

# Preparation and Characterization of Cassava Bagasse Reinforced Thermoplastic Cassava Starch

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**Abstract:** A starch-based composite film was prepared by using fibrous residual of starch extraction (cassava bagasse) as filler. Composite films were prepared through casting technique using fructose as a plasticizer and various sizes and concentrations of bagasse. The physical, thermal, tensile and structural properties of the composite film were investigated. Also, temperature variation of dynamic-mechanical parameters of cassava starch/bagasse composites was investigated by Dynamic Mechanical Analysis (DMA) test. The size and concentration of bagasse were significantly influenced the physical properties of cassava bagasse. There were also increases- in thickness, water solubility, and water absorption of cassava bagasse. There were reduction of water content and density of the film. However, there was no significant effect of adding bagasse on thermal properties. X-ray diffraction (XRD) studies indicated increase in crystallinity of the composites with increase in fiber content. SEM micrographs indicated that the filler was incorporated into the matrix. Films with a small size of bagasse showed better compact structure and homogeneity surface. On the other hand, films with big size and higher concentration of bagasse exhibited more heterogeneous surfaces. The modulus and maximum tensile strength of composite films were increased from 69.03 to 581.68 MPa and 4.7 to 10.78 MPa respectively. Addition of 6 % bagasse was the most efficient reinforcing agent owing to its remarkable physical and mechanical properties. The composites prepared by using cassava for both matrix and reinforcement increased the significance of the remaining residue of starch extraction.

**Keywords:** Cassava film, Bio-composite, Cassava bagasse, Natural fillers, Mechanical properties

## Introduction

Cassava (*Manihot Esculenta* Cranz, Manioc, Tapioca, Ubi Kayu) is ranked fifth most widely produced starch crop in the world but as third among the food sources consumed in the tropical regions. It is usually more used in the under-developed regions of the world. Around 800 million people of Africa, South American, Asia, and the Pacific Islands use this crop. It contains more than 80 % starch (dry weight) which makes it an energy rich food source. However, short post-harvest life is one of the major factors which limit its production [1,2]. The value of harvested cassava can be enhanced by processing cassava to produce starch and consequently developing the rural economies. The plant along with its by-products enhance the value of domestic and industrial products made from this plant and allow rural communities to avail themselves of more opportunities and benefits. One of the major by-products of cassava starch is pulp or bagasse. Cassava bagasse contains 50-60 % residual starch (dry weight basis). It may be dried in the sun and used as filler in cattle feed [3,4]. Nonetheless, most of the bagasse is simply discarded as a waste product [3]. Recently, natural fibers are increasingly being used as reinforcing materials in polymers and composites. In comparison to inorganic fillers,

lignocelluloses are more significant owing to their renewable nature, biodegradability, low energy consumption, wide availability, low cost and density and high specific strength and modulus [5-7]. Additionally, high sound attenuation is shown by natural fibers and it is easy to engage them in a process owing to suppleness and smooth nature which permit high filling stages [8]. Agro-industrial or agricultural residues can be considered important for acquiring natural fibres. Starch composites with various cellulose fibre such as wood and kenaf fibres [9], softwood short fibres [10], pehuen cellulosic husk [11] date palm and flax fibres have been examined earlier [12]. There has not been much work about preparation and characterization of cassava starch films reinforced with the residue from starch extraction (bagasse). However, there is no information on preparation and characterization of CS/CB composite film using cassava bagasse as filler with different particle sizes, higher concentration and fructose as the plasticizer. The use of cassava bagasse fiber has been studied as a natural filler intended to reinforce biomaterials, modifying their hydrophobicity and final properties [13-15]. Cassava starch and cassava bagasse have been characterized in our previous work. Thus, the effect of various filler loading and different particle sizes of cassava bagasse on physical, thermal, tensile and structural properties of CS/CB composite films were investigated. This bio-composite makes this industrial wastes advantageous

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with the resultant attenuation of waste volumes. The fundamental objective of the present work was to develop and characterize eco-compatible plasticized films based on cassava starch and bagasse as filler reinforcing material with proposition of an integral approach to the use of whole tuber root. This research was also carried out to evaluate the use of cassava bagasse, which is highly unutilized and inexpensive source of cassava starch and fiber, as a feedstock for making fiber reinforced TPS. The use of CB as reinforcement agents for CS thermoplastic cassava adds value to the wasted by-products and increases the suitability of CS composite films as environmentally friendly food packaging material. It should be noted that the cassava bagasse particles used as the fiber in this study were not chemically treated or modified, which would lead to the development of more environmentally friendly and cheaper production processes and materials.

## Experimental

### Materials

Native cassava starch was extracted from cassava tubers. Cassava bagasse was obtained through the same extraction process and was used as a filler. Fructose supplied by LGC Scientific Sdn. Bhd, Malaysia was used as a plasticizer.

### Film Preparation and Characterization

Casting method was employed to prepare starch films by utilizing a film-forming solution that included 5 g of cassava starch/100 ml distilled water. The concentration of fructose used as a plasticizer was 0.30 g/g dry starch. Bagasse was used as a filler at concentrations of 3, 6 and 9 % w/w dry starch. Two particle sizes of the bagasse were utilized  $B_1 < 300 \mu\text{m}$  and  $300 \mu\text{m} < B_2 < 600 \mu\text{m}$ . Films with 3, 6 and 9 % w/w dry starch of small size bagasse were termed  $B_{1-3}$ ,  $B_{1-6}$  and  $B_{1-9}$  respectively. Films with 3, 6 and 9 % w/w dry starch of big size bagasse were termed  $B_{2-3}$ ,  $B_{2-6}$  and  $B_{2-9}$  respectively. The mixture was heated to 80 °C in a thermal bath and was left in this condition for 20 minutes under continuous stirring. The film-forming solution was placed in a desiccator in a vacuum to remove air bubbles that were formed during heating. The solution was then poured consistently in 10 cm diameter circular plates. These plates were then dried in an oven whose air-flow was at 45 °C. The dry films were taken off the plates and kept at the ambient condition (temperature and pressure) in plastic bag for a week before characterization.

