Tensile, Barrier, Dynamic Mechanical, and Biodegradation Properties of Cassava/Sugar Palm Fiber Reinforced Cassava Starch Hybrid Composites

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The hybrid composite was prepared from cassava bagasse (CB) and sugar palm fiber (SPF) by casting technique using cassava starch (CS) as a matrix and fructose as a plasticizer. The chemical composition and physical properties of SPF and CB were studied in this work. SPF was added at different loadings of 2, 4, 6, and 8% dry starch to the CS/CB composite films with 6% CB. The addition of SPF influenced the hybrid properties. It was observed that the addition of 6% SPF to the composite film increased the tensile strength and modulus up to 20.7 and 1114.6 MPa, respectively. Also, dynamic-mechanical properties of the hybrid composites were investigated using a DMA test. The incorporation of SPF increased the storage modulus (E) value from 0.457 GPa of CS to 1.490 GPa of CS-CB/SPF8 hybrid composite film. Moreover, the incorporation of SPF slightly decreased the water vapor permeability (WVP) compared to the CS/CB composites film. It can be concluded that the incorporation of SPF led to changes in cassava starch composite film properties, potentially improving the bio-degradability, WVP, and mechanical properties of the film. Based on its excellent properties, CB/SPF-CS hybrid composite films are suitable for various purposes such as packaging, automotive, and agro-industrial applications, at lower cost.

Key words: Cassava film; Hybrid composite; Cassava bagasse; Sugar palm fiber; Physical properties; Thermal properties

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INTRODUCTION

A growing trend of natural fiber reinforced composites utilization has been ignited by the increasing environmental awareness. Numerous environmental and sustainability merits are attached to the use of biocomposites as compared to conventional synthetic composites. Due to their low cost and density together with renewability and biodegradability, biocomposites materials are currently receiving wide acceptance for various applications (Jumaidin *et al.* 2016; Sanyang *et al.* 2016; Edhirej *et al.* 2017b). On the other hand, natural fiber reinforced composites exhibit inherent drawbacks, which most times limits their effective utilization. Such drawbacks are mainly related to their hydrophilic nature, which results in low mechanical behavior, as well as high moisture sensitivity. However, natural fiber composites are hydrophobic and their mechanical strength is much lower than that of synthetic fiber composites (Abdallah *et al.* 2010; Hachemane *et al.* 2013). Bio-based materials from renewable sources such as starch, protein, and lipid are increasingly being used for the preparation of bioplastics. Among several biopolymers, starch is one of the most promising for the development of biodegradable plastics. However, starch-based materials are known to be brittle with poor mechanical properties. Thus, the incorporation of a plasticizer is required to overcome the brittleness of these materials. According to previous studies, fructose plasticized film could obviously improve the thermal stability and shows better mechanical properties. Films with fructose present smooth and homogenous surfaces without pores and absorb less water as compared with other plasticizers (Galdeano *et al.* 2009; Edhirej *et al.* 2017c).

Cassava, in particular, is an important starch source in some countries such as Brazil, Thailand, Malaysia, Indonesia, and some regions of Africa. One of the major byproducts of cassava starch is bagasse. Cassava bagasse contains 50 to 60% residual starch (dry weight basis). Cassava bagasse is one of the natural fibers that has attracted researchers to explore its capability as a reinforcement material in composites. A study by Versino *et al.* (2014) has used the remaining fibrous residue of cassava starch extraction as a film filler to obtain fully biodegradable starch-based composite. The addition of natural filler reinforcement constitutes an interesting option to tailor the properties of the resulting composite films (Versino and García 2014). Another study by Versino *et al.* (2015) prepared cassava starch/bagasse composite film containing 0.5 and 1.5 % bagasse and using glycerol as the plasticizer. According to their results, the addition of cassava bagasse enhanced the properties of the resulting composites.

Sugar palm fibers (SPF) are documented in the literature to possess high durability and resistance to sea water. Hence, they were traditionally employed to make boat components and ropes for ship cordages. In addition, they are also used for manufacturing brooms, brushes, and mats, and also for roofing in rural villages. Most recently, SPFs have witnessed increasing utilization as a reinforcement material in polymer composites due to their outstanding features (Ishak *et al.* 2013; Sanyang *et al.* 2016). Therefore, several studies have been conducted on reinforcing different types of thermoplastic or thermoset polymer matrix with SPF to improve their properties (Bachtiar *et al.* 2008; Leman *et al.* 2008; Ishak *et al.* 2012; Sahari *et al.* 2012; Sanyang *et al.* 2015a). The CB contains low concentrations of cellulose but high concentrations of hemicellulose as compared to SPF and the water content, water absorption and thickness swelling of the CB are higher than SPF; this is probably due to the reduction of cellulose content (Edhirej *et al.* 2017a).

