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Preparation and Characterization of Dual-Modified Cassava Starch-Based Biodegradable Foams for Sustainable Packaging Applications

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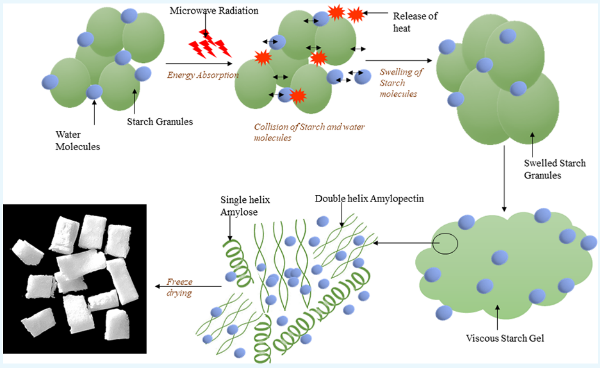

ABSTRACT: Starch and its derivatives have recently emerged as a sustainable and renewable alternative for petroleum-based expanded polystyrene (EPS) and expanded polypropylene (EPP) foam materials. In this study, biodegradable foam materials were prepared from cassava starch using a novel dual modification technique, combining microwave treatment and freeze-drying. The foam materials were prepared from starch solutions microwaved over different intervals. The starch-based foam materials were characterized using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectroscopy, and compression set test. Moreover, the water absorption capacities and density values of the foam materials were measured according to ASTM standards. The biodegradability test was carried out according to the aerobic compost environment test. The lowest water absorption capacities of 65.56% and 70.83% were exhibited for the cassava starch foam sample (MWB) prepared at a 20 s microwave treatment time and immersed in distilled water for 2 and 24 h, respectively. Furthermore, the lightweight cassava starch-based foam materials displayed density ranging from 124 to 245 kg/m^3. The biodegradation test exhibited significant biodegradation of over 50% after 15 days for all the foam materials prepared. These results suggest that the dual-modified cassava starch-based biodegradable foams show potential in sustainable packaging applications by replacing petroleum-based materials.

■ INTRODUCTION

Expanded polystyrene (EPS) and expanded polypropylene (EPP) foams[1,2] are employed in a diverse range of applications due to their intriguing properties such as low density, thermal insulation, strength, and low cost. EPS is widely used as disposable packaging and building insulation materials.[2−4] EPP is an elastomer foam molded using heat and pressure[5] and is commonly utilized in automobile bumpers owing to its high energy absorbance properties.[6]

EPS is one of the major types of plastic wastes, causing a considerable impact on the environment.[7,8] Most of the EPS and EPP are utilized for single-use applications, including food, personal care, agriculture packaging, and fishing equipment.[9] Moreover, these manmade polymers take a much longer time to degrade naturally and release hazardous chemicals into the environment,[10] affecting human and animal health. The degradation of EPS is estimated to be over 100 years, and it is also recognized as a photo-oxidation-resistant material.[11] Therefore, the development of eco-friendly renewable materials, including foam materials for single-use applications, is of great importance. Recently, biopolymers, including starch, have been investigated as a substitution for EPS and EPP foam materials. Starch is the second most abundant natural polymer after cellulose[12] and a low-cost polysaccharide.[4,5,12,13] It is readily biodegradable by a wide variety of enzymes and microbes.[14] Starch is a common constituent found in all organs of higher plants, and it is the major form that stores carbohydrates. It can also be found in mosses, ferns, protozoa, algae, and bacteria. Starch is widely present in green plants and every type of tissue, including leaves, fruits, roots, stems,

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shoots, and pollen grains.[15] The main botanical origins of starch production are maize, cassava, wheat, and potato.[16] Starch consists of two types of molecules, namely, linear amylose (20−25% w/w) and branched amylopectin (75−80% w/w). The amylose to amylopectin ratio of starch varies depending on the source.

Cassava (*Manihot esculenta Crantz*) ranks fourth among staple foods for over 800 million people worldwide. Cassava is considered one of the major sources of starch that proliferates rapidly with minimum fertilizer requirements over a range of soil conditions. The cassava starch has widely been considered in the food and non-food industry. The non-food strains of cassava starch are widely used in bioplastic production, paper, textiles, packaging, drug delivery, and tissue engineering.[17] Interestingly, non-food strains of cassava starch have been employed in preparing biodegradable foam materials.[4,7] According to previous studies, the formation of starch foam can be divided into two main steps known as starch gelatinization and evaporation of water from the batter or gel.[11,18]

Conventional methods such as casting and forming, injection, extrusion, compression molding, and novel techniques, including hot mold baking and reactive extrusion, have been employed for processing starch-based foam materials.[19−21] In hot mold baking, a baking technology is used to develop starch-based foam materials.[4,22,23] This process involves placing a dough-like starch material with a high moisture content of 70−80% (w/w) in a heated mold.[3] The steam produced from the moisture of the starch acts as the blowing agent, creating foam inside the mold.[4] In the extrusion process, starch granules are converted into a homogeneous gelatinous solution. Usually, a co-rotating twin-screw extruder machine is used to produce starch foams. The extruded materials show comparable physical properties to commercial plastic foams.[24] Therefore, starch foams are industrially manufactured via extrusion processes.[3,5,19−21] Apart from the above two methods, the explosion puffing method is also employed to produce starch foam materials. The explosion puffing can produce low-density starch-based foam within several seconds, which is similar to the production process of popcorns. However, it is not suited for preparing molded products compared to extrusion processes.[3]

Generally, starch-based foam materials have high water absorption and biodegradability.[25−27] It has also been reported that mechanical properties such as tensile strength increase with increasing amylose content in starch.[25] Moreover, the properties of starch foam materials are mainly dependent on the starch source. For example, tuber starch-based foam materials show low-density values compared to cereal starch-based foam materials.[25,28]