### Physical Properties

#### Film Thickness

The film thicknesses were determined according to the method described by Lu *et al.* (2006) using a digital micrometer (Mitutoyo Co., Japan). Five random measurements were taken for each film and an average value was calculated and used [16].

### Film Density

The dimensions of square samples of the films were 20×20 mm. The film density was calculated directly from the film weight and volume and the values considered were the averages of five measurements. Film density was calculated by dividing the film weight by the film volume using equation (1) below while the film volume was calculated by multiplying the film area by its thickness [17].

$$\rho = \frac{m}{v} = \text{g/cm}^3 \quad (1)$$

### Water Content (WC)

WC of films was determined using weight loss method. Initial weights ( $w_1$ ) of film samples were determined using a weighing balance. The samples were then dehydrated at 105 °C for 24 h and the final weight ( $w_2$ ) was determined using the same balance. Water content was calculated as the percentage of initial film weight loss through drying according to equation (2) and reported on a wet basis.

$$\text{WC (\%)} = \frac{W_1 - W_2}{W_2} \times 100 \quad (2)$$

### Film Solubility in Water (WS)

WS of films was prepared in triplicate and measured following the method of Shojaee *et al.* (2013). Initially, film samples were dried at 90 °C for 24 h in a laboratory oven and then weighted to calculate initial solid matter. The reason behind selection of temperature was to prevent loss of plasticizer [18]. These film samples (1 cm×3 cm) were then soaked in 50 ml of distilled water under constant stirring for 6 hours at 25 °C. After that period, the remaining pieces of films were filtered and dried at 90 °C to constant weight (final dry weight). Equation (3) was used to determine water solubility (%) of the films [19]:

$$\text{WS (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (3)$$

### Water Absorption

Water absorption (WA) test was conducted in accordance with ASTM D 570-98 in which the film samples were first dried for 24 h at 50 °C, cooled in a desiccator and directly weighed and then soaked in distilled water at room temperature. The samples were taken out of the water on regular basis after a particular soaking period, wiped with a cloth and weighed again. The differences between the preliminary and final masses of the samples were calculated using equation (4).

$$\text{Water absorption (\%)} = [(M_{\text{final}} - M_{\text{initial}})/M_{\text{initial}}] \times 100 \quad (4)$$

where  $M_{\text{initial}}$  is the initial mass while  $M_{\text{final}}$  is the final mass.

### Soil Barrier Test

Biodegradation tests were carried out following the method described by Sahari *et al.* [20]. The biodegradability

of the samples was determined by measuring the weight loss of the films buried in compost soil under moisture-controlled conditions. Triplicate specimens (30×20 mm) of each film were buried 10 cm under the surface of the soil which was moistened by adding water periodically. 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 and then dried to a constant weight at 60 °C in a vacuum oven. The weight loss was then determined using equation (5) below.

$$\text{Weight loss (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (5)$$

where  $W_i$ =initial weight before being buried, while  $W_f$ =final weight after being buried.

### Morphological Properties

#### Scanning Electron Microscopy (SEM)

SEM S-3400N Hitachi-Japan operating at an acceleration voltage of 20 kV and mounted on bronze stubs using a double-sided tape and coated with a gold layer (40-50 nm) under high vacuum mode was used to study the morphology of the fractured surfaces of the samples.

#### Tensile Properties

The mechanical properties of the films were determined using ASTM D882 [24] with a slight modification. Film strips (70 mm×10 mm) were then characterized using 5 kN INSRON tensile machine with an initial grip separation and crosshead speeds of 30 mm and 2 mm/min. Then tensile strength and elongation at breaking as well as Young's modulus were calculated. At least five replicates were carried out for each sample.

### Structural Properties

#### X-ray Diffraction (XRD)

Reflection geometry was used to take XRD measurements on Rigaku, Tokyo, Japan diffractometer using current of 40 mA, generator voltage of 40 kV and goniometer speed of 0.02 (2θ) s<sup>-1</sup>. The relative crystallinity index was calculated using equation (6) proposed in a previous work [21] based on the calculus of amorphous and crystalline areas.

$$Rc = \frac{A_c}{A_c + A_a} \quad (6)$$

where  $Rc$  is the relative crystallinity,  $A_c$  is the crystalline area and  $A_a$  is the amorphous area in the XRD pattern.

#### Fourier Transform Infrared Spectroscopy (FTIR)

An IR spectrometer (Bruker Vector 22) was used to determine the FTIR spectra at the frequency range of 4000-400 cm<sup>-1</sup>. The samples were prepared using KBr-disk method.

### Thermal Properties

#### Thermal Gravimetric Analysis (TGA)

TGA was conducted by using 10 mm<sup>2</sup> of the films. The

heating rate was 10 °C min<sup>-1</sup> while the temperature ranged from room temperature to 500 °C. The air flow rate was 25 ml/min in a nitrogen atmosphere.

#### Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis is a technique to determine thermal and mechanical properties of polymers. The specimens generally deformed sinusoidally in response to an applied force. The resultant strain in the specimen due to the sinusoidal load depends upon both the elastic and viscous behavior of the specimen. In this study, the storage modulus ( $E'$ ) and the loss modulus ( $E''$ ) of cassava starch/bagasse composites films were conducted according to ASTM D5026 standard. The storage modulus (or elastic modulus) reflects the elastic modulus of the composites which measures the recoverable strain energy in a deformed specimen, and the loss modulus (or 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 room temperature (about 25 °C) to 150 °C with a heating rate of 1.5 °C/min and using a frequency of 1 Hz. Dynamic mechanical analysis (DMA) was performed initially to investigate if the addition of the cassava bagasse to cassava TPS will improve the mechanical properties.

## Results and Discussion

### Physical Properties

#### Film Formulation

Preliminary experiments were carried out to determine bagasse fiber concentration range for film formulation. The maximum compatible concentration of bagasse used in the formulations was 9 % (w/w). Films became brittle with rough surface as well as pores and cracks, once this limit was exceeded.

#### Thickness and Density of the Starch Films

There was no significant difference in the film thicknesses and density among different films, the thickness was increased while the density was decreased upon fiber addition with very small variations as shown in Table 1.

The higher the fiber concentrations in the cassava film, the thicker the film. In addition, films containing 6 % and 9 % of fiber were thicker compared to films containing 3 % fiber and the control film. Film with 3 % small size bagasse fiber was the thinnest (0.30 mm) whereas film containing 9 % big size bagasse fiber was the thickest (0.49 mm) amongst all. The thickness was also influenced by the fiber size. The thickness of the films with the small size bagasse was smaller compared to the films with large size bagasse having the same concentration. The incorporation of a higher content and/or a large size of filler resulted in thicker and rougher films. According to Versino *et al.* [22], this could be attributed to the presence of large size filler particles within the polymer matrix which led to a less homogenous material and could promote structural defects. Films with a higher

**Table 1.** Physical properties of cassava starch/bagasse composite film with different size and concentration of bagasse

Film	Thickness (mm)	Density (g/cm <sup>3</sup> )	Moisture content (%)	Water solubility (%)
Control	0.18±0.08	1.73±0.13	10.96±0.02	33.9±0.04
B <sub>1</sub> -3	0.30±0.09	1.44±0.10	10.97±0.03	28.39±0.07
B <sub>1</sub> -6	0.45±0.06	1.28±0.07	11.34±0.06	26.47±0.11
B <sub>1</sub> -9	0.47±0.11	1.18±0.08	11.77±0.04	24.86±0.06
B <sub>2</sub> -3	0.31±0.10	1.23±0.08	11.31±0.08	26.12±0.08
B <sub>2</sub> -6	0.45±0.09	1.20±0.09	11.93±0.09	25.84±0.10
B <sub>2</sub> -9	0.49±0.07	1.10±0.03	12.23±0.03	24.04±0.05

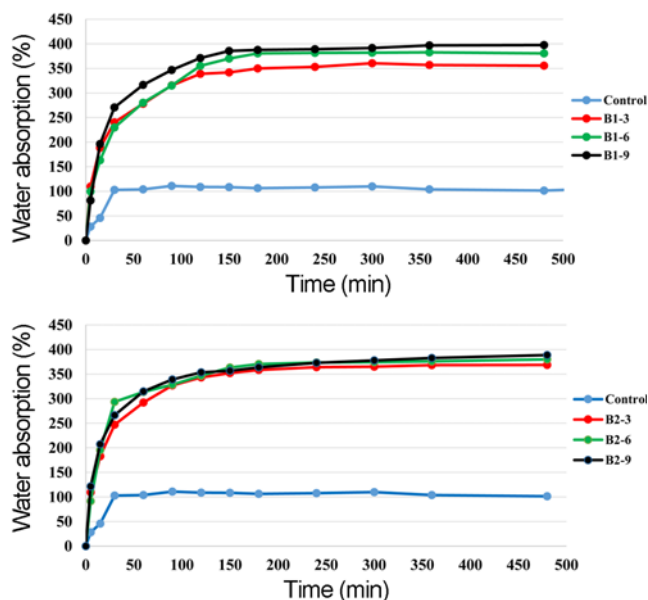
concentration of fiber showed lower densities and the size of fiber also influenced the film densities. That could be due to low density of bagasse as compared to starch. A similar result was reported by Salgado *et al.* [23] for foams based on cassava starch, sunflower proteins and cellulose fibers. In addition, the highest density (1.44 g/cm<sup>3</sup>) was recorded for film with 3 % small size bagasse and the lowest density (1.10 g/cm<sup>3</sup>) was recorded for films with higher concentration of big size bagasse as shown in Table 1.

#### Moisture Content and Solubility in Water

Moisture content of cassava starch film mixed with various sizes and concentrations of bagasse were about 10.97 to 12.23 %, which were greater than moisture content of the control film (10.96 %) (Table 1). A significant decrease in the moisture content of cassava films was observed when the concentrations of big size bagasse were amplified from 3 to 9 % (w/w). The hydrophilic content increased as a result of incorporation of bagasse. The MCs of films with large size bagasse were slightly higher than the films with small size bagasse at the same concentration and showed small variations. This was probably because large bagasse exhibited a higher surface area ratio [24]. Moreover, it is well known that dry cassava bagasse immersed in water is rehydrated like a sponge, which means that it absorbs high amount of water in a short period of time. Therefore, the solubility of films was also enhanced. Furthermore, it affects and changes the contact between the polymer chains which may possibly enhance or reduce the suspension of the polymer. Solubility in water is an important property of starch based-films. Potential applications may require water insolubility to improve product integrity and water resistance [25]. It was found that films did not remain intact once immersed in water. The aforementioned behavior depends on the size as well as the concentration of bagasse. The solubility decreased with increase in concentration despite the fact that these films exhibited the highest equilibrium moisture content. In addition, the B<sub>2-9</sub> and B<sub>1-9</sub> show lower solubility with 24.04 and 24.86 % respectively as compared to B<sub>1-3</sub> and B<sub>2-3</sub> that had 28.39 and 26.12 % respectively.