Nevertheless, few investigations have been so far reported on the hybridization of SPF with other natural or synthetic fibers in a single polymer matrix. Jumaidin *et al.* (2017) studied the effect of sugar palm fibers on the physical, thermal, and mechanical properties of seaweed/thermoplastic sugar palm starch agar composites. The obtained results indicated that the hybrid composites displayed improvements in tensile and flexural properties, higher water and biodegradation resistance, and enhanced thermal stability of hybrid composites by the addition of FPF (Jumaidin *et al.* 2017). A previous study on morphological analysis of the CS-CB/SPF hybrid composite using SEM revealed good interfacial interaction and dispersion of CB and SPF within the matrix (Edhirej *et al.* 2017a). The properties of hybrid composites are greatly influence by many factors, such as the matrix, size and shape of individual fibers, fiber–matrix interface bonding, and volume fraction of the fibers (Rao *et al.* 2011; Júnior *et al.* 2012). The right combination of reinforcing fibers can achieve significant improvement of the physical and mechanical properties of the hybrid composite (Mehta and Parsania 2006). Hybrid composite materials provide a good balance between the cost of the composite and the performance properties

that cannot be obtained with a single fiber (Thwe and Liao 2002). The main objective of this work was to investigate the influence of different sugar palm fiber loadings on the tensile, dynamic mechanical, barrier and degradation properties of the cassava/sugar palm fiber reinforced cassava starch hybrid composites. To the best of our knowledge, not enough study has been conducted on this type of hybrid composite, and this study aims to provide new information to the research community. It should be noted that the CB and SPF particles used as the fiber in this study were not chemically treated or modified, which would lead to the development of a more environmentally friendly and cheaper production process and materials. The use of CB and SPF as reinforcement agents for CS thermoplastic film added value to these waste by-products and increased the suitability of CS composite films as environmentally friendly food packaging material.

EXPERIMENTAL

Materials

Native cassava starch was extracted from cassava tubers as described in a previous study (Edhirej *et al.* 2016). Cassava bagasse was obtained from the same extraction process and was used as a filler. Sugar palm fiber was collected at Jempol, Negeri Sembilan, Malaysia. Fructose was supplied by LGC Scientific Sdn. Bhd, Malaysia, and was used as plasticizer.

Film Preparation and Characterization

Starch films were prepared through the casting technique using a film-forming solution containing 5 g of cassava starch/100 mL distilled water. Fructose was used as plasticizer at concentrations of 30% dry starch. According to previous studies fructose plasticized film could obviously improve the thermal stability and shows better mechanical properties. Film with fructose presents smooth and homogenous surfaces without pores and absorbs less water as compared with other plasticizers (Edhirej *et al.* 2017c). Bagasse was used as filler, at 6% w/w of dry starch and the particle size of cassava bagasse was determined using 300 µm mesh sieve. The SPF was added at different concentrations of 2, 4, 6, and 8 % w/w of dry starch and were termed CS-CB/SPF2, CS-CB/SPF4, CS-CB/SPF6 and CS-CB/SPF8, respectively. The films compositional are shown in Table 1.

Table 1. Compositions of TPS Matrix Based on Cassava Starch, Its Composites

 Cassava Bagasse, and Cassava Bagasse/Sugar Palm Fiber Reinforced Cassava

 Starch Hybrid Composite

Film	Fructose g/g dry starch	Starch g/100ml distilled water	CB g/100g of dry starch	SPF g/100g of dry starch
CS film	0.3	5	0	0
CS/CB	0.3	5	6	0
CS-CB/SPF2	0.3	5	6	2
CS-CB/SPF4	0.3	5	6	4
CS-CB/SPF6	0.3	5	6	6
CS-CB/SPF8	0.3	5	6	8

The mixture was heated to 80 °C in a thermal bath and kept at this temperature for 20 min under constant stirring. Air bubbles formed during heating were removed by placing the film-forming solution into a desiccator under vacuum until there were no bubbles. The solution was poured homogenously onto 10 cm diameter circle plates. The plates with the film forming solution were then dried in an oven with air circulation, at 45 °C. The dry films were removed from the plates and stored at ambient conditions (around 25 °C and 60% of relative humidity) in a plastic bag for two weeks before characterization (Edhirej *et al.* 2017c).

Characterization of Fibers

Chemical composition

The methods described by (Versino and García 2014), were used to investigate Acid Detergent Fiber (ADF), Neutral Detergent Fiber (NDF), lignin (LIG), ash, cellulose, and hemicellulose of cassava bagasse and sugar palm fiber. NDF and ADF were used to determine the chemical composition of the fibers. This is the most practiced method for calculating the major fiber constituents, *i.e.* cellulose, hemicelluloses, and lignin. The proportions of cellulose and hemicelluloses were calculated by using Eqs. 1 and 2, respectively:

$$Cellulose = ADF - lignin$$
(1)

$$Hemicelluloses = NDF - ADF$$
(2)

Density (ρ)

The density of CB and SPF was calculated by gas pycnometer using helium gas. The density ρ is a basic physical property of matter, which is defined as the ratio of its mass (*m*) to its volume (*V*) as shown in Eq. 3.

$$\rho = \frac{m}{v} = g/cm^3 \tag{3}$$

Water Content (WC)

The weight loss was determined to allow calculation of the moisture content of CB and SPF. Powder samples were weighed (W_1) , dried at 105 °C for 24 h, and weighted again (W_2) , WC was calculated as the percentage of initial powder weight lost during drying and that on a wet basis as shown in Eq. 4.