To improve the water resistivity and mechanical properties of starch-based foams, other polymers such as cellulose,[8] fiber,[3,11,21] and natural rubber latex[13] are incorporated as additives during foam production. Therefore, the physical, mechanical, and thermal properties of starch-based foams significantly depend on the additives added during the production process.[7,24,29] Albeit starch foam materials are prepared by varying the amount of additive and extruder parameters, including temperature and moisture, this method possesses several setbacks. The drawbacks of the extruder methods include longer time requirement, high energy consumption, and generation of toxic chemicals.[24]

Recently, microwave techniques have been introduced as an alternative heating method during polymer processing,[30] food processing,[31] and nanomaterial synthesis.[32] The application of microwave technology in foaming processes involves three main steps: mixing the material with blowing agents such as water,[33] expanding the material by microwave radiation, and stabilizing the foam structure during drying.[30] The microwave treatment helps reduce the heating time and facilitates homogeneous heating. Usually, microwaved starch-based foams are produced using extruded plasticized starch. For instance, Sjöqvist and Gatenholm,[34] Chanvrier *et al.*[35] Kraus *et al.*[33] and López-Gil *et al.*[36] prepared the starch-based foam materials with extruded thermoplastic starch (TPS) pellets using different conditions and additives, including blowing agents and plasticizers to obtain the optimum conditions.

The freeze-drying technique is used to remove moisture and prepare highly porous materials. During the freeze-drying process, the temperature of the particular solution is maintained at the freezing temperature of water, causing the separation of water from the solutes.[37] The freeze-drying process is widely applied in tissue engineering applications to produce scaffolds and films using starch-based materials.[38] Apart from the above, freeze-drying has been employed to prepare multiwall carbon nanotubes (MWCNTs).[39]

The current study presents the preparation and characterization of cassava starch-based foam materials using a combination of microwave radiation and freeze-drying techniques used as a novel approach. During this dual treatment, microwave energy promotes the generation of a significant amount of gelatinized starch quickly, saving time and energy, whereas the freeze-drying process facilitates foam formation.[40,41] To the best of our knowledge, this is the first attempt to prepare and measure the properties of cassava starch-based foam materials produced using a combined method of microwave radiation and freeze-drying. Herein, we report the density, biodegradability, morphology, chemical, and thermal properties of the dual-modified cassava starch-based foam materials. Moreover, the prepared dual-modified cassava starch-based foam materials show potential in packing applications.

■ EXPERIMENTAL DETAILS

Extraction of Native Cassava Starch. The extraction of native cassava starch (NCS) was performed using a slightly modified method described by Gunawardene *et al.*[42] Initially, cassava roots were peeled off, washed, and cut into 1 cm cubes. After that, the pulp obtained after pulverizing the cassava cubes in a high-speed blender for 5 min was suspended in water 10 times its volume and stirred for 5 min. Then, the pulp was filtered using a double-fold cotton cloth, and the resulting filtrate was allowed to settle for 2 h. Next, the top liquid was discarded, water was added to the sediment, and the mixture was stirred again for another 5 min. Finally, the extracted cassava starch was dried at 65 °C for 3 h. Native cassava starch was passed through a 100-mesh sieve before any further use. Association of Official Analytical Chemists (AOAC) standard tests were used to determine the composition of native cassava starch. For instance, AOAC standard 920.36 (2000)[43] is used to determine the moisture content of cassava starch before being subjected to drying. The moisture content of cassava starch is ∼12%. AOAC standards 984.13, 948.22, 923.03 (2000),[43] and AOAC 962.09(2005)[44] were used to determine the protein, fat, ash, and crude fiber content of the dry cassava starch, respectively. The amylose and amylopectin contents in dry cassava starch were determined by the blue value method reported elsewhere.[45] The percentages of amylose and amylopectin in cassava starch are ~78% and 20%. The composition of the starch samples determined using AOAC standard tests is enumerated in Table 1. All the analyses were carried out in triplicate, and the data present in Table 1 are the averages of three replicates.

Table 1. Composition of Native Cassava Starch

wet or dry basis	components	percentage (%)
native cassava starch	moisture	12.00 ± (0.01)
native cassava starch (dry)	protein	0.66 ± (0.00)
	fat	0.19 ± (0.00)
	ash	0.23 ± (0.00)
	crude fiber	0.10 ± (0.01)
	amylose	78.48 ± (0.01)
	amylopectin	20.04 ± (0.01)

Microwave Treatment and Freeze-Drying. Initially, 5 g of native cassava starch was dissolved in 50 mL of distilled water. Then, the resulting cassava starch solution was stirred for 5 min at room temperature (RT). After that, starch solutions were irradiated under microwave radiation at four different time intervals. Table 2 shows the sample IDs and the microwave irradiation times. Microwave treatments were carried out in Electrolux MW 1800 Microwave apparatus of 2450 MHz frequency and at a working power of 1800 KW. Next, the microwave-treated cassava starch solutions were frozen at −14 °C. Finally, the frozen gel solutions were freeze-dried to obtain foam materials using an EYELA freeze dryer FD-1. Each trial was carried out in triplicate. All foam samples were conditioned in a desiccator for 5 days before testing. Figure 1 shows the photographs of the cassava starch foam material, MWB, obtained after the freeze-drying process.

Table 2. Sample IDs and the Microwave Irradiation Time Intervals

sample ID	irradiation time (s)
MWA[a]	10
MWB	20
MWC	30
MWD	40

[a] MWA was in the powder foam as 10 s irradiation time was not enough for the gelatinization of starch.

Morphology of Cassava Starch Foam. The morphology of the native cassava starch and cassava starch foam materials was examined using a scanning electron microscope (SEM) (ZEISS-evo 18, Jena, Germany). The samples were coated with gold and then examined at an acceleration potential of 5 kV.

X-ray Diffraction (XRD). The X-ray diffraction patterns of native cassava starch and microwaved cassava starch were obtained using a diffractometer (Rigaku Ultima IV, Texas, USA). The XRD spectra were recorded over a 2 theta (2θ) range of 5 to 45° with a continuous scan rate of 0.02°/min.

