

## POLY(LACTIC ACID) COATED CASSAVA LEAVES BIOCOMPOSITE PACKAGING SHEETS

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Biocomposite packaging sheets made from cassava leaves and poly(lactic acid) (CL/PLA), and having desirable sheet properties, were successfully prepared using a surface impregnation method. CL sheets were solvent impregnated with PLA at various concentrations to improve their performance. This newly developed biocomposite packaging material exhibits a low moisture uptake and high tear strength upon impregnation with 8% PLA. Electron micrographs of the biocomposite revealed PLA with dimple-like morphology. This biobased packaging material could contribute to reducing the dependency on paper and plastic based packaging.

**Keywords:** cassava leaves, tapioca, packaging, poly(lactic acid), coating, impregnation, mercerization, moisture absorption

### INTRODUCTION

Cassava (*Manihotesculenta Crantz*) roots are the most agronomically important of the cyanogenic crops, particularly as a food source. Cassava is a very rustic crop that grows well under marginal conditions, where few other crops could survive. Its flexible harvesting time and vegetative propagation via stem cutting make it an excellent food source.<sup>1,2</sup> A large proportion of cassava varieties is drought tolerant, can be produced in degraded soils, and is resistant to the most important diseases and pests.<sup>3</sup> The importance of cassava leaves (CL) is related to its roots. In African countries, CL stand at the top of the list of leaf consumption, cassava has become the basic vegetable and is highly valued.<sup>4,5</sup> In Asian countries, particularly in Malaysia, the leaves can be regarded as waste or a by-product of the harvested roots. According to the statistics made by the Food and Agricultural Organization (FAO), cassava plant is listed in the top ten most produced commodities in the world. In Southeast

Asia, the growth of CL exceeded 70,000 tonnes/year, whereas only 7.0 tonnes/year of the CL were processed for production in the industrial field.

The motivation of industrially utilizing CL lies in their hydrophobic waxy surface, which could act as 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 and 30  $\mu\text{g}/\text{cm}^2$ .<sup>6</sup> Therefore, being apprehensive of the enormous amount of waste, our current effort is directed towards utilizing CL for industrial applications. With the advent of technological approaches, the focus has been shifted to widening the use of CL for newer, value adding applications; one such application being as food packaging material.

For a long time, most of the common food packaging materials have been dominated by petroleum based plastics.

However, the increased use of synthetic packaging materials has led to serious ecological problems because of their total non-biodegradability. Although their complete replacement is nearly impossible to achieve, specific applications, such as food packaging made from agricultural resources might be a feasible future perspective. Our previous study has shown the potential of CL as packaging material. Initial treatments of CL yield sheets with good mechanical integrity, and with improved sheet making properties, but without significant loss of waxy components.<sup>7</sup> The resulting properties of the processed CL are promising, but their mechanical strength could obviously be further improved for viable use. It is encouraging to further enhance the CL sheets with biopolymers, which possess good mechanical strength, plus hydrophobicity and good film-forming properties.

One of the most promising biopolymers for such a purpose is poly(lactic acid)(PLA) because it is biodegradable, biocompatible, commercially available and has good performance characteristics as packaging material.<sup>8,9,10</sup> In addition to its environment-friendly nature, PLA can also be used for food contact surfaces and is generally recognized as safe. With these characteristics and due to recently reduced production costs by the application of new technology and large-scale production, PLA is becoming an important alternative as a green food packaging material, since it shows better performance than synthetic plastics in many applications.<sup>11</sup> In addition, the potential use of PLA-coated sheets includes specific products, such as meat and dairy products, ready meals, beverages, snacks, dry products, frozen products, fruits and vegetables, where packaging may be in the form of trays, cartons, cups, boxes, or deli containers.<sup>12,13</sup>

Thus far, to the best of the authors' knowledge, there are no reported studies on sheets made of cassava leaves/poly(lactic acid) (CL/PLA). It is envisioned that the properties of processed CL sheets could be enhanced by surface impregnation with PLA. Therefore, our main target is to impede the moisture activity of CL, while enhancing their mechanical properties. Initially, the CL will be chemically treated using a conventional mercerization process, then the CL will be formed into sheets and impregnated with PLA at various concentrations. It will be shown that the CL and PLA materials are able to form

packaging sheets with desirable properties at a certain PLA concentration.