$$WC(\%) = \frac{W_1 - W_2}{W_1} X100 \tag{4}$$

Water Absorption (WA)

The water absorption of CB and SPF were determined as per the method explained by (Yaich *et al.* 2011). The samples (3.0 g) were dissolved in 25 mL of distilled water and placed in pre-weighed centrifuge tubes. After being kept in the centrifuge for 25 min at 3000 rpm, the dispersions were mixed and were left at room temperature for 1 h. The supernatants were removed and the residue was dehydrated in an oven for 25 min at 50 °C, to determine the moisture content of the samples. The water absorption capacity was denoted as grams of water bound per gram of the sample on a dry basis using Eq. 5 (Yaich *et al.* 2011).

water absorption (%) =
$$\frac{M_{\text{final}} - M_{\text{intial}}}{M_{\text{intial}}} \times 100$$
 (5)

7148

Characterization of Films

Tensile properties

The tensile properties of the films were determined using ASTM D882, taking into account the modification proposed by Sanyang *et al.* (2015b). Film strips were cut into 70 mm \times 10 mm sections and then characterized using a 5KN INSTRON tensile machine with an initial grip separation and crosshead speeds of 30 mm and 2 mm/min, respectively. Tensile strength and elongation at breaking as well as Young's modulus were calculated. A five replicates were carried out for each sample.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was performed initially to investigate whether the addition of the SPF to cassava TPS would improve the mechanical properties. The storage modulus (E') and the loss modulus (E'') of CS films, CS/CB composite film and CS-CB/SPF hybrid composite with various amount of SPF were evaluated according to the ASTM D5026 standard as described in the literature by Sanyang *et al.* (2015a). The storage modulus (elastic modulus) reflects the elastic modulus of the composites, which measures the recoverable strain energy in a deformed specimen, and the loss modulus (viscous modulus) is related to the energy lost due to energy dissipation as heat. DMA was run in the dual cantilever tensile mode. The temperature interval was from -75 °C to 75 °C with a heating rate of 1.5 °C/min and using a frequency of 1 Hz.

Soil Barrier Test

The biodegradation tests were carried *via* the method described by Sahari *et al.* 2014). The biodegradability was determined by measuring the weight loss of the films buried in compost soil under moisture controlled conditions. Triplicate specimens $(30 \times 20 \text{ mm})$ of each film were buried 10 cm under the surface of the soil, which was moistened by adding about 150 mL of distilled water twice a day. Each specimen was taken from the soil at different times and cleaned by wiping gently with a brush after being buried for 1, 2, 3 and 5 days, respectively, and then dried to a constant weight at 60 °C in a vacuum oven. The weight loss was then determined using Eq. 6,

Weight loss (%)
$$-\frac{W_i - W_f}{W_i} \times 100$$
 (6)

where W_i is the initial weight before being buried and W_f is the final weight after being buried.

Water Vapor Permeability (WVP)

Prior to the water vapor permeability (WVP) test, the film samples were conditioned in a desiccator with a relative humidity of 50% at 25 °C. The WVP test was conducted according to ASTM E96–95 with slight modifications (Sanyang *et al.* 2015b). Circular film samples were mounted and sealed on the open mouth of cylindrical cups containing 20 g of silica gel. The test cups were measured before being kept in a relative humidity chamber (25 °C, relative humidity 75%). The weight of the test cups was determined by periodic measurement until the equilibrium state was reached. Weight increments of the test cups were recorded, and WVP was calculated using Eq. 7,

$$WVP = \frac{(m \times d)}{(A \times t \times P)} \tag{7}$$

where *m* is the weight increment of the test cup (g), *d* is the film thickness (mm), *A* is the area of film exposed (m²), *t* is the duration for permeation (s), and *P* is the water vapor partial pressure across the films (Pa). The results were expressed in $g \cdot mm \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$.

RESULTS AND DISCUSSION

Properties of Fibers

Chemical composition of fibers

The physical, mechanical, and thermal properties of a natural fiber are greatly affected by its chemical composition. Natural fibers are mainly constituted of cellulose, hemicelluloses, lignin, and ash. Cellulose serves as the main structural component, providing strength to the walls of the stem plant as well as to the fiber (Reddy and Yang 2005). Table 2 shows the chemical composition of CB and SPF. It shows that the CB contained low concentrations of cellulose but high concentrations of hemicellulose as compared to SPF. Nonetheless, the lignin and ash content of CB were lower than that of SPF. The lignin content was calculated to determine the resistant components proportion of the fibrous residue, which plays a major role in providing strength to the fiber walls (Doporto *et al.* 2012).

Density (ρ)

The densities of CB and SPF were calculated from the average of five replicates as illustrated in Table 2. The density of cassava bagasse (1.45 g/cm^3) was found to be higher than SPF (1.28 g/cm^3) .

Moisture content (MC)

The MC of natural fiber is an important criterion that needs to be considered in choosing natural fiber as a reinforcement material. This is because moisture content affects dimensional stability, electrical resistivity, tensile strength, porosity, and swelling behavior of natural fiber in a composite material (Jawaid and Khalil 2011). The MC of SPF was lower than CB, with values of 6.01 and 14.92%, respectively.

