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A comparative study of some properties of cassava and tree cassava starch films

P.C. Belibi[a,b], T.J. Daou[c], J.M.B. Ndjaka[a], B. Nsom[d], L. Michelin[c], B. Durand[b]

[a] *Département de Physique, Faculté des Sciences, Université de Yaoundé I. B.P. 337 Yaoundé – Cameroun*
[b] *LPMT – ENSISA, Université de Haute – Alsace. 2, rue des Frères Lumière 68093 Mulhouse - France*
[c] *Equipe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M), UMR CNRS 7361-UHA, 3B, rue Alfred Werner 68093 Mulhouse Cedex, France*
[d] *Université de Bretagne Occidentale. 3 Rue des Archives 29238 Brest cedex 3 – France*

Abstract

Cassava and tree cassava starch films plasticized with glycerol were produced by casting method. Different glycerol contents (30, 35, 40 and 45 wt. % on starch dry basis) were used and the resulting films were fully characterized. Their water barrier and mechanical properties were compared. While increasing glycerol concentration, moisture content, water solubility, water vapour permeability, tensile strength, percent elongation at break and Young's modulus decreased for both cassava and tree cassava films. Tree cassava films presented better values of water vapour permeability, water solubility and percent elongation at break compared to those of cassava films, regardless of the glycerol content.

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Keywords: cassava film; moisture content; water solublity; water vapor permeability; mechanical properties.

1. Introduction

Cassava (*M. Esculenta*) is an important food crop in the tropics. However, despite its high production level (Nigeria is the world-leading producer of cassava [1]), supply has not matched demand; this is because cassava serves both as a staple and an industrial raw material [2]. Cassava starch has been extensively used to produce biodegradable films [3 - 8] which are described as isotropic, odorless, tasteless, colorless, non-toxic and biologically degradable [9]. To avoid competition between food and industry, there is need to expand the production of other carbohydrate-rich crops to provide an alternative substitute of cassava in food and industry. Tree cassava (*M. Glaziovii*), a wild species of cassava, can be produced on large scale in Cameroon with good yield of starch in its tubers. Starch based films properties depend on various parameters such as the botanic origin of starch, the respective content of amylose and amylopectin, the crystallinity, the type and content of the plasticizer and the conditions of storage such as relative humidity [10].

* Corresponding author. Tel.: +33-89336739; fax: +33-89336885.
E-mail address: jean.daou@uha.fr

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Several publications reported the water barrier and the mechanical properties of cassava starch based films [3, 6, 7]. The aim of this study is to compare the water barrier and the mechanical properties of cassava and tree cassava starch based films as a function of glycerol content, the plasticizer used.

1. Materials

1.1. Starch extraction

Starch was extracted from cassava and tree cassava tubers, grown in Cameroon. For each specie, the tubers were washed, peeled and grated. The resulting paste was mixed with water and the solution was filtered on a clean cloth. The collected filtrate was then allowed to stand for 6 hours followed by the removal of the supernatant. The white precipitate (starch) was then recovered, sun-dried and stored in polyethylene bags at room temperature. The moisture content, expressed as g of water per 100 g of dry starch (weight percent), was determined by drying starch to constant weight at 110°C. This moisture content was found to be (13.8 ± 1.0) wt% and (12.9 ± 0.8) wt% for cassava and tree cassava starches respectively. Elemental analysis were performed by X-ray wavelength fluorescence (XRF) with a MagiX Philips (2.4 kW) on samples packed into pellet. On dry basis, carbohydrate represented (99.62 ± 0.05) wt% and (99.36 ± 0.04) wt% of the chemical composition of cassava starch and tree cassava starch respectively and this was consistent with the literature [7, 11].