Thermogravimetric Analysis (TGA). The thermal degradation of native and microwaved cassava starch samples was evaluated using a TGA 5500 (TA instruments, New Castle, DE, USA). Platinum crucibles with 100 μL were used with a heating rate of 10 °C/min in the temperature range of 30−650 °C under N_2 gas with a flow rate of 10 mL/min. The thermal degradation temperature of the microwaved samples was calculated using TRIOS (4.4.0) software.

Figure 1. Photograph of the freeze-dried cassava starch foam material, MWB (microwaved for 20 s).

Solid-State Carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR). The Bruker Avance III 400 NMR (Billerica, MA, USA) spectrometer was used to obtain the ^{13}C CP-MAS solid-state NMR spectra. The ^{13}C CP-MAS-NMR spectra were recorded using a total suppression of spinning sidebands (TOSS) pulse sequence spun at a rate of 5 kHz in a 4 mm zirconia rotor. The chemical shifts were externally referenced to 176.03 ppm for the carbonyl carbon of glycine.

Fourier Transform Infrared Spectroscopy (FTIR)-ATR. FTIR spectra of native cassava starch and microwaved cassava starch samples were obtained on an FTIR Spectrum Two (PerkinElmer, Lantricant, UK) equipped with a deuterated triglycine sulfate (DTGS) detector. Spectra were collected in the wavenumber range of 500−4000 cm^{-1}. For each sample, the scan rate was maintained at 4 and taken at a resolution of 4 cm^{-1}.

Water Absorption of the Foam Materials. The water absorption of the foam materials was measured according to ASTM D570-98.[46] All samples were placed in an oven at 50 °C for 24 h. Next, the samples were immersed in distilled water for 2 h. After 2 h, the samples were removed from the water and wiped with a cloth and the weight was measured. Then, the water absorption (%) at 2 h of the foams was obtained. Again, the samples were immersed in water for further 22 h and weighed. Finally, the water absorption (%) of the foam materials was calculated at 2 and 24 h using the following eq 1.

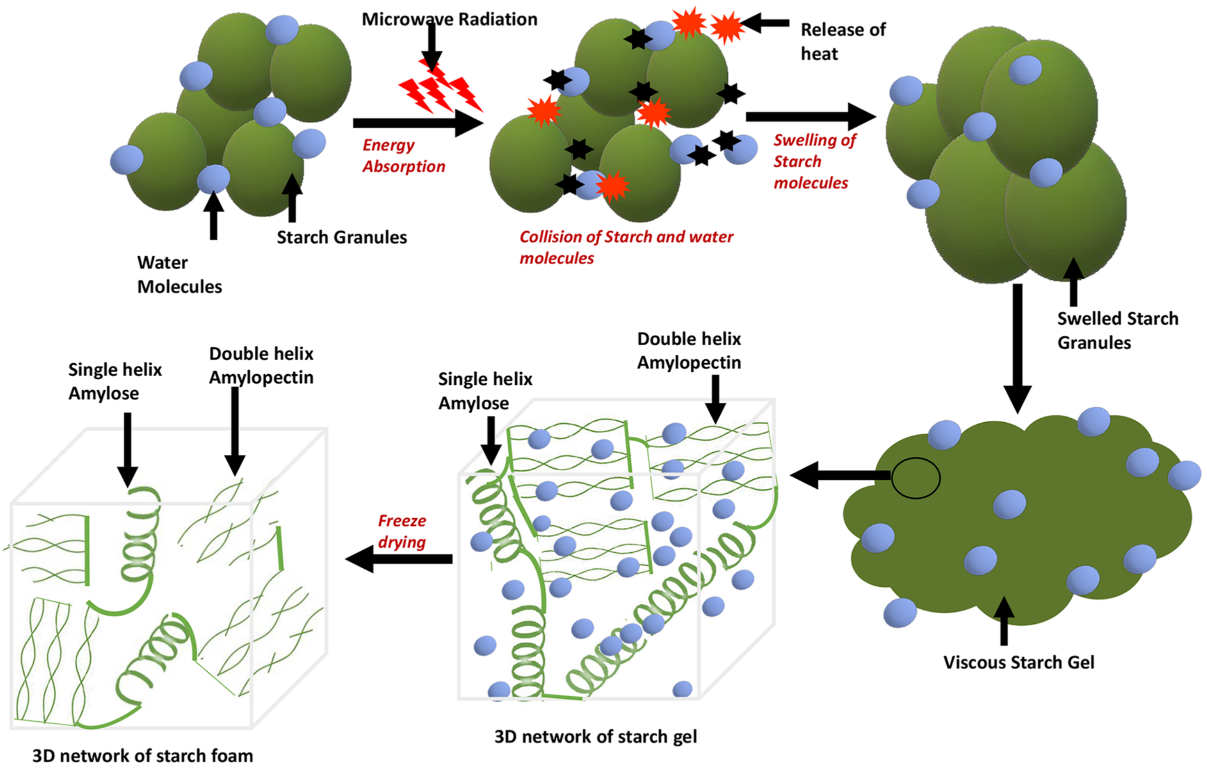
$$\text{water absorption (\%)at 2 and 24 h} = \frac{(W_1 - W_o)100}{W_o} \quad (1)$$

where W_o is the weight of the samples before being tested and W_1 represents the weight of the sample after soaking in water for 2 and 24 h.

Note that the MWA sample was not subjected to the water absorption test since it was in the powder form.