Chemical Composition and physical properties of Cassava Bagasse and sugar palm fiber					
No	Content	Cassava Bagasse	Sugar palm fiber		
1	ADF (%)	13.16 ± 0.9	86.47 ± 2.2		
2	NDF (%)	42.42 ± 2.3	92.04 ± 4.1		
3	LIG (%)	3.12 ± 0.6	42.60 ± 1.3		
4	Ash (%)	3.36 ± 0.4	2.03 ± 0.2		
5	Cellulose (%)	10.04 ± 0.9	43.87 ± 2.8		
6	Hemicelluloses (%)	29.26 ± 2.1	5.57 ± 0.1		
7	Density (g/cm ³)	1.45 ± 0.07	1.28 ± 0.05		
8	Water content (%)	14.92 ± 1.2	6.01 ± 0.6		
9	Water Absorption (%)	258.05 ± 7.3	123.23 ± 4.3		

Table 2. Chemical Composition and Physical Properties of Cassava Bagasse

 and Sugar Palm Fiber

Water absorption (WA)

The WA is a critical criterion for several applications of TPS products. The results of the water absorption test are presented in Table 2 for CB and SPF. From the results, SPF absorbed a lower amount of water as compared to the CB, which indicates that CB is more hydrophilic (Munthoub and Rahman 2011). CB exhibited higher retention capacity of water than SPF due to the reduction of cellulose content in the CB; this result is in agreement with Razali *et al.* (2015), and also consistent with their chemical composition.

Properties of Films

Mechanical properties

Tensile characteristics of CS films, CS/CB composite film with 6% cassava bagasse, and CS-CB/SPF hybrid composite with various amount of SPF are shown in Fig. 1. A significant increase in tensile strength of the hybrid composite films was observed with an increase in SPF up to 6%, but there was a reduction at 8% loading. This could be a result of a higher content of larger particles at this stage, which resulted in a less homogenous material that could be prone to mechanical flaws. Prachayawarakorn *et al.* (2013) also observed a similar result at different fiber loading (kapok 15%). From Fig. 1 it can be seen that the highest tensile stress (20.72 MPa) was observed for CS-CB/SPF6 films.

Moreover, the increasing contents of both cellulosic fibers resulted in the significant improvement of the stress at maximum load and Young's modulus of the cassava films. This was due to the structural similarity of the two carbohydrate components, the increase in the crystallinity (from XRD), as well as the fiber surface smoothness and homogenous (from SEM) in our previous work (Edhirej *et al.* 2017a).

Young's modulus or elastic modulus determines the film stiffness. Therefore, high Young's modulus indicates high stiffness of a material. Thus, the addition of CB and SPF resulted in increasing Young's modulus. From the result, it can be seen that the highest Young's modulus (1115 MPa) was recorded for CS-CB/SPF6. However, increasing SPF content to 8% resulted in films with lower Young's modulus.

Decreases in Young's modulus with increasing fiber content in hydrophilic films have been reported previously (Mali *et al.* 2002, 2005). This could be a result of structural changes of starch arrangement that occurred when fiber was added, which made the matrix of the film less compact.

The addition of CB and SPF significantly influenced the elongation property of the films. Therefore, the elongation at break was reduced from 17.63 to 10.64% by the addition of 6% CB. Nevertheless, the addition of SPF decreased the value to 5.56, 5.08, 4.46, and 4.11% for CS-CB/SPF2, 4, 6, and 8%, respectively. This result could be attributed to the alignment and diffusion of the CB and SPF in the TPS matrix.

These outcomes showed that tensile strength and elongation at break were inversely related. Similar variations in mechanical characteristics were noticed for various hydrocolloid-based films earlier (Shakuntala *et al.* 2014; Versino and García, 2014). The result showed that the film containing 6% SPF (CS-CB/SPF6) had the best tensile strength and Young's Modulus.





CS film CS/CB CS-CB/SPF2CS-CB/SPF4CS-CB/SPF6CS-CB/SPF8 Fig. 1. Tensile properties of CS film, CS/CB composite film and CS-CB/SPF hybrid composite film

with different SPF loading. A: tensile strength, B: modulus and C: elongation at break

Dynamic Mechanical Analysis (DMA)

DMA is a technique to investigate the thermal and mechanical properties of polymers. The specimens generally deform sinusoidally in response to an applied oscillating force. The resultant strain in the specimen due to the sinusoidal load depends upon both the elastic and viscous behavior of the specimen.