## EXPERIMENTAL

### Preparation of CL/PLA sheets

Freshly picked Malaysian grown CL were cleaned by running tap water and then stored at a temperature of +4 °C in a refrigerator until use. Their mercerization and sheet making process have been described in detail elsewhere.<sup>7</sup> Briefly, the CL were treated with 15% sodium hydroxide solution for 24 h at room temperature. The PLA, Nature Works<sup>TM</sup>4031 D, was supplied by Nature Works LLC, USA. The molecular weight ( $M_w$ ) is between 195000 and 205000g/mol. The PLA was mixed into methylene chloride (Merck) in various concentrations (2, 4, 6, 8, 10% w/v) and the polymeric solution was mechanically stirred overnight at 50 rpm. The initially prepared CL were immersed into the solution containing PLA for 5 minutes. The impregnated CL were then placed in a fume hood under ambient conditions to allow evaporation of the organic solvent. The steps of making the CL/PLA biocomposite sheets are depicted in Figure 1.

### Characterizations

Moisture absorption tests were done in triplicate on CL/PLA samples of 2 cm x 2 cm, placed on top of a wire mesh in five different relative humidity (RH) environments. The samples had been previously conditioned in dessicators in accordance with ASTM E-108 standards. The RH was controlled using saturated salt solutions of LiCl (11%), KCH<sub>3</sub>CO<sub>2</sub> (25%), Mg(NO<sub>3</sub>)<sub>2</sub> (53%), NaCl (75%), and K<sub>2</sub>SO<sub>4</sub> (97%). Samples were weighed at intervals of 6 hours until saturation. The equilibrium moisture content at each water activity was calculated on a dry basis. The percentage of moisture absorption (%) was calculated as:

$$\text{Moisture absorption(\%)} = \frac{W_f - W_i}{W_i} \times 100 \quad (1)$$

$W_f$  = final weight

$W_i$  = initial weight

The water wetting test was performed on square CL/PLA sheets with dimensions of 1 × 1 cm. A drop of water was allowed to fall from a burette at 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/PLA sheet. 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). The sample sheets were cut according to the dimensions required by the standards and dried at 60 °C for 24 h before testing. At least five replicates were done for each CL/PLA type.

Fourier transform infrared (FTIR) spectra were obtained from a KBr disc of samples, using a model 2000 Perkin Elmer spectrometer with a resolution of  $4.0\text{ cm}^{-1}$ . Scanning electron microscope (SEM) images were obtained using Leo Supra 50VP. Thermogravimetric analysis (TGA) was performed by

TGA7 Perkin Elmer Pyris. Samples were heated from 30 up to 600 °C under nitrogen flow to observe the degradation steps of the samples at the heating rate of 10 °C/min.