#### Water Absorption (WA)

WA is a significant study in starch films because water acts as a plasticizer. Films reinforced with cassava bagasse



**Figure 1.** Water absorption of cassava starch/bagasse composite film with different size and concentration of bagasse.

has higher hydrophilicity. Highest propensity for water absorption of the films is due to the existence of hydroxyl groups in film molecules. Figure 1 shows the percentage of water uptake as a function of time in cassava starch/bagasse composite films. It can be observed from Figure 1 that all films absorbed high amount of water after 60 min of water immersion at room temperature due to hydrophilic properties of starch and bagasse. It is evident from Figure 1 that water absorption value of the films increased with higher content of bagasse fiber due to the properties of fibers which are solubility in water and being hygroscopic naturally. Moreover, the control film absorbed about 104.04 % in an hour while the films with 3, 6, and 9 % small size bagasse absorbed about 277.96, 280.18 and 316.45 % respectively. In a similar pattern, films with 3, 6 and 9 % big size bagasse absorbed 291.99, 313.67 and 314.56 %, respectively. Films containing 3 % bagasse absorbed less amount of water as compared to other films. The maximum water uptake observed was 388.55 % at 480 min for the film containing 9 % big size

bagasse. The minimum value was 339.68 % for film containing 3 % small size bagasse at 480 min. Films with big particle size cassava bagasse exhibited greater tendency to absorb water which probably caused a lower response to stress [24].

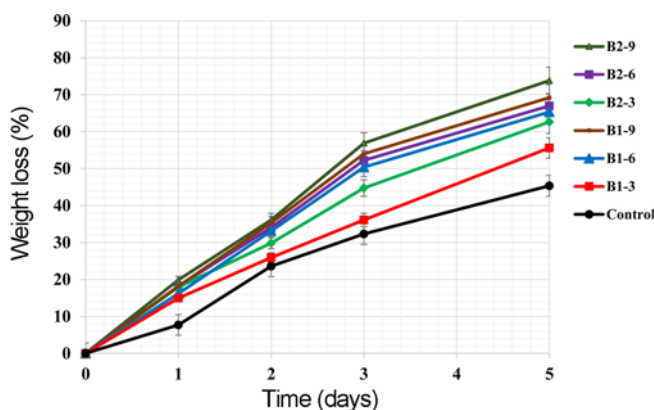
Water absorption tends to decrease with increase amount of cassava bagasse. It is well known that the dry cassava bagasse immersed in water is rehydrated like a sponge which means that it absorbed water of about 160 % of its weight in a short period of time and, therefore, had a higher weight. It should be noted that water absorption depends on particle size of cassava bagasse. After absorption by cassava bagasse, the resultant moisture of the material could be up to three times or more. Water absorption tests revealed that stabilizing the mixtures with cassava bagasse increased the water absorption capacity. The results from this study are quite similar to those from our previous works [26].

#### Biodegradation of Bio-composite

Biodegradation is the breakdown of materials by the action of microorganisms. Once in contact with the biodegradable

polymer, the microorganisms produce enzymes that break down the polymers into progressively smaller segments which have lower average molecular weights. The enzymes react to the starch and degrade to small molecules. Thus, this favours material's degradation in the environment [27].

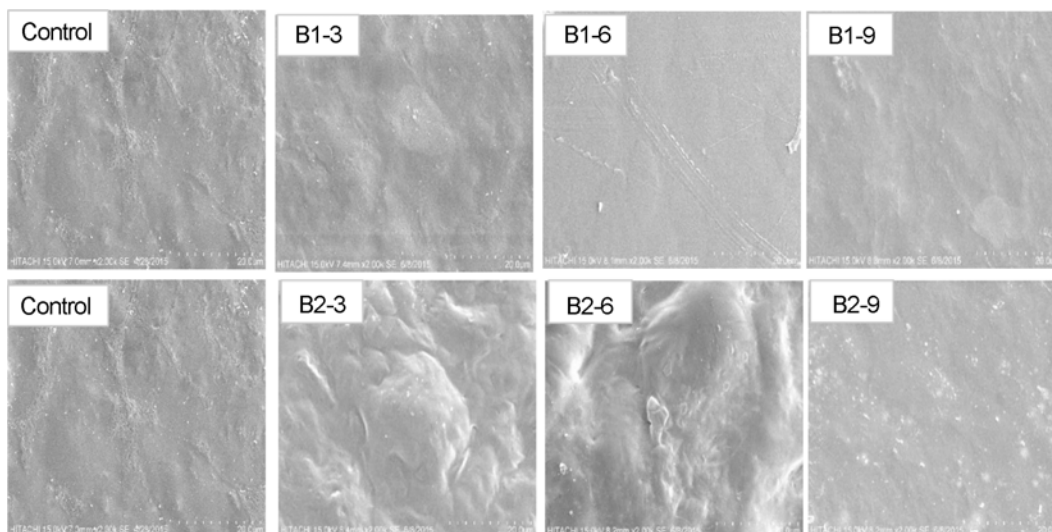
The weight loss of the films after biodegradation testing is shown in Figure 2. At the end of 5 days, the control film had lost 45.38 % weight, while the films with small size bagasse had lost 55.59, 65.34 and 69.22 % weight for B1-3, B1-6 and B1-9 respectively, and 62.60, 66.97 and 73.79 % for B2-3, B2-6 and B2-9 respectively. The control film was totally degraded after 10 days while it took bio composites films 7 days to degrade completely. The weight loss for the matrix was lower compared to the composite films which can be attributed to the fact that the control film absorbs less water. This result is in agreement with the water absorption result in this study. The film degradation was also influenced by fiber size. The films with large size bagasse degraded faster, especially at high content. This is probably because the large bagasse exhibited a higher surface area ratio. The result implies that the film with large size and/or higher bagasse contents would exhibit a potential for better biodegradability, making it more prone to microorganism attack. These microorganisms, in form of bacteria and fungi, access the composite films in the presence of a water medium [28].