Compression Set Test of Cassava Starch-Based Foam Materials. The compression set test was carried out according to ASTM D395-14 (2014) with slight modifications.[47] Test specimens with a 13 mm diameter and thickness (T_o) were

Scheme 1. Schematic Representation of the Foam Formation Mechanism of Starch



measured. Then, the sample was compressed between two parallel compression plates for 72 h at RT until a constant strain was obtained. Next, the compression plates were removed, and the test sample was allowed to cool down to RT for 30 min before measuring the thickness (T_f). The compression set in % was calculated using eq 2. The reported results represent the average of three replicates in each sample.

$$\text{compression set (\%)} = \frac{(T_o - T_f)100}{(T_f - T_t)} \tag{2}$$

where T_t is the spacer thickness

Density Measurements of the Foam Materials. The density of the foam materials was measured according to ASTM D792-13.[48] Due to the water absorption of the foam materials, they were immersed in a non-hygroscopic solvent. Initially, the specific gravity at 23 °C of the liquid (d) was calculated using a pycnometer. The apparent mass of foams was recorded without a wire or sinker in air (a). Then, the samples were completely immersed in liquid at a temperature of 23 °C. After that, the mass was rerecorded (b). Next, the apparent mass of the totally immersed sinker and partially immersed wire (c) was recorded. Finally, the specific gravity (sp gr) and density of the foam materials were calculated using eqs 3 and 4, respectively.

$$\text{specific gravity of the foam materials at 23°C (sp gr)} = \frac{(a \times d)}{(a + c - b)} \tag{3}$$

$$\text{density of the foam materials at 23°C} = \text{sp gr} \times 997.5 \tag{4}$$

Biodegradability. The biodegradability test was carried out according to the aerobic compost environment test reported elsewhere.[49] The organic C and N contents of soil were measured using the Walkley−Black titration method and Kjeldahl method. According to the results, the compost consists of 14.07% and 1.10% organic C and N, respectively. The foams were cut into pieces of 2.0 × 2.0 cm dimensions and were buried inside the soil at a depth of 3 cm at 25 °C. During the experiment periods, water was sprayed daily to maintain the moisture content of the compost. The weights of the samples were measured after 15 days. The degradation rate was measured using the following eq 5:

$$\text{weight loss (\%)} = \frac{(B - B_o)100}{B_o} \tag{5}$$

where B_o and B are the weights of the foam materials before and after the test, respectively. The reported results represent the average of three replicates in each sample.

■ RESULTS AND DISCUSSION

Foam Formation Mechanism. The schematic representation of the foam formation mechanism of starch upon microwave and freeze-drying processes is depicted in Scheme 1. During the microwave treatment, the starch molecules absorb the microwave energy, inducing dipole rotation of the molecules. Due to the continuous rotation, starch molecules collide with each other, resulting in friction. Consequently, the heat generated through the molecular vibration and friction causes the swelling and increases the viscosity of starch granules, giving a highly viscous 3D polymeric gel. During this process, the water molecules in the mixture act as a plasticizer for starch,[50] converting native starch into thermoplastic starch (TPS). The freeze-drying (lyophilization) method provides dry foam materials from the high viscosity gel. As low pressure and heat are applied, the frozen gel undergoes sublimation, leaving

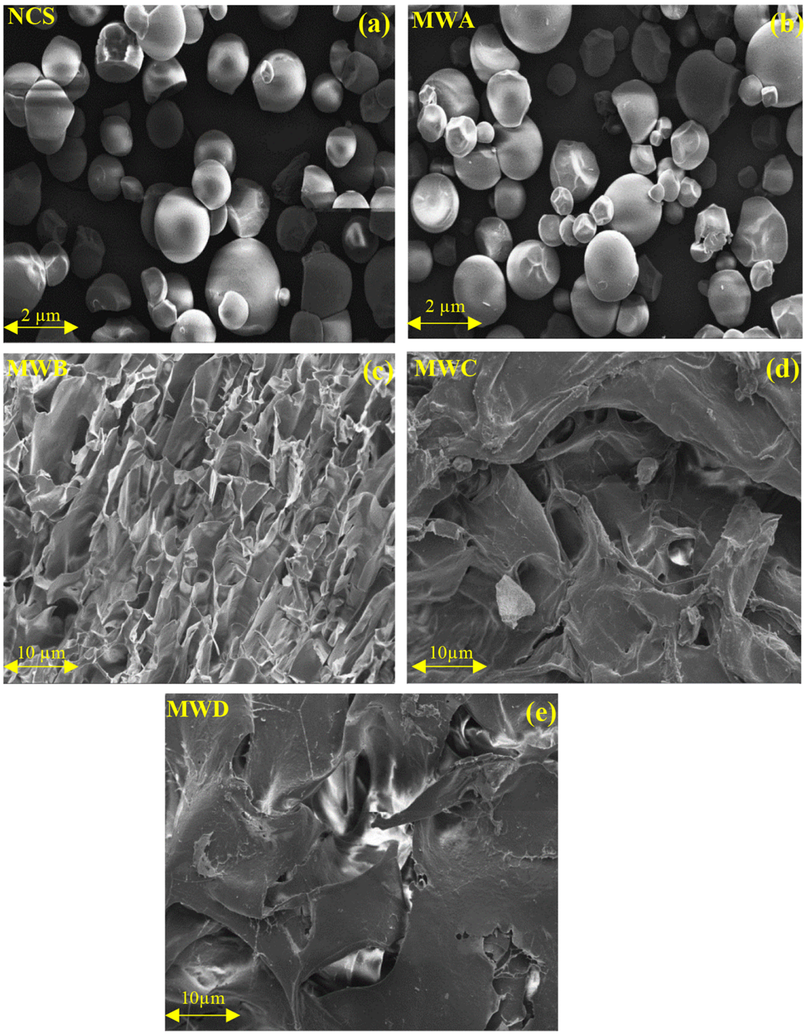


Figure 2. SEM images of the native cassava starch granules at different microwave irradiation times: (a) native cassava starch (NCS) (×1000 magnification), (b) microwaved cassava starch (MWA) at 10 s (×1000 magnification), (c) microwaved cassava starch (MWB) at 20 s (×2500 magnification), (d) microwaved cassava starch (MWC) at 30 s (×2500 magnification), and (e) microwaved cassava starch (MWD) at 40 s (×2500 magnification).

moisture from the gel.[51] The sublimation process facilitates the conversion of the frozen gel into a dry foam.

Morphology of the Foam Materials. The scanning electron microscopic (SEM) images of the native cassava starch granules and microwave-treated cassava starch at four different irradiation times are shown in Figure 2. As shown in Figure 2, the native cassava starch granules exhibit a regular oval- or sphere-like morphology before the microwave treatment, see Figure 2a. The sample MWA showed granular morphology similar to NCS (see Figure 2b). This is due to the lack of gelatinization of starch at 10 s microwave irradiation.