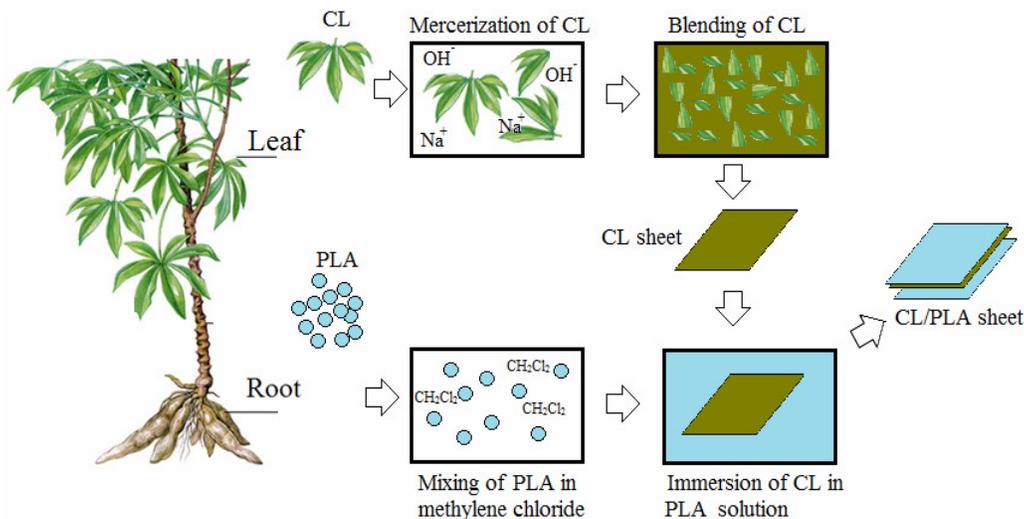


Figure 1: Schematic diagram for the preparation of CL/PLA biocomposite sheets

Table 1  
Wetting time of CL/PLA biocomposite sheets

PLA (%)	Wetting time (min)
0	15
2	30-60
4	60-120
6	120-300
8	> 300
10	> 300

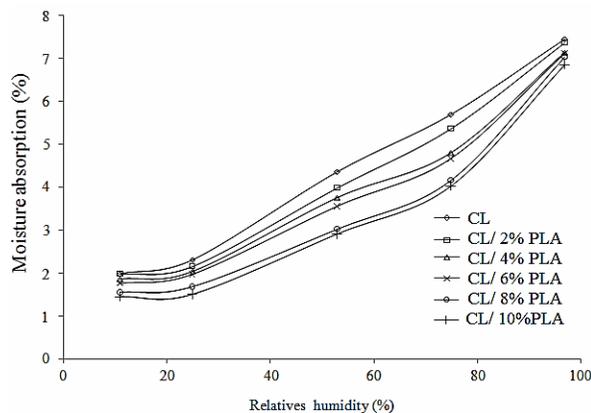


Figure 2: Moisture absorption of CL/PLA biocomposite sheets with increasing RH

## RESULTS AND DISCUSSION

### Moisture absorption and wetting time

Figure 2 indicates that the moisture absorption of all the samples, including the neat CL, increases significantly with increasing RH, except at very low levels of RH. Accordingly, the moisture uptake of the CL/PLA sheets is strongly dependent on their RH environment. Increasing the humidity conditions leads to increased moisture uptake of the sheets. Nevertheless, the maximum moisture uptakes of the neat CL sheets are much lower than those of many reported cellulosic fibre based kraft pulps or paper.<sup>14,15</sup> The low moisture uptake is due to the presence of wax on the CL, which provides an effective barrier to prevent the adherence of water molecules from the surrounding environment. It can be observed that the moisture gain decreases with increasing PLA concentrations. The reason is that the PLA provides additional surface coverage on the CL surface, which interacts favourably with the adhered wax component, reducing the environmental moisture uptake by its acetyl groups, thus increasing the sheets' hydrophobic capability. These two stages of moisture activity barrier (PLA and wax) are preferable for packaging applications, mainly for replacing synthetic plastic films or sheets. The wetting time of the CL/PLA sheets is presented in Table 1. The neat CL required about 15 min to wet. The time needed for water to wet the CL/PLA sheets increased by the impregnation of increasing concentrations of PLA. This corresponds to the presence of hydrophobic PLA, which decreased the surface tension of the CL by providing a high mismatch of surface tension between it and the water, thus making it more difficult for water molecules to wet the CL surface. Interestingly, the wetting time for 8 and 10% PLA coated samples lasted more than 300 min. This proved that PLA is suitable for increasing the water resistance of CL.

### Tear index

Figure 3 depicts the tear index trend of the CL sheets impregnated with various concentrations of PLA. The neat CL sheet exhibits a tear index value of about 785 mN·m<sup>2</sup>/g. This can be attributed to the mercerization process of the CL, which renders a better crystalline structure<sup>16</sup> compared to the raw leaves. Upon mercerization

by sodium hydroxide, the CL 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. As waxes consist of very long-chain aliphatic mixtures with broad chain length distribution, it seems plausible that the processed CL be amorphous in large parts and exhibit properties of soft materials. The impregnation of CL with 2% PLA induces no significant changes in tear index. A minimal amount of PLA could cause the surface to be dominated with solvent rich components, thereby leaving behind a significant portion of bare leaf area (uncoated surfaces). This nonuniform PLA formation renders no improvement in sheet strength. Increasing the amount of PLA concentrations from 4 to 8% leads to higher tear index. At these PLA concentrations, the polymer forms a continuous layer on the CL surface, which reinforces the sheet by impeding tear propagation. Upon higher impregnation concentration (10%), the tear index drops severely, reaching that of neat CL. This poor resistance to crack propagation is due to the weak spots during the mechanical testing caused by the poor interaction between the CL surface and the excessive PLA coating. Furthermore, the weight of the PLA component contributes to lowering the tear index due to the specific weight relation of the testing, based on Equation 1.