Figure 2A shows the variation of the storage modulus, E', of cassava CS films, CS/CB composite film containing 6% cassava bagasse and CS-CB/SPF hybrid composite with various amount of SPF, as a function of the temperature. The addition of SPF in the

hybrid composite significantly increased the E' value, as shown in Fig. 2A. The E' value of CS and CS-CB/SPF8 hybrid composite film was 0.457 GPa and 1.490 GPa at -75 °C, respectively. This means that the fiber increases the capacity of the matrix to support mechanical constraints with recoverable viscoelastic deformation. In particular, the composite stiffness was substantially increased with incorporation of fibers. Figure 2A shows that, at high temperatures, there were no significant differences between the values of the storage modulus for all films. The reduction in the modulus of the films, which was due to the increase in temperature, was more significant for films with higher contents of SPF, because at higher SPF content, the filler inclusions can form aggregates, thus decreasing the modulus. This observation shows that at high temperatures, the physically entangled network of fibers in the composites bears a significant amount of load (Bonilla et al. 2013). The hybrid composite films have higher E' values than the CS film and present certain trends with respect to the content of SPF. This beneficial tendency is due to the quill particles having a high compatibility with the matrix, causing good dispersion and interface. Comparing the E' spectra of the hybrid composites with the CS film and CS/CB composite film, it was observed that the incorporation of higher concentrations of SPF resulted in the increase of the stiffness of the material within the temperature range taken into consideration. This result agreed with the earlier report by Rezaei et al. (2009).

Figure 2B presents the variation of the loss modulus, E'' of the CS films, CS/CB composite film, and CS-CB/SPF hybrid composite with various amount of SPF, as a function of the temperature. All E'' curves in this figure exhibited broad peaks with distinct amplitude and temperatures positions, as compared to the control film peak. These can be associated with the " α " peak and suggest a more complex structural relaxation behavior in the composites. According to Mohanty et al. (2006), this relaxation can be attributed to the chain mobility of the polymeric matrix. It is noticed from Fig. 2B that all the hybrid composite peaks were displaced to lower temperatures in comparison to the CS/CB film peak. This is possibly due to an increase in the flexibility of the polymer chains caused by the incorporation of the SPF. On the contrary, the peaks of E' for the polymer is displaced to higher temperatures indicating a reduction in the chain flexibility (Kishi and Fujita 2008). As higher concentration of fibers were incorporated, the slower the flow and the higher the E''. Generally, as the temperature increases, the viscosity of the materials decreases gradually. Broad peaks were observed on the curves within the temperature range of -30 to -10 °C representing the transition region from the glassy state to the rubbery state. These results were in agreement with previous work by Rezaei et al. (2009).

In Fig. 5C, broad peaks of the tan δ curves were shown scattered within the range of -15 to 60 °C. Since the tan δ peaks are not precisely defined and are rather scattered, quantitative assessment and detailed analysis on the peaks to relate the peaks with respect to the fiber loading were not carried out. Furthermore, the incorporation of stiff fibers reduced the tan δ peak height by restricting the movement of polymer molecules [26]. The composites show two transitions at low and high temperatures. The transitions were observed for the amorphous phase (β -transition) at low temperatures (0 to 20 °C) and for the crystalline phase (α -transition) at higher temperatures (40 to 60 °C). There is no trend in the position or intensity of both these transitions as a function of the fiber content, which makes it impossible to draw any conclusions on the influence of the presence of SPF on the dynamic mechanical properties of these composites.



Fig. 2. DMA properties of CS film, CS/CB composite film and CS-CB/SPF hybrid composite film with different SPF loading. A: Storage modulus, B: Loss modulus, C: Tan Delta

Biodegradation of the Hybrid Composites

The weight loss of the CS/CB composite film and CS-CB/SPS hybrid composites after biodegradation testing is shown in Fig. 3. At the end of 7 days, the CS/CB film had lost 76.4%, while CS-CB/SPS hybrid composites had lost 74.0, 70.3, 67.7, and 60.8% weight for the CS-CB/SPF2, 4, 6, and 8%, respectively.

The CS/CB were totally degraded after 1 week, meanwhile for the hybrid composites films took 10 to 15 days to completely degrade. The weight loss for the CS/CB

composite film was higher compared to the hybrid composites films for all successive degradation tests, which can be attributed to the fact that CB film absorbs more water, making it more prone to microorganism attack presence of a water medium; the result implies that the samples with lower SPF contents would exhibit potential for better biodegradability.

The water absorption for SPF was about 123.2%, while for CB it was 258.0%, which could be attributed to the hydrophobic behavior of films contain SPF (Sahari *et al.* 2013b). Biodegradation is the breakdown of materials by the action of microorganism (Sahari *et al.* 2013a). These micro-organisms, in the form of bacteria and fungi, access the SPS in the in contact with the biodegradable polymer, the microorganisms produce enzymes that break down the polymers in progressive smaller segments which have lower average molecular weights. Since starch consists of macromolecule amylose and amylopectin, the enzymes reacted to the starch and degraded to a small molecule of glucose and maltose. Thus favoring the material's degradation in the environment (Bonhomme *et al.* 2003).