**Figure 2.** The biodegradability of CS/CB composite film with different size and concentration of bagasse.

#### Scanning Electron Microscopy (SEM)

SEM images in Figure 3 shows insignificant difference among samples containing the same fiber loading. It can be observed that film with 3 % bagasse had compact structure and smooth surfaces without pores. Microstructure of starch films with 6 % small size bagasse (B<sub>1-6</sub>) had smooth surfaces and homogeneous texture without pores as shown in Figure 3. Film with 9 % bagasse had less compact structure with rough texture having large pores and visible fractures with

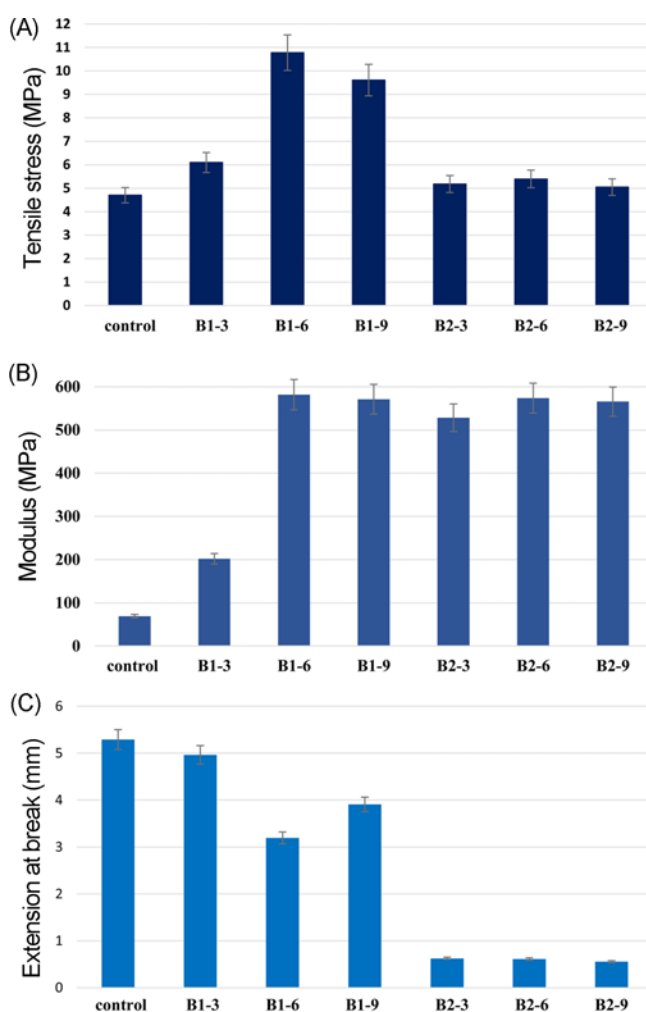


**Figure 3.** SEM of cassava starch/bagasse composite film with different size and concentration of bagasse.

haphazard arrangement. This is due to the fact that fibre agglutinations are not desired and they limit stress transference from matrix to fiber and hence decrease mechanical strength of the composites [29,30]. It is quite clear that bagasse were pulled out from the TPS matrix with crack, leaving spaces in the matrix in case of film with 9 % bagasse. In films, the homogeneity of matrix is a beneficial pointer of their structural reliability [31,32]. In this regard, it can be expected that films having 6 % bagasse will show comparatively better mechanical characteristics. As shown by SEM, the arrangement of composite film was inconsistent and rough. Smooth surfaces and solid structures that showed the structural strength of the arrangement are basic characteristics of such films.

### Tensile Properties

Tensile characteristics of cassava TPS films and the bio-composites containing cassava bagasse with various size and



**Figure 4.** Tensile properties of cassava starch/bagasse composite film with different size and concentration of bagasse; (A) tensile stress, (B) modulus, and (C) extension at break.

amount are shown in Figure 4. In case of low fiber concentrations, the incorporation of cassava bagasse as strengthening agents of TPS matrix resulted in durable films.

A significant increase in tensile strength of the cassava starch-based films was observed with an increase in fiber content from 3 % to 6 % but there was reduction at 9 % loading. This could be a result of higher content of larger particles at this stage which resulted in a less homogenous material that could prone to mechanical flaws. Prachayawarakorn *et al.* also observed similar result behavior at different concentrations [33].

Increase in maximum tensile strength and tensile modulus values of TPS films after adding 3 and 6 % bagasse supported the aforementioned outcome. It can be seen that the highest tensile stress (10.78 MPa) observed for B<sub>1-6</sub> which was greater than the control film (4.7 MPa). This result is also greater than 1.79 and 4.35 MPa which were recorded by Versino *et al.* for cassava starch/bagasse contains 0.5 and 1.5 % bagasse respectively [14].