1.2. Film preparation

The method of preparation was adapted from V.P Cyras et *al*. [12] and P.C Araujo-Farro et *al*. [13]. Native cassava starch or native tree cassava starch (5 g/100 g total film solution) was dispersed in distilled water with the corresponding content of glycerol (30, 35, 40 and 45 wt% on starch dry basis) at room temperature and stirred for 1 h on a magnetic stirrer (250 rpm). The mixture was then heated to (80 ± 1) °C in a thermal bath under constant stirring for 15 min, the heating continued for another 15 min at 80°C. Then the films were obtained by casting, pouring the hot suspension into rectangular moulds (12.4 x 18.4 cm^2 bottom area). These moulds were left at room temperature for at least 4 h to allow bubbles to dissipate and then dried in an oven with air circulation, at 30°C for 50 h. The dry films were removed from the moulds and stored at controlled conditions (21°C and 63% of relative humidity) for at least 48 h before measurements.

2. Characterization

2.1. Thickness of the films

The thickness of cassava and tree cassava biodegradable films was determined using a flat parallel surface manual micrometer (Mitutoyo, model 102 – 707, Japan, precision 0.001 mm) by performing at least twelve random measurements for each film. The average value for each film was used to calculate the tensile properties and the water vapor permeability.

2.2. Film moisture content

Film moisture content (MC) was determined gravimetrically by drying small pieces of film in an oven with air circulation at 110°C for 6 h. Samples were analyzed in triplicate and results were expressed as g of water per 100 g of dried film.

2.3. Film solubility in water

Film solubility in water (WS) was defined as the content of dry matter solubilized after 24 h of immersion. Water solubility of each film was measured according to the method described by Rhim at *al.* [14]. Three randomly selected samples from each film were first dried at 110°C for 6 h to determine their initial dry weights. Then, they were placed in a 80-mL beaker containing 40 mL of distilled water. Beakers were covered with parafilm and stored at room temperature for 24 h with occasional gentle stirring. The weight of undissolved dry matter was determined by removing the film pieces from the beakers, gently rinsing them with distilled water, and oven-drying them (110°C, 6 h). The weight of water-soluble matter was calculated by subtracting the weight of undissolved dry matter from the weight of initial dry matter and expressed as a percentage of the initial dry matter content.

2.4. Water vapor permeability

The gravimetric method based on ASTM E96/E96M-05 [15] was used to determine water vapor permeability which was reported as the rate of water vapor transmission through a unit area of flat material of unit thickness induced by unit vapor pressure difference between two surfaces under specific condition of 100% of relative humidity. Test cups were made of polymethylmethacrylate with 2.8 cm internal diameter and 3.4 cm height with an exposed film area of 6.15 cm^2. Cup walls were sufficiently thick enough to make cups impermeable to water vapor. Each film sample, without pinholes neither defects, was sealed with parafilm over a circular opening of the test cup, which was stored, at room temperature, in a desiccator. To maintain 100% of relative humidity (RH) gradient across the film, silica gel was placed inside the cup and distilled water was used in the desiccator. The RH inside the cup was always lower than the outside, and the water vapor transferred through the film and absorbed by the desiccant was determined from the weight gain of the silica gel recorded at various times. Steady state conditions were assumed to be reached after 2 h. The cups were weighted initially, at 2 h intervals for the first 8 hours. Changes in the weight of the cups were recorded to the nearest 0.0001 g and plotted as a function of time. The slope ω (g/s) of each line was calculated by linear regression ($r^2 > 0.99$). All tests were conducted in triplicate. The WVP of the film was determined as follows:

$$WVP = (\omega * e) / [A * P(R_1 - R_2)]$$

wherein:

WVP is the water vapor permeability (g/m.s.Pa); e is the average film thickness (m); A is the exposed film area (m^2); P is the saturation vapor pressure of water (Pa) at the test temperature (21°C); R_1 is the RH in the desiccators and R_2 the RH in the cup test.

2.5. Mechanical test

Mechanical property measurements, tensile strength and percentage elongation at break and Young's modulus, were obtained using a dynamometer MTS-20/M (Adamel Lhomargy, France), with a 100 N load cell and a crosshead speed of 50 mm/min (ISO 527-1996 standard). The films were cut in strips (90 x 15 mm^2) which were clamped between tensile grips; the force (N) and the deformation (mm) were recorded during extension. For each test seven samples were analyzed.