Fig. 3. Degradation properties of CS/CB composite film and CS-CB/SPF hybrid composite film with different SPF loading

Water Vapor Permeability (WVP)

WVP of packaging films should be considerably low for the film to effectively act as a barrier to resist moisture transfer between the packed product and the surrounding atmosphere. Starches are known for their poor water barrier properties due to their high hydrophilic character. Hence, the incorporation of reinforcement fibers or fillers helps to address this drawback. However, the effect of fillers on the WVP of biodegradable matrixes depends on filler type and concentration (Versino and García 2014). The obtained value for cassava TPS was similar to those reported for materials based on starch from different botanical origins (Versino *et al.* 2015). From Table 3, the WVP of CS film was 1.34 g/s m Pa. A similar result was reported for corn TPS films, which presented a WVP of 1.36×10^{-10} g/s m Pa (López *et al.* 2015). In addition, the cassava and corn starch based films, obtained by casting method, exhibited WVP values of 1.4 and 1.2×10^{-10} g/s m Pa, respectively, (López and García 2012). Contrary to the expected, the increasing in WVP of films was observed with the incorporation of CB. A similar effect was reported by Müller *et al.* (2009), working on cassava starch reinforced films with softwood short fibers. In this work an increase of 21.5% was reported by addition of 6% CB. However, a decrease in WVP with an increase of SPF loading were observed, and a similar observation was reported by Versino and García (2014). This behavior could be attributed to the fact that the presence of filler increases the tortuosity of the pathway for water molecules, thus decreasing WVP values. As can be seen in Table 3, CS film showed higher permeability values than films containing SPF. According to (Bangyekan *et al.* 2006) this can be attributed to the higher hydrophobicity of SPF when compared to starch and bagasse. Additionally, hydrogen bond interactions between CS and SPF reduce the availability of the hydrophilic groups, diminishing their interactions with water molecules. In this work the lowest value of WVP was reported by addition of 8% SPF. The addition of SPF probably introduced a tortuous path for water molecule to pass through.

Film	WVP ×10 ⁻¹⁰ (g.mm.s ⁻¹ .m ⁻² .pa ⁻¹⁾	
CS film	1.34 ± 0.11	
CS/CB	1.52 ± 0.09	
CS-CB/SPF2	1.27 ± 0.08	
CS-CB/SPF4	1.13 ± 0.07	
CS-CB/SPF6	1.01 ± 0.13	
CS-CB/SPF8	0.98 ± 0.14	

Table 3. WVP of CS Film, CS/CB Composite Film, and CS-CB/SPF Hybrid

 Composite Film with Different SPF Loading

CONCLUSIONS

- 1. Cassava baggase/sugar palm fiber (CB/SPF) reinforced cassava starch (CS) hybrid composites were developed with the main objective of obtaining a material with improved properties and performance. The incorporation of SPF significantly improved the mechanical properties. It increased the tensile strength and modulus up to 20.7 and 1114.6 MPa, respectively, for CS-CB/SPF6. this being the most efficient reinforcing agent.
- 2. Comparing the CS-CB/SPF hybrid composite with the CS/CB composite film and the CS film, it is clear that the same physical and mechanical properties of the films were improved with the incorporation of SPF.
- 3. The dynamic mechanical analysis (DMA) was also studied and the results demonstrated that the addition of SPF led to a slight increase in the E' and E'' of the hybrid.
- 4. The incorporation of SPF helped improve the barrier properties of the starch films.
- 5. It can be concluded that, hybrid composites can be prepared using cassava starch as matrix and cassava bagasse and sugar palm fiber as reinforcement, adding value to the waste material.
- 6. Based on its excellent mechanical and biodegradation properties, CS-CB/SPF hybrid composite is suitable and potential for various purposes such as packaging, automotive and agro-industrial application, at lower cost.

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REFERENCES CITED

- Abdallah, M., Zitoune, R., Collombet, F., and Bezzazi, B. (2010). "Study of mechanical and thermomechanical properties of jute/epoxy composite laminate," *Journal of Reinforced Plastics and Composites* 29(11), 1669-1680. DOI: 10.1177/0731684409341672
- Bachtiar, D., Sapuan, S. M., and Hamdan, M. (2008). "The effect of alkaline treatment on tensile properties of sugar palm fibre reinforced epoxy composites," *Materials & Design* 29(7), 1285-1290. DOI: 10.1016/j.matdes.2007.09.006
- Bangyekan, C., Aht-Ong, D., and Srikulkit, K. (2006). "Preparation and properties evaluation of chitosan-coated cassava starch films," *Carbohydrate Polymers* 63(1), 61-71. DOI: 10.1016/j.carbpol.2005.07.032
- Bonhomme, S., Cuer, A., Delort, A., Lemaire, J., Sancelme, M., and Scott, G. (2003). "Environmental biodegradation of polyethylene," *Polymer Degradation and Stability* 81(3), 441-452. DOI: 10.1016/S0141-3910(03)00129-0
- Bonilla, J., Fortunati, E., Vargas, M., Chiralt, A., and Kenny, J. M. (2013). "Effects of chitosan on the physicochemical and antimicrobial properties of PLA films," *Journal* of Food Engineering 119(2), 236-243. DOI: 10.1016/j.jfoodeng.2013.05.026
- Doporto, M. C., Dini, C., Mugridge, A., Viña, S. Z., and García, M. A. (2012). "Physicochemical, thermal and sorption properties of nutritionally differentiated flours and starches," *Journal of Food Engineering* 113(4), 569-576. DOI: 10.1016/j.jfoodeng.2012.07.021
- Edhirej, A., Sapuan, S., Jawaid, M., and Zahari, N. I. (2017a). "Cassava/sugar palm fiber reinforced cassava starch hybrid composites: Physical, thermal and structural properties," *International Journal of Biological Macromolecules* 101, 75-83. DOI: 10.1016/j.ijbiomac.2017.03.045
- Edhirej, A., Sapuan, S. M., Jawaid, M., and Zahari, N. I. (2017b). "Cassava: Its polymer, fiber, composite, and application," *Polymer Composites* 38(3), 555-570. DOI: 10.1002/pc.23614
- Edhirej, A., Sapuan, S. M., Jawaid, M., and Zahari, N. I. (2017c). "Effect of various plasticizers and concentration on the physical, thermal, mechanical and structural properties of cassava starch based films," *Starch-Stärke* 69(1), 1-11. DOI:10.1002/star.201500366
- Galdeano, M. C., Mali, S., Grossmann, M. V. E., Yamashita, F., and García, M. A. (2009). "Effects of plasticizers on the properties of oat starch films," *Materials Science and Engineering:* C 29(2), 532-538. DOI: 10.1016/j.msec.2008.09.034
- Hachemane, B., Zitoune, R., Bezzazi, B., and Bouvet, C. (2013). "Sandwich composites impact and indentation behaviour study," *Composites Part B: Engineering* 51, 1-10. DOI: 10.1016/j.compositesb.2013.02.014