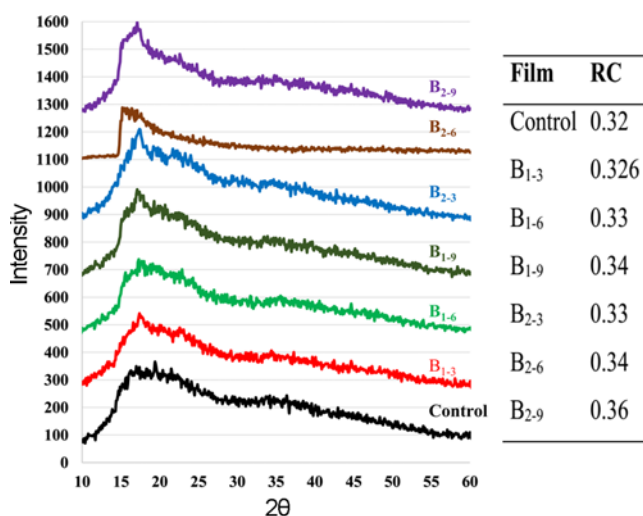
Young's modulus or elastic modulus determines the film stiffness. Therefore, high young's modulus indicates high stiffness of a material. Thus, addition of 3 and 6 % fiber (bagasse) resulted in increasing tensile stress and young's modulus. However, increasing bagasse content from 6 % to 9 % resulted in films with lower tensile stress and young's modulus. Decrease in tensile stress and Young's modulus with increasing fiber content in hydrophilic films have been reported previously [31,34]. This could occur as 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 3 % w/w small size bagasse significantly influenced the elongation property of TPS films. Therefore, the elongation at break reduced from 5.29 to 4.96 mm. Nevertheless, addition of the higher amount of this element decreased the value to 3.19 mm with 6 % and 3.9 mm with 9 % bagasse. The films with big size bagasse showed the same trend in which the elongations at break were 0.62, 0.61 and 0.55 mm for the films containing 3, 6 and 9 % big size bagasse respectively. This result could be attributed to the alignment and diffusion of the bagasse on TPS matrix. Films containing 6 % small size bagasse had the best tensile strength and Young's modulus. 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 [22,35].

### Structural Properties

#### X-ray Diffraction (XRD)

The XRD of the film samples can help determining the influence of fiber size and concentration on the crystallinity of films. Figure 4 shows XRD spectra of the control film as well as that of composite films. Well-defined diffraction peaks exhibited by the control film at 17.18° and a small



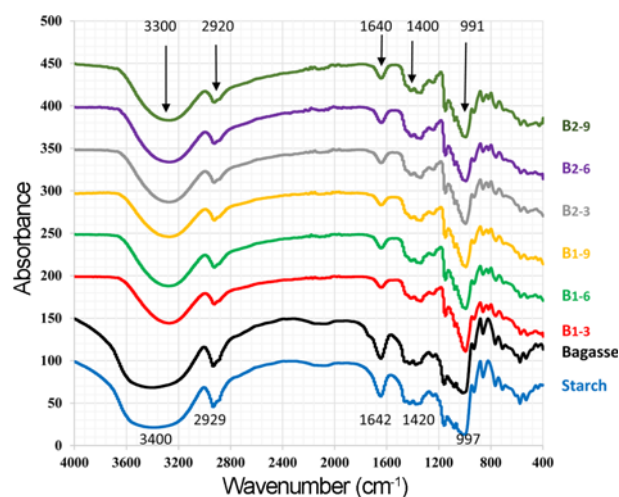
**Figure 5.** XRD curves of cassava starch/bagasse composite film with different size and concentration of bagasse. RC is relative crystallinity.

number of minor peaks at almost  $19.3^\circ$ ,  $20.8^\circ$  demonstrated characteristic A-type pattern [36,37]. It is evident from Figure 5 that all the films showed similar pattern. It could be said that the crystallinity of TPS- based composites increase with increase in the amount of bagasse fibers [38]. The major crystalline peaks of the composite films containing small size bagasse were observed at  $15.4^\circ$ ,  $17.4^\circ$  and  $33.1^\circ$ . Moreover, films with big size bagasse showed peaks at  $16.9^\circ$ ,  $18.5^\circ$  and  $49.8^\circ$ . This shows that when starch molecules are added to the spaces the bagasse chains, the inside arrangement of films turn out to be more and more crystalline and more arranged. It is clear from Figure 5 that high crystalline arrangement is found in films having bigger size and concentration of bagasse. In the same vein, relative enhancement of bagasse in the matrix leads to an increase in relative crystallinity. It is to be noted that crystallinity of natural fibers is higher than that of starch as they are orientated materials [39]. In the present case, all TPS materials were not oriented even though reinforcing fiber content in the TPS matrix increased, leading to improved crystallinity index of the composites. Similarly, all TPS materials were not positioned, although supporting fiber concentration in the TPS matrix was enhanced, resulting in enhanced crystallinity index of the composites. From Figure 4 which shows relative crystallinity of TPS-based composites, it can be observed that the proportional increase in bagasse caused enhancement of the relative crystallinity.

#### Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectroscopy was employed to examine and analyses variations in TPS structure on a short-range molecular level and to determine the probable links between matrix and fiber.