However, upon the microwave treatment, the morphology of starch changed into an exfoliated morphology with increasing irradiation time, see Figure 2c−e. It is also evident that the microwave radiation resulted in the swelling and disintegration of the starch granules (see Figure 2c−e). The presence of voids in the microwave-treated samples also depends on the degree of gelatinization that occurs during microwave heating.

X-ray Diffraction (XRD). Figure 3 shows the XRD profiles obtained for NCS, dual-modified cassava starch foam materials (MWA, MWB, MWC, and MWD) at four different microwave irradiation time intervals. According to the XRD spectra shown in Figure 3, both NCS and MWA samples exhibit five distinct XRD peaks at 15, 17, 18, 20, and 23°. These results are in agreement with the XRD patterns reported for NCS in the literature.[52,53] Nevertheless, as shown in XRD spectra, cassava starch is a semicrystalline material. However, a significant amount of changes in the crystal structure of cassava starch was observed during microwave and freeze-drying processes (see Figure 3). According to the XRD spectra, it is indicative that the crystalline nature of the starch decreases as the microwave time increases. The MWD sample exhibited the highest amorphous character of about 100%, attributed to the complete gelatinization.[54] Moreover, the XRD data suggest that the amorphous nature of the foam materials enhanced significantly with increasing irradiation time.

Thermogravimetric Analysis (TGA). The thermogravimetric (TG) and corresponding differential thermogravimetric (DTG) profiles of native cassava starch (a) and microwaved cassava starch foam materials (MWA, MWB, MWC, and MWD) are shown in Figure 4. The TG profiles of all samples studied showed two distinct weight loss regions in the temperature ranges of 30−100 °C and 330−400 °C. The former event represents the weight loss due to the evaporation of moisture present in the foam sample. The moisture content present in the foam samples is approximately 9% (w/w). The latter event is attributed to the thermal decomposition of starch with a weight loss of ~63% (w/w). The DTG profiles of all samples exhibit the degradation temperature of starch at 330 °C, suggesting that the thermal stability of starch remained the same during the microwave and subsequent freeze-drying treatments.

Solid-State ^{13}C Nuclear Magnetic Resonance (^{13}C-NMR). ^{13}C solid-state NMR can be used to determine the crystalline and non-crystalline properties of the starch granules after the microwave treatment. Figure 5 shows the ^{13}C CP/MAS NMR spectra of the NCS, MWA, MWB, MWC, and MWD samples. The NCS sample exhibited four distinct peaks at 91–106 ppm (C1), 78–86 ppm (C4), 66–78 ppm (C2, C3, C4, and C5), and 58–66 ppm (C6).[55] Typically, the C1 carbon peak arising from the glycosidic ring is used to identify the changes in the crystalline polymorph and the relative order of starch. Generally, the C1 band is a triplet for the A-type and a doublet for the B-type crystalline polymorph of starch.[55] As shown in Figure 5, the C1 peak of the NCS sample is a triplet, indicating A-type polymorphism. However, the C1 peak of all microwaved starch samples (MWA, MWB, MWC, and MWD) is a doublet, and the intensity of the peak is significantly increased compared to that of the NCS sample. This is due to the B-type polymorphism and the disordered structure.

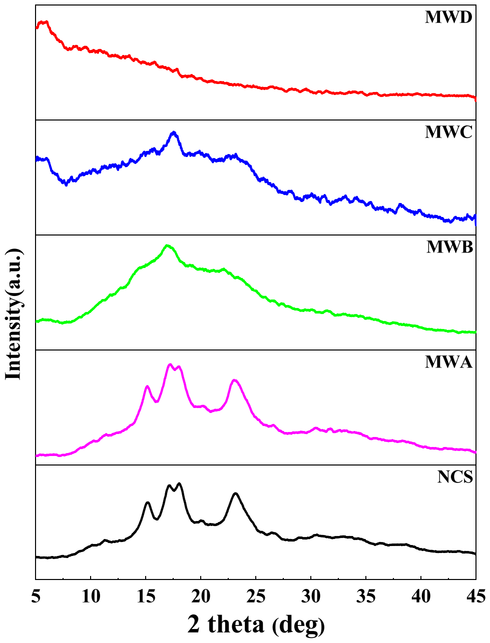


Figure 3. XRD diffractograms of native cassava starch (NCS) and cassava starch foam materials (MWA, MWB, MWC, and MWD) prepared at different microwave irradiation times (10, 20, 30, and 40 s).