### Morphological analysis

Figure 4a depicts the SEM image of uncoated CL. The SEM image of the CL/8% PLA sample (Figure 4b) shows that its surface is smooth, flat and uniform, being covered with PLA. This easy to process and high mechanical strength biopolymer provides the reinforcement needed for utilizing the CL sheet. Further magnification on the surface (Figure 4c) reveals a uniform internal dimple-like pattern, which conveys kinetically trapped morphology as a result of solvent evaporation and corroborates the high wetting time.<sup>17</sup> These microsized pores can enhance the hydrophobicity of the substrate surface (CL) coated with these reversed microspheres. It can be seen from Figure 4d that 10% PLA caused the detachment of the PLA and relatively nonuniform deposition, which leads to a major reduction in the tear index.

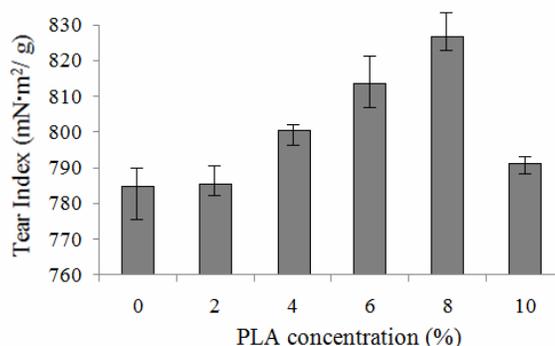


Figure 3: Tear index of CL/PLA biocomposite sheets with increasing PLA concentrations

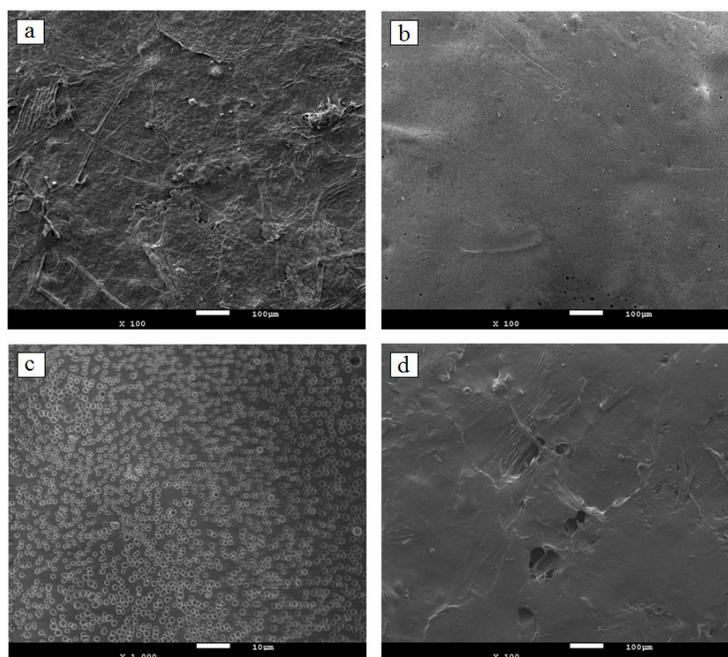


Figure 4: SEM images of a) neat CL sheet, b) CL/8 % PLA, c) higher magnification of CL/8 % PLA and d) CL/10 % PLA