The FTIR spectra of cassava starch and bagasse is shown in Figure 6. Both cassava starch and bagasse had similar



**Figure 6.** FTIR of cassava starch/bagasse composite film with different size and concentration of bagasse.

behavior and chemical composition as they were from the same source. The broad peak observed around  $3400\text{ cm}^{-1}$  is associated with stretching of the O-H groups. Bands identified at  $2929$  and  $2886\text{ cm}^{-1}$  could be attributed to C-H stretching. The peak at  $1642\text{ cm}^{-1}$  could be attributed to the bending mode of the absorbed water. The peaks around  $1420\text{ cm}^{-1}$  could be assigned to O-H bonding. The peaks at  $1153$  and  $1041\text{ cm}^{-1}$  could be attributed to C-O bond stretching of the C-O-H group in cassava starch and the C-O bond stretching of the C-O-C group in the anhydroglucose ring respectively [33,40]. The peak observed around  $3270\text{ cm}^{-1}$  could have resulted from stretching of the O-H groups. Bands identified at  $2922\text{ cm}^{-1}$  might be because of C-H stretching. The peak at  $1655\text{ cm}^{-1}$  could have resulted from the bending mode of the absorbed water. The peaks around  $1366.05\text{ cm}^{-1}$  might be attributed to C-H bonding. The peaks at  $1151.46$  and  $1078.71\text{ cm}^{-1}$  might be attributed to the C-O bond stretching of the C-O-H group in cassava starch [40]. Peaks at  $2990.27$ ,  $3270$  and  $3680.1\text{ cm}^{-1}$  are the fundamental dissimilarities between the row material and cassava starch/bagasse composite film which is connected to the elongation of O-H group of free hydroxyl. For instance, the existence of O-H groups in starch was shown by the penetrating peaks at  $3200\text{-}3500\text{ cm}^{-1}$  which points out that the starch is highly hydrophilic [41]. It has been reported that similar peaks which relate to the elongation of hydroxyl groups are due to the presence of hydrogen bonding between the molecules [41,42]. The peaks at  $990\text{-}1030\text{ cm}^{-1}$  depict elongation of anhydroglucose ring O-C stretch [43]. Whereas the peaks at  $1500\text{-}1600\text{ cm}^{-1}$  might be due to diversion of water in starch [28,44].

#### Thermal Properties

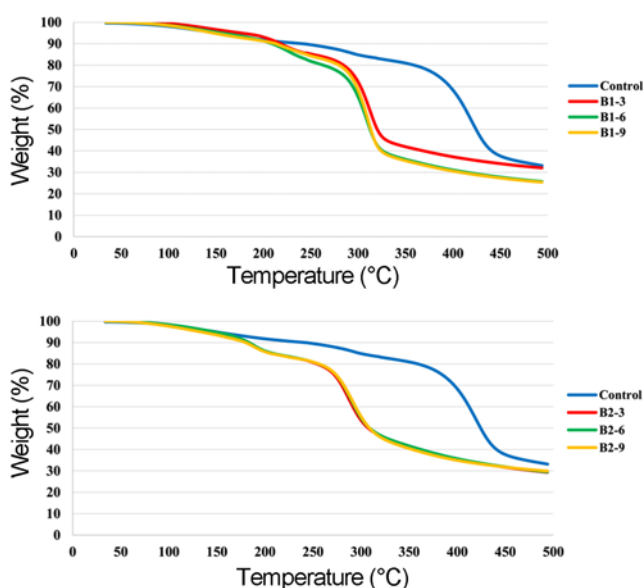
##### Thermal Gravimetric Analysis (TGA)

The TGA thermographs of CS/CB composite films are

shown in Figure 7. Despite the differences in fiber size and concentration, the behavior of the mass loss curves was similar in all the cases. Nevertheless, the initial temperatures for decomposition of all films were lowered than that of the control film. The mass loss at temperature lower than 100 °C could be attributed to water loss while the one from 100 °C to the onset temperature (around 215 °C) might be due to the volatilization of water as well as the plasticizers. In the second level, the mass loss occurred between 215 and 330 °C with the peak at 310 °C. During this process, Ether bonds and unsaturated structures are created by means of thermal condensation between hydroxyl groups of starch chains throughout this procedure to remove water and other small molecules. The last level which occurred between 350 °C and 500 °C could be due to disintegration of the earlier produced residue as an oxidative atmosphere was utilized [45]. As shown in Figure 7, the major difference of fiber loading in TPS film was the reason behind the onset of decomposition and mass loss at onset temperature. The mass that remained at 500 °C decreased with the addition of fiber. The lowest mass residue was noted in film with 9 % small size bagasse which finally reached 24.41 % (Figure 7(A)) while the control film had 33.67 %. Variances in mass residue for films containing small size bagasse ranged from 24.41 to 32.07 % and from 29.4 to 29.92 % for films containing big size bagasse. These results are in agreement with the work reported by Prachayawarakorn *et al.* [33,38] that the addition of fiber to a starch matrix improves its thermal stability since there is good adhesion between the fiber and matrix which reduces the mass loss of the sample.