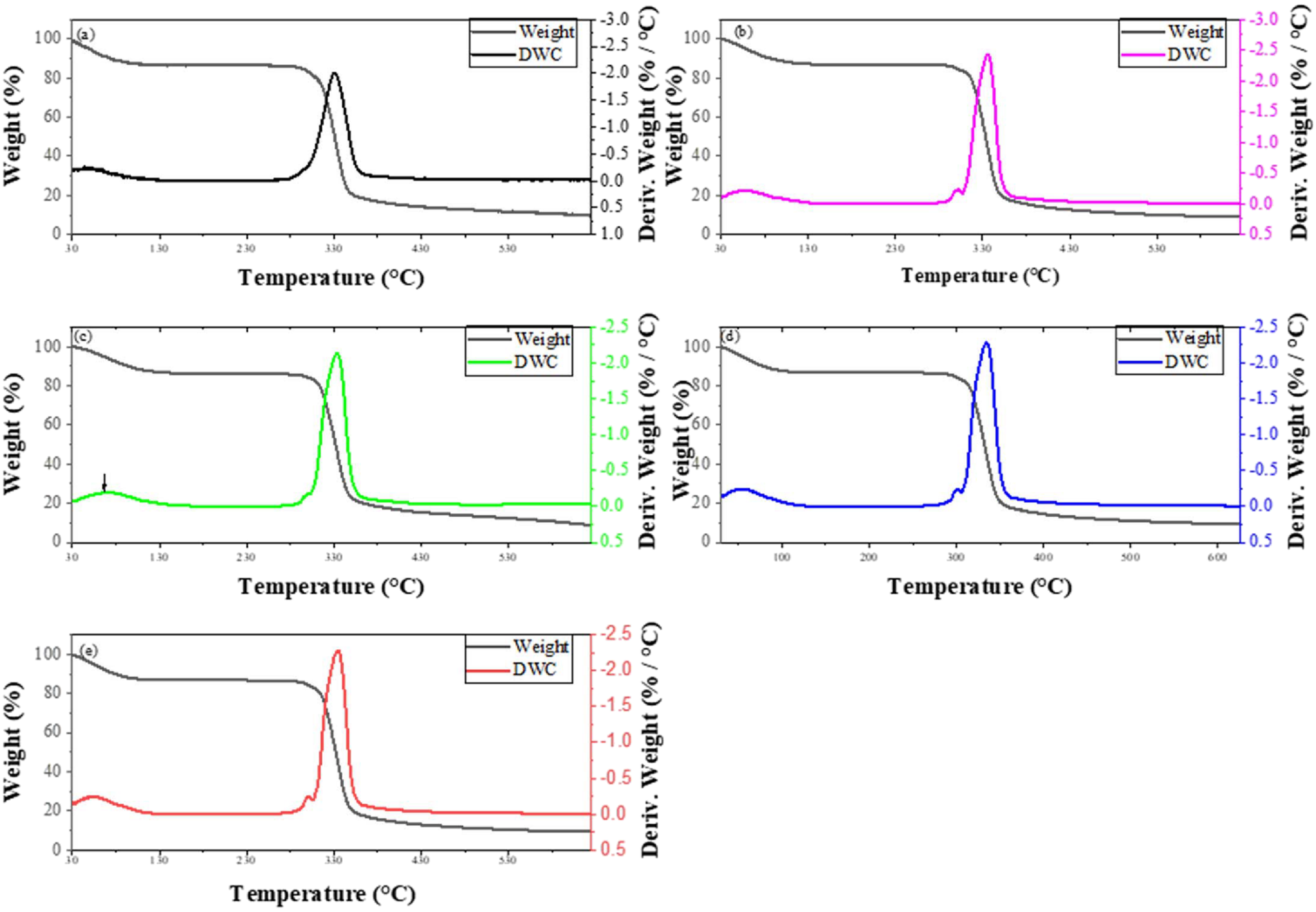


Figure 4. TG and DTG profiles of native cassava starch and microwaved cassava starch samples prepared at four different irradiation times: (a) native cassava starch (NCS), (b) microwaved cassava starch (MWA) at 10 s, (c) microwaved cassava starch (MWB) at 20 s, (d) microwaved cassava starch (MWC) at 30 s, and (e) microwaved cassava starch (MWD) at 40 s.

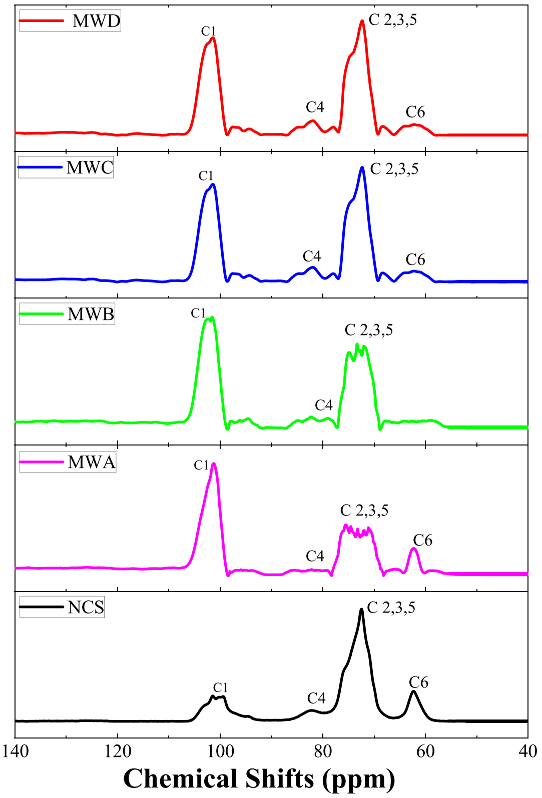


Figure 5. ^{13}C CP/MAS NMR spectra of NCS and microwaved cassava starch (MWA, MWB, MWC, and MWD) samples.

Therefore, the data suggest a decrease in the crystalline character of the starch foam materials upon microwave and freeze-drying treatments.

Fourier Transform Infrared (FTIR) Spectroscopy Studies. FTIR studies were conducted on native cassava starch and all microwaved cassava starch samples. Figure 6 shows the FTIR spectra of native (NCS) and microwaved cassava starch foam materials (MWA, MWB, MWC, and MWD). All samples exhibited identical vibrational bands and are consistent with the literature values reported for starch elsewhere.[56]

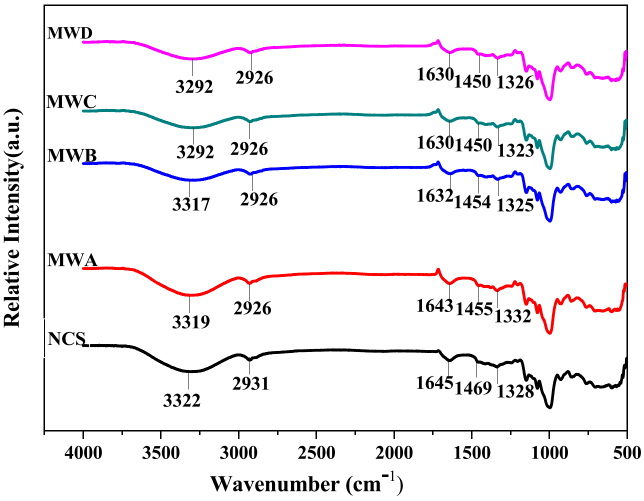


Figure 6. FTIR spectra of the NCS and cassava starch foam materials (MWA, MWB, MWC, and MWD) at different microwaved time periods (10, 20, 30, and 40 s).

