index of the sheets doubled upon mercerization with only 2% of NaOH solution and increased gradually with up to 20% treatment. This can be attributed to the mercerization process of the CLs, which renders a better crystalline structure.¹⁶ With increasing the mercerization concentration of sodium hydroxide, the CLs become less dense and less rigid, thereby making the cellulose chains more capable of rearranging themselves and undergoing reorientation and recrystallization along the direction of tear. Furthermore, the treatment of

CLs prior to sheet making was observed to be favourable in promoting more uniform and smoother sheets, thus higher mechanical strength was obtained. It can be seen that the electron micrograph of the 15% mercerized CLs (Figure 3b) exhibits relatively flat and smooth surface, compared to that of untreated CLs. However, the tear index reduced as the mercerization concentration was increased up to 25%. High NaOH concentration led to cellulose degradation, which resulted in less favourable sheet formation. The treatment of the CLs with 30% NaOH caused severe difficulties in the sheet making process, because of the development of a random breakdown of the cellulose chains¹⁷ and thus a sharp fall in mechanical properties, reaching a lower tear index value than that of untreated CLs. This is clearly depicted by the SEM image in Figure 3c.

Table 1
Cyanide content of processed CL sheets

Sample (NaOH concentration, %)	Cyanide content (mg HCN/kg dry weight (ppm))
Raw	223.83
0	106.71
2	0.12
8	<0.1
10	<0.1
15	<0.1
20	<0.1
25	<0.1
30	<0.1

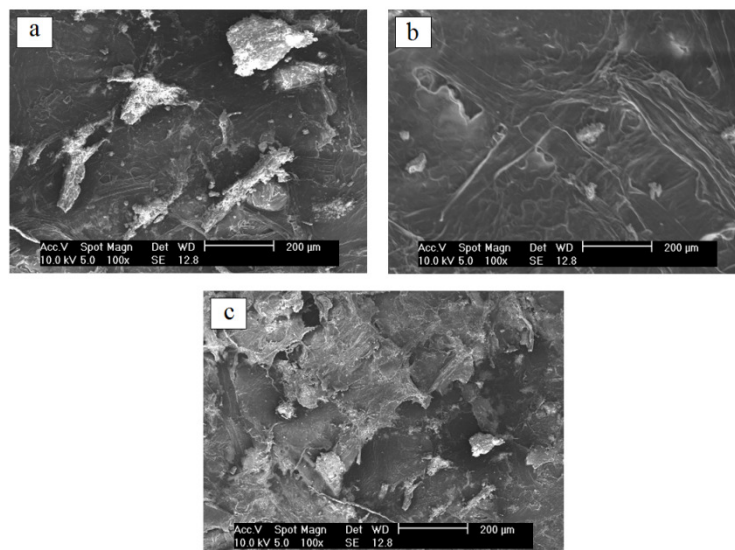


Figure 3: SEM images of CL sheets((a) untreated and after(b) 15% and c) 30% NaOH treatment)

Moisture absorption

Figure 4 indicates that the moisture absorption of all the CL samples increases almost linearly with increasing RH. Such a trend shows that the CL sheets moisture uptake is strongly dependent on the RH environment. Increasing humidity conditions increases the CL moisture uptake. Nevertheless, the maximum moisture uptakes of the CL sheets are much lower than those of many reported cellulosic fiber based kraft or paper (>8%, reaching 16% for kapok).¹⁸ Low moisture uptake is due to the presence of wax on the CLs, which provides an effective barrier, preventing the adherence of water molecules from the surroundings and is a suitable property for packaging applications, mainly for replacing synthetic plastic films or sheets. Also, it can be observed that the moisture regain increases with increasing NaOH concentration. The reason is that the mercerization process leads to more available free surface hydroxyl groups (OH) of cellulose, which interact favourably with the water molecules, thus increasing the CL hygroscopic capability.

Wetting test

Figure 5 shows that the wetting time needed for water to wet the CL is lowered by the treatment with the NaOH solution. It took the untreated CLs about 2 days to wet. This

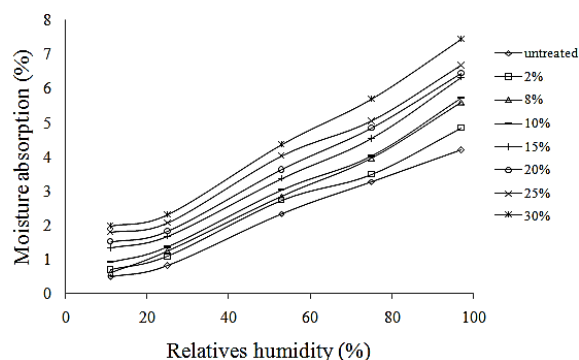


Figure 4: Moisture absorption of CL sheets with increasing RH

CONCLUSION

It has been shown that CLs have a potential to be used as packaging material after a mercerization treatment. A mild concentration of NaOH solution (15%) was proved to be the most suitable mercerization value for the preparation of CL sheets. This was established by the good tear index value, elimination of toxic compound (HCN), smooth sheet formation, low moisture

corresponds to the high mismatch of surface tension between water (surface energy of water ~73dyne/cm) and CLs, determined by the wax present in the sheets. Waxes containing large amounts of alkanes are the least wettable constituent (surface energy of wax ~30 dyne/cm).¹⁹ 2% NaOH treated CLs revealed a wetting time of about 20 min. As expected, the oily and greasy matter present in the CLs was removed by the NaOH treatment, which increased the surface tension of the CLs, allowing the water to wet the CL surface. It can be seen that the wetting time was still maintained up to 15 min for the CL samples treated with 8, 10, 15% NaOH, which is explained by the retention of wax and smooth finished surface, as observed in the SEM image of Figure 3b. This condition is preferable for packaging applications that require some degree of hydrophobicity. The sample treated with higher NaOH concentrations (20-30%) exhibit rapid wetting time (less than 10 min). This indicates that the wax component was sufficiently eliminated from the CLs and the high mercerization concentration opens up more available OH groups, which lead to better wetting with the water molecules. Furthermore, the serrated surface and loosening structure, as seen in Figure 3c, promote more water molecules to enter the void spaces.

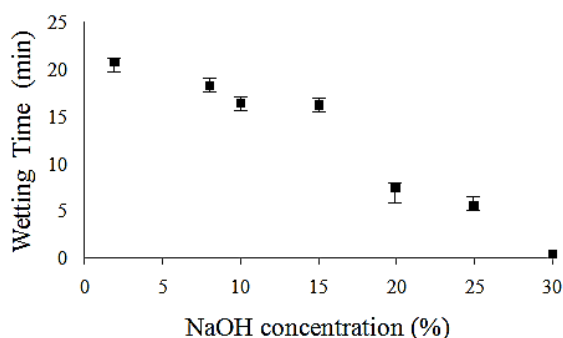


Figure 5: Wetting time of CL sheets with increasing NaOH concentration

uptake and reasonable wetting time. The total removal of HCN, considering its economic value, presents a high potential for large scale production. This new approach is promising for packaging applications, which require the utilization of bio-derived resources and cost effectiveness. Even so, more studies should be done to investigate CL viability in replacing plastics or paper packaging.

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