#### Dynamic Mechanical Analysis (DMA)

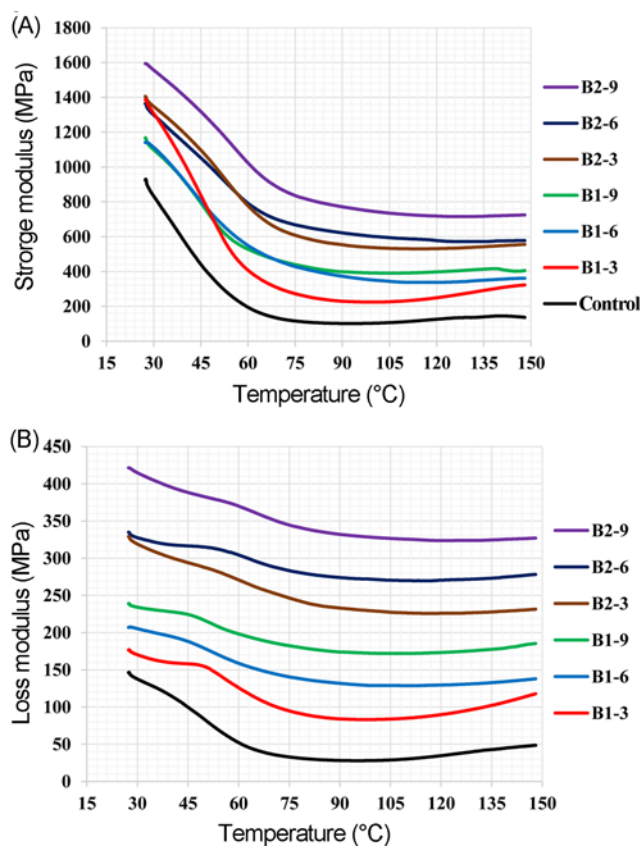
The elastic modulus of the film samples is shown by the



**Figure 7.** TGA of cassava starch/bagasse composite film with different size and concentration of bagasse.

storage modulus ( $E'$ ) which is obtained from the DMA study. It defines the recoverable strain energy in the distorted samples. Simply, it is basically the calculation of elastic behavior of film samples when exposed to change in temperature [46]. Additionally,  $E'$  helps in determining the toughness of the film samples. The impacts of bagasse size and concentration on the storage modulus of films are shown in Figure 8(A). From that figure, it was evident that an increase in the amount of fiber from 3 to 9 % increased the storage modulus of the films. The storage modulus of films having big size fiber was higher compared to the films with small size fiber of the same content. In reality,  $E'$  for control film is approximately 0.950 GPa at 25 °C while in 9 % big size fiber composite, it is about 1.600 GPa. This indicates that the matrix capacity to reduce mechanical limitations with recoverable viscoelastic deformation was increased by bagasse. Specifically, the composite toughness of the film increases significantly with the addition of bagasse.

The reduction in the modulus of the films, which was due to increase in temperature, was more significant for films with small size and/or low contents of bagasse. This observation proves that at high temperatures, the physically entangled network of fibers in the composites bears a



**Figure 8.** DMA of cassava composite film, with different size and concentration of bagasse; (A) storage modulus and (B) loss modulus.



significant amount of load [47]. The composite films have higher  $E'$  values than the matrix (control film) and had certain trends with respect to the size and content of bagasse. This beneficial tendency is due to the quill particles having high compatibility with the matrix leading to good dispersion and interface. However, excess reinforcement causes a slight decrease in the film composite with higher concentration which is probably because the matrix is not enough to cover and wet the quill particles completely. This result was in agreement with our previous work [48]. Comparing the  $E'$  spectra of the composites with the control film, it was observed that the incorporation of large size bagasse and/or higher concentrations of bagasse resulted in increase in stiffness of the material within the temperature range taken into consideration. This result agreed with the earlier report by Rezaei *et al.* [49].

The change of the loss modulus ( $E''$ ) for various composite film, as a function of the temperature is presented in Figure 8(B). In this figure, all  $E$  curves showed broad peaks with separate positions of amplitude and temperature. In addition, these can be connected to the  $\alpha$  peak and recommends comparatively strong structural relaxation behavior through the composites. The aforementioned relaxation is connected to the chain movement of the polymeric matrix [50]. All composite peaks are moved to higher temperatures compared to peaks from the control film. The reason behind its occurrence is the reduction in the movement of the polymer chains triggered by the addition of bagasse. In the case of polymer composites, the peaks of  $E''$  were moved to higher temperatures and that signifies decrease in the chain flexibility [51]. The slower the flow the higher the  $E''$  when large size fibers and/or higher concentration of fibers were incorporated. Generally, as the temperature increases, the viscosity of the materials decreases gradually. Broad peaks were observed on the curves within the temperature range of 70 to 90 °C representing the transitional region from glassy to rubbery state. These results were in agreement with our previous work [49].

### Conclusion

Biodegradable composite films can be developed from cassava starch/bagasse which was obtained through starch-extraction process by casting and dehydration method using 30 % w/w fructose as plasticizer. The size and concentration of cassava bagasse affected physical properties. For instance, bigger size bagasse and higher content of bagasse in films increased film thickness from 0.18 to 0.49  $\mu\text{m}$  while film density decreased from 1.73 to 1.10  $\text{g}/\text{cm}^3$ . Moreover, higher content of bagasse slightly increased moisture content and decreased water solubility of the films. Thermal properties of TPS composites are in agreement with band shifts observed by FTIR. Observed increments in  $T_g$  and  $T_m$  were attributed to a more heterogeneous matrix composition as

well as interaction among the components. SEM morphology of TPS exhibited heterogeneous matrix composition due to their similar chemical nature especially those containing small size bagasse. Furthermore, it should be noted that cassava bagasse particles used as fibers in this study were not chemically treated or modified, which would lead to the development of more environmental friendly and cheaper production process and materials. Addition of natural fiber (cassava bagasse) as a fiber reinforcement constitutes an interesting option to manipulate the properties of the resulting composite films which allows broadening of the application range of eco-compatible starch-based materials.

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