The broad band at 3000−3600 cm^{-1} is attributed to the O−H stretching vibrations of absorbed water present in starch. The decrease in the intensity of this broad band with increasing microwave irradiation time is due to the loss of adsorbed water during freeze-drying.[55] Moreover, the peak at 2800−3000 cm^{-1} is assigned to the band of flexion of the CH_2 deformation.[56] Additionally, the peak at 1630−1643 cm^{-1} is assigned to the bending vibration of O−H bonds of absorbed water molecules in the amorphous region of cassava starch.[55] Apart from the above, the peak at 1323−1332 cm^{-1} corresponds to the C−O−H bending and C−O−C bending vibrations.[57] Moreover, the peak in the region of 1450−1469 cm^{-1} corresponds to the $-CH_2$ symmetric scissoring.[58] Our results indicate no distinct changes to the chemical structure of the starch material upon microwave and freeze-drying treatments.

Water Absorption (WA) Studies. Figure 7 illustrates the percentage of water absorption by the starch-based foam materials immersed in distilled water at 2 and 24 h. According to the data depicted in Figure 7, the MWD (40 s) sample showed the highest water uptake rate at 2 h, as compared to the water absorption capacities of MWC and MWD samples. The highest water uptake rates of 133.33% and 190% were observed for the MWD sample immersed in distilled water after 2 and 24 h. This could be attributed to the increased amorphous character and porosity of the foam materials upon microwave treatment, which agrees with the XRD results.

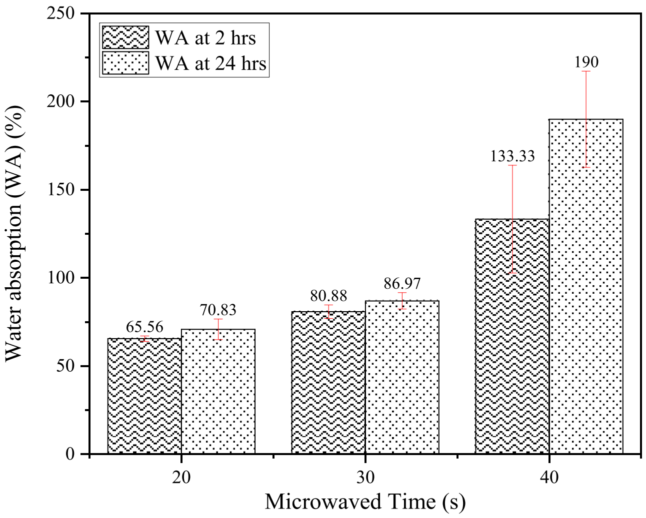


Figure 7. Percentage of water absorption of the foam materials with respect to microwaved treatment time (WA experiment conducted in samples immersed in distilled water for 2 and 24 h).

The MWB sample exhibits the lowest water absorption rate after 2 and 24 h. This could be attributed to the highly crystalline nature of the MWB sample compared to the other irradiated samples. Therefore, overall, the water absorption capacity of the foam materials has increased with the increment of the microwave treatment time. According to the literature, the percentage of water absorption of the compression molded starch foam is reported to be around 15.3%,[28] which is comparatively lower than the data observed in the present study. This significant increment in water absorption of foam materials in the current study can be explained by the enhanced porosity and amorphous structure of starch foam materials, as explained in the aforementioned XRD and SEM sections. Other biomaterials, including rice husk,[59] essential oil,[60] polylactic acid,[61] and sunflower protein,[62] have been employed to tailor the water adsorption capacity of starch. Also, the addition of these biomaterials resulted in increased flexural stress.[59]

Compression Set Values of the Foam Materials. The compression set provides a measurement of the ability of foam materials to retain their elastic properties at a specific temperature when subjected to prolonged compression. The lower the compression set value, the higher the elasticity of the material with minimal permanent deformation. Therefore, the elastomeric properties of the material are higher when the compression set value is low. Table 3 shows the compression set values of the three foam materials (MWB, MWC, and MWD). As can be seen from Table 3, all three samples exhibited a compression set value of over 0%, indicating that the thermoplastic elastomer never recovers, and the deformation is permanent. Therefore, compression set data reveal that the dual-modified cassava starch-based foam loses its thermoplastic elastomeric properties upon compression.

Table 3. Compression Set Values of Dual-Modified Cassava Starch-Based Foam Materials

sample name	compression set (%)
MWB	73.86 ± (0.18)
MWC	66.5 ± (0.11)
MWD	64.51 ± (0.41)

Compression set (%) data have been reported for different form materials. For instance, the dry-aged compression set was carried out for toluene diisocyanate (TDI) polyurethane foams according to ASTM D3574.[63] According to the data obtained at 90 °C, the samples showed around 90% of compression set, but at 80 °C, it was about 80%. Kmetty and coworkers conducted the compression set for cross-linked polyethylene foams, and their results exhibited 95% compression set after 24 h.[64] Furthermore, Park and Kim[65] prepared the ethylene vinyl acetate copolymer (EVA)/multiwalled carbon nanotube (MWCNT) nanocomposite foams and these foams showed around 55% of compression set value at 50 °C. In the present study, the maximum compression set value obtained for cassava starch-based foam is 73.86% and the value is comparatively better than previously reported data for TDI, cross-linked polyethylene, and EVA/MWCNT nanocomposite foams.[63−65] However, the elastomeric properties of starch-based foam materials can be further improved by using different additives and polymers such as resorcinol−formaldehyde, silane,[66] and poly(butylene succinate).[67]

Biodegradation of the Foam Materials. The biodegradation of the dual-modified cassava starch-based foam materials (MWB, MWC, and MWD) was tested in a compost environment over 15 days. The biodegradation was evaluated