3. Results and discussion

3.1. Film thickness

Films obtained from 5 wt% cassava and tree cassava starch dispersions plasticized with glycerol were translucent (Fig. 1). The thickness of the films ranged from (193.8 ± 15.0) µm to (210.0 ± 14.9) µm for cassava starch based films and from (177.4 ± 12.6) µm to (192.9 ± 13.7) µm for tree cassava starch based

films. These thickness differences is may be due to the fact that the film-forming solution was spread manually in the mould.

Fig. 1 : (a) Cassava starch based film image ; (b) Tree cassava starch based film image

3.2. Moisture content

Moisture contents of cassava and tree cassava starch biodegradable films are shown in table 1, values ranged from (11.8 ± 2.2) % to (41.1 ± 1.5) % for cassava films and from (15.3 ± 0.3) % to (24.8 ± 1.5) % (g water/100 g dried film). At low glycerol content (30 wt%), MC of cassava films is lower than that of tree cassava films while at high glycerol content, (45 wt%), MC of tree cassava films is lower than that of cassava films.

Table 1. Moisture contents of cassava and tree cassava films, as a function of glycerol content

Glycerol content (wt%)	*M. Esculernta* MC (%)	*M. Glaziovii* MC (%)
30	11.8 (0.2)*	15.3 (0.3)*
35	22.2 (1.9)	21.5 (1.3)
40	25.7 (0.9)	24.8 (1.5)
45	41.1 (1.5)	23.9 (2.8)

*The numbers in parentheses represent the standard deviation

3.3. Water solubility

Water solubilities of cassava and tree cassava biodegradable films are shown in table 2, values ranged from (23.0 ± 0.5) % to (32.1 ± 1.5) % for cassava films and from (19.3 ± 0.5) % to (24.7 ± 0.7) for tree cassava films. The increase of glycerol in the formulation of the film promoted solubility thereof in water; this is more marked with cassava films. Regardless of the glycerol content, tree cassava films presented better WS values.

Table 2. Water solubilities of cassava and tree cassava films, as a function of glycerol content

Glycerol content (wt%)	*M. Esculenta* WS (%)	*M. Glaziovii* WS (%)
30	23.0 (0.5)*	19.3 (0.5)*
35	26.0 (1.8)	24.7 (0.7)
40	29.2 (1.6)	19.6 (0.7)
45	32.1 (1.5)	23.1 (1.3)

*The numbers in parentheses represent the standard deviation

3.4. Water vapor permeability

Water vapor permeabilities of cassava and tree cassava films are shown in table 3, values ranged from (3.28 ± 0.33) x 10^{-10} g/s.m.Pa to (4.47 ± 0.44) x 10^{-10} g/s.m.Pa for cassava films and from (1.97 ± 0.03) x 10^{-10} g/s.m.Pa to (3.86 ± 0.22) x 10^{-10} g/s.m.Pa for tree cassava films. The increase of glycerol content increased water vapor permeability of the films as it can be observed in table 3. Glycerol is a relatively small hydrophilic molecule, which can be inserted between adjacent polymeric chain, decreasing intermolecular attractions and increasing molecular mobility, which facilitates the migration of water vapor molecules. Similar results were reported in literature [16]. Regardless of the glycerol content, tree cassava films presented better WVP values.

Table 3. Water vapor permeability of cassava and tree cassava films, as a function of glycerol content

Glycerol content (wt%)	*M. Esculenta* WVP (x 10^{-10}g/s.m.Pa)	*M. Glaziovii* WVP (x 10^{-10}g/s.m.Pa)
30	3.28 (0.33)*	1.97 (0.03)*
35	4.22 (0.11)	2.83 (0.17)
40	4.39 (0.14)	3.39 (0.14)
45	4.47 (0.44)	3.86 (0.22)

*The numbers in parentheses represent the standard deviation

3.5. Mechanical test

Tensile strength (