### FTIR spectroscopy

The components of green leaves are mainly bound with lignocellulosic components. The two most significant peaks for the FTIR analysis are those at  $3400\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ . The spectrum of the neat CL sheet in Figure 5a shows a band at  $3400\text{ cm}^{-1}$ , which represents the intermolecular and intramolecular H bond of the free OH of cellulose.<sup>18</sup> The pronounced peak at  $1700\text{ cm}^{-1}$  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.<sup>19</sup> The existence of this wax associated peak is a sign that the wax is still present in the CL after being processed into sheets. The hydrophobic waxes on CL surfaces form a water repellent surface and thereby prevent the formation of a water film. It can be seen that the impregnation of 8% PLA (Figure 5b) resulted in lower detection of the OH band compared to the neat CL, which is due to the PLA coating, which further limits the exposed cellulose surfaces. On the other hand, the  $1700\text{ cm}^{-1}$  peak (representing the acetyl groups of PLA)

seems to be significantly increased with the treatment, indicating that the CL surfaces have been dominated by the hydrophobic functional group of PLA. The CL/10% PLA sample (Figure 5c) shows a similar IR pattern, except for the noticeable intensity of the CH<sub>3</sub> band at 1450 cm<sup>-1</sup>. This is due to the increased amount of PLA. The

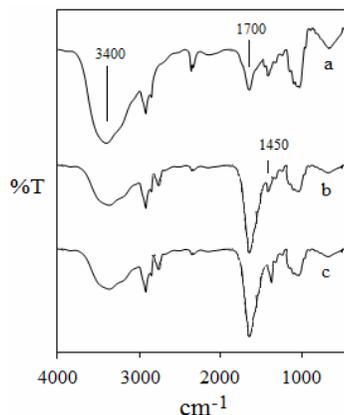


Figure 5: FTIR spectra of a) neat CL, b) CL/8% PLA and c) CL/10% PLA

proposed CL-PLA interactions are illustrated in Figure 6. The functional groups of the wax compound (methyl and carboxyl) provide good interaction with the acetyl group of PLA through H bonding, also accompanied by the wax short chain alkanes repeating unit.

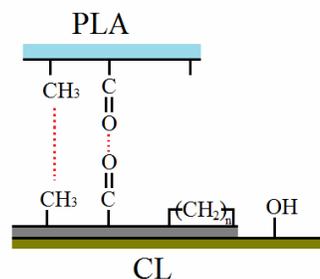


Figure 6: Interactions between CL-PLA

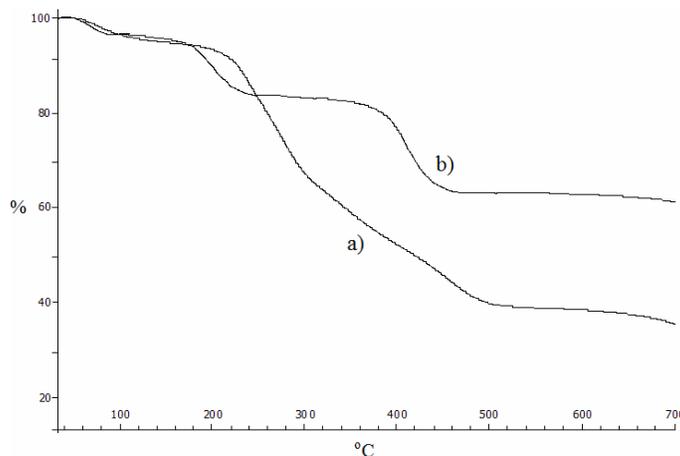


Figure 7: TGA curves of a) neat CL and b) CL/8% PLA

### TGA analysis

Figure 7 illustrates the thermogravimetric profiles of the neat CL and CL/8% PLA. Both samples show the first step at 100 °C, which corresponds to water evaporation and the degradation of the short chain wax compound. It can be seen that the PLA component of the impregnated CL (Figure 6b) degrades around 390 °C,<sup>20</sup> then follows the relatively slow degradation of the lignocellulosic component of the leaves. This delay in decomposition temperature is believed to be caused by the strong interaction between CL and PLA. Thus, it can be said that the

PLA shows a positive effect on the thermal stability of the resulting CL/PLA biocomposite sheets.

### CONCLUSION

It has been demonstrated that the processed CL coated with PLA have the potential to be used as packaging material. The optimum PLA concentration (8%) was proved to be suitable for the preparation of CL/PLA sheets. This was established by the low moisture uptake, good wetting time, high tear strength, uniform sheet formation, enhanced CL-PLA interaction and

improved thermal stability. The ease of forming sheets and their economic value are great advantages that recommend CL/PLA for large scale production. This new approach is promising for packaging applications, which require the utilization of bio-derived resources and cost-effectiveness.

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