Table 4. Comparison of the Density, Percent Weight Loss, and the Preparation Method of Starch-Based and Petroleum-Based Foam Materials Reported in the Literature

sample name	density (kg/m^3)	weight loss (%) per days	preparation method	additives	reference
potato starch/cellulose composite foams			compression molding	PLA	61
natural rubber/nanocellulose		50% (2 months)	solvent casting	natural rubber	68
cassava starch bio-foams	440	fragmentation within 8 weeks	compression molding	natural rubber cotton fiber	69
EPS (commercially available)	60	0% in 52 weeks			present study
microwaved foam TPS extruded pellets	114		extrusion, microwave treatment	hydrocerol BIH, NaCl, and $CaCl_2$	71
MWB	124.30	49.55 ± (0.29) in 15 days	microwave treatment, freeze-drying		present study
phenolic foam	127.30		microwave treatment	carbon nanoparticles	75
cassava starch-based foams	180	completely degraded in 8 weeks	hydraulic press	grape stalks, magnesium stearate, distilled water, and glycerol	70
sweet potato starch-based foams	200		mechanical thermopressing	oregano & thyme essential oil	60
potato starch-based foams	205		microwave treatment, air drying	chitosan	76
MWC	220.36	60.46 ± (0.03) in 15 days	microwave treatment, freeze-drying		present study
MWD	245.91	61.26 ± (0.06) in 15 days	microwave treatment, freeze-drying		present study
extruded TPS foam material (native wheat starch)	292		extrusion, microwave treatment	natural fibers (grape wastes, cardoon wastes, & barley straw fibers)	36
corn starch-based foam	330		extrusion	distilled water, calcium carbonate ($CaCO_3$), and polyvinyl alcohol (PVA)	77
cassava starch-based foams	340		baking process	polylactic acid (PLA), cellulose microfibers (CEL), and $CaCO_3$	78
cassava starch-based foams	580		hydraulic press	rice husk	59
bottom ash-based foams	610		microwave treatment		72
thermoplastic polyurethane	664		microwave treatment	carbon black	73
cassava starch foam	456 to 587		baking process	sunflower proteins and cellulose fibers	62

by determining the percent weight loss. In the biodegradation test, all foam materials showed a significant degradation within 15 days. Usually, in the compost environment, the water molecules diffuse into the cassava starch chain causing swelling and enhancing biodegradation via microbial activity.[56] The MWB sample showed a weight loss of approximately 50% after 15 days. Both MWC and MWD exhibited a weight loss of over 60% after 15 days due to the accelerating enzymatic degradation of the materials. Previously, in three separate studies (see Table 4), Abraham *et al.*[68] Sanhawong *et al.*[69] and Engel *et al.*[70] examined the biodegradation of cassava starch-based foams incorporated with natural rubber latex, cotton fiber, and grape stalks, respectively. They all reported a complete biodegradation of their thermoplastic cassava starch-based foams after 8 weeks. The dual-modified cassava starch-based foam materials prepared in this study show a much faster degradation behavior than other foam materials reported in the literature. This could be attributed to the increased amorphous and porous characteristics of the foam materials that facilitate the biotic degradation.

Density Measurements. Apart from biodegradability, the density of the foam materials also plays an important role in their practical applications. The density of the foam materials is inversely proportional to their expansion ability.[27] Usually, the density of EPS foam materials varies from 160 to 245 kg/m^3, and the density of commercially available EPS is around 60 kg/m^3.[18] In contrast, the density of starch-based foam materials is slightly higher. For instance, it is reported that the density values ranged around 114 kg/m^3 for the extrude microwaved starch foam materials[71] and the density value for compression-molded starch foam materials is reported to be 210 kg/m^3.[28] Densities of the dual-modified MWB, MWC, and MWD samples are 124, 220, and 245 kg/m^3, respectively. These values are considerably lower and comparable with the density values reported in the literature for starch foam materials.[36,59,62,69] For instance, the density values obtained from this study are lower than the values reported for baked and microwaved foam materials by Salgado *et al.*[62] Haq *et al.*[72] and Prociak *et al.*[73] Table 4 compares the density, percent weight loss, and preparation method of the starch and petroleum-based foam materials reported in the literature. Moreover, according to the data summarized in Table 4, it is evident that the combined treatment of both microwave and freeze-drying contributes to a significant reduction of the density of native cassava starch, which is around ~640 kg/m^3.[74] Starch foam materials prepared from only microwave treatment, extrusion, hot press, and baking exhibit higher densities than the dual-modified starch (see Table 4). Therefore, dual-modified cassava starch samples show relatively lower densities and higher degradation over 15 days, indicating their usability in lightweight and biodegradable packaging applications. The formation of pores during the microwave treatment was attributed to a reduction in the density and weight compared to extruded and compression-molded starch-based foam materials.

As shown in Table 4, dual-modified cassava starch foam materials show low density and high degradation compared to foam materials reported in the literature. As shown in Table 4, cassava starch exhibited a density of 124 kg/m^3 at a 20 s microwave time with a comparatively higher degradation rate (49.55%) at the concerned period. The cassava starch-based foam materials prepared in this study are more feasible for packaging applications with the addition of different additives as mentioned in Table 4. However, further studies need to be conducted to investigate and improve the mechanical, antimicrobial, and barrier properties of the cassava starch-based foam materials.

■ CONCLUSIONS

In this study, cassava starch-based foam materials were successfully prepared using a combination of microwave radiation and freeze-drying as a novel method. Cassava starch-based foam materials were characterized using SEM, XRD, TGA,^{13}C-NMR, and FTIR. The amorphous structure and porosity of the cassava starch-based foams enhanced upon the dual treatment. The dual-modified cassava starch-based foam materials showed relatively higher water adsorption capacities with increasing amorphous character. All the cassava starch-based foam materials showed significant degradation of 50% after 15 days. The lowest density value of 124 kg/m^3 was observed for the sample irradiated for 20 s. Although the freeze-drying method is commonly used in the food and pharmaceutical industries, it is a high cost and energy-extensive process. Therefore, developing a low-cost, energy-efficient, and scaled-up freeze-drying process is imperative. Moreover, further investigations are required to investigate and improve the mechanical, antimicrobial, and barrier properties of the cassava starch-based foam materials. Owing to their easy preparation, non-toxicity, biodegradability, and lightweight, dual-modified cassava starch-based foam materials could be applied in sustainable packing applications.

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