- Ishak, M., Sapuan, S. M., Leman, Z., Rahman, M., and Anwar, U. (2012). Characterization of sugar palm (*Arenga pinnata*) fibres," *Journal of Thermal Analysis and Calorimetry* 109(2), 981-989. DOI: 10.1007/s10973-011-1785-1
- Ishak, M., Sapuan, S. M., Leman, Z., Rahman, M., Anwar, U., and Siregar, J. (2013). "Sugar palm (*Arenga pinnata*): Its fibres, polymers and composites," *Carbohydrate Polymers* 91(2), 699-710. DOI: 10.1016/j.carbpol.2012.07.073
- Jawaid, M., and Khalil, H. A. (2011). "Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review," *Carbohydrate Polymers* 86(1), 1-18. DOI: 10.1016/j.carbpol.2011.04.043
- Jumaidin, R., Sapuan, S. M., Jawaid, M., Ishak, M., and Sahari, J. (2016). "Character-istics of thermoplastic sugar palm starch/agar blend: Thermal, tensile, and physical properties," *International Journal of Biological Macromolecules* 89, 575-581. DOI: 10.1016/j.ijbiomac.2016.05.028
- Jumaidin, R., Sapuan, S. M., Jawaid, M., Ishak, M. R., and Sahari, J. (2017). "Thermal, mechanical, and physical properties of seaweed/sugar palm fibre reinforced thermoplastic sugar palm starch/agar hybrid composites," *International Journal of Biological Macromolecules* 97, 606-615. DOI: 10.1016/j.ijbiomac.2017.01.079
- Júnior, J. H. S. A., Júnior, H. L. O., Amico, S. C., and Amado, F. D. R. (2012). "Study of hybrid intralaminate curaua/glass composites," *Materials & Design* 42, 111-117. DOI: 10.1016/j.matdes.2012.05.044
- Kishi, H., and Fujita, A. (2008). "Wood-based epoxy resins and the ramie fiber reinforced composites," *Environmental Engineering and Management Journal* 7(5), 517-523.
- Leman, Z., Sapuan, S. M., Saifol, A., Maleque, M. A., and Ahmad, M. (2008). "Moisture absorption behavior of sugar palm fiber reinforced epoxy composites," *Materials & Design* 29(8), 1666-1670. DOI: 10.1016/j.matdes.2007.11.004
- López, O. V., Castillo, L. A., García, M. A., Villar, M. A., and Barbosa, S. E. (2015). Food packaging bags based on thermoplastic corn starch reinforced with talc nanoparticles," *Food Hydrocolloids* 43, 18-24. DOI: 10.1016/j.foodhyd.2014.04.021
- López, O. V., and García, M. A. (2012). "Starch films from a novel (*Pachyrhizus ahipa*) and conventional sources: Development and characterization," *Materials Science and Engineering: C* 32(7), 1931-1940. DOI: 10.1016/j.msec.2012.05.035
- Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. N., and Zaritzky, N. E. (2002).
 "Microstructural characterization of yam starch films," *Carbohydrate Polymers* 50(4), 379-386. DOI: 10.1016/S0144-8617(02)00058-9
- Mali, S., Sakanaka, L., Yamashita, F., and Grossmann, M. (2005). "Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect," *Carbohydrate Polymers* 60(3), 283-289. DOI: 10.1016/j.carbpol.2005.01.003
- Mehta, N., and Parsania, P. (2006). "Fabrication and evaluation of some mechanical and electrical properties of jute-biomass based hybrid composites," *Journal of Applied Polymer Science* 100(3), 1754-1758. DOI: 10.1002/app.23014
- Mohanty, S., Verma, S. K., and Nayak, S. K. (2006). "Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites," *Composites Science and Technology* 66(3), 538-547. DOI: 10.1016/j.compscitech.2005.06.014
- Müller, C. M., Laurindo, J. B., and Yamashita, F. (2009). "Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films," *Food Hydrocolloids* 23(5), 1328-1333. DOI: 10.1016/j.foodhyd.2008.09.002

- Munthoub, D. I., and Rahman, W. A. W. A. (2011). "Tensile and water absorption properties of biodegradable composites derived from cassava skin/polyvinyl alcohol with glycerol as plasticizer," *Sains Malaysiana* 40(7), 713-718.
- Prachayawarakorn, J., Chaiwatyothin, S., Mueangta, S., and Hanchana, A. (2013). "Effect of jute and kapok fibers on properties of thermoplastic cassava starch composites," *Materials & Design* 47, 309-315. DOI: 10.1016/j.matdes.2012.12.012
- Rao, H. R., Kumar, M. A., and Reddy, G. R. (2011). "Hybrid composites: Effect of fibers on mechanical properties," *International Journal of Macromolecular Science* 1(1), 9-14.
- Razali, N., Salit, M. S., Jawaid, M., Ishak, M. R., and Lazim, Y. (2015). "A study on chemical composition, physical, tensile, morphological, and thermal properties of roselle fibre: Effect of fibre maturity," *BioResources* 10(1), 1803-1824. DOI: 10.15376/biores.10.1.1803-1824
- Reddy, N., and Yang, Y. (2005). "Biofibers from agricultural byproducts for industrial applications," *Trends in Biotechnology* 23(1), 22-27. DOI: 10.1016/j.tibtech.2004.11.002
- Rezaei, F., Yunus, R., and Ibrahim, N. A. (2009). "Effect of fiber length on thermomechanical properties of short carbon fiber reinforced polypropylene composites," *Materials & Design* 30(2), 260-263. DOI: 10.1016/j.matdes.2008.05.005
- Sahari, J., Sapuan, S. M., Ismarrubie, Z., and Rahman, M. (2012). "Physical and chemical properties of different morphological parts of sugar palm fibres," *Fibres & Textiles in Eastern Europe* 91(2), 21-24.
- Sahari, J., Sapuan, S. M., Zainudin, E., and Maleque, M. (2013a). "Thermo-mechanical behaviors of thermoplastic starch derived from sugar palm tree (*Arenga pinnata*)," *Carbohydrate Polymers* 92(2), 1711-1716. DOI: 10.1016/j.carbpol.2012.11.031
- Sahari, J., Sapuan, S. M., Zainudin, E., and Maleque, M. A. (2013b). "Mechanical and thermal properties of environmentally friendly composites derived from sugar palm tree," *Materials & Design* 49, 285-289. DOI: 10.1016/j.matdes.2013.01.048
- Sahari, J., Sapuan, S. M., Zainudin, E. S., and Maleque, M. A. (2014). "Degradation characteristics of SPF/SPS biocomposites," *Fibres & Textiles in Eastern Europe* 22(5), 96-98.
- Sanyang, Sapuan, S. M., Jawaid, M., Ishak, M., and Sahari, J. (2015a). "Effect of plasticizer type and concentration on dynamic mechanical properties of sugar palm starch based films," *International Journal of Polymer Analysis and Characterization* 20(7). 627-636.
- Sanyang, Sapuan, S. M., Jawaid, M., Ishak, M. R., and Sahari, J. (2015b). "Effect of plasticizer type and concentration on tensile, thermal and barrier properties of biodegradable films based on sugar palm (*Arenga pinnata*) starch," *Polymers* 7(6), 1106-1124. DOI: 10.3390/polym7061106
- Sanyang, M. L., Sapuan, S., Jawaid, M., Ishak, M. R., and Sahari, J. (2016). "Recent developments in sugar palm (*Arenga pinnata*) based biocomposites and their potential industrial applications: A review," *Renewable and Sustainable Energy Reviews* 54, 533-549. DOI: 10.1016/j.rser.2015.10.037
- Shakuntala, O., Raghavendra, G., and Samir Kumar, A. (2014). "Effect of filler loading on mechanical and tribological properties of wood apple shell reinforced epoxy composite," *Advances in Materials Science and Engineering* 2014, 1-9. DOI: 10.1155/2014/538651
- Thwe, M. M., and Liao, K. (2002). "Effects of environmental aging on the mechanical properties of bamboo–glass fiber reinforced polymer matrix hybrid composites,"

Composites Part A: Applied Science and Manufacturing 33(1), 43-52. DOI: 10.1016/S1359-835X(01)00071-9

- Versino, F., and García, M. A. (2014). "Cassava (Manihot esculenta) starch films reinforced with natural fibrous filler," Industrial Crops and Products 58, 305-314. DOI: 10.1016/j.indcrop.2014.04.040
- Versino, F., López, O. V., and García, M. A. (2015). "Sustainable use of cassava (Manihot esculenta) roots as raw material for biocomposites development," Industrial Crops and Products 65, 79-89. DOI: 10.1016/j.indcrop.2014.11.054
- Yaich, H., Garna, H., Besbes, S., Paquot, M., Blecker, C., and Attia, H. (2011). "Chemical composition and functional properties of Ulva lactuca seaweed collected in Tunisia.," *Food Chemistry* 128(4), 895-901. DOI: 10.1016/j.foodchem.2011.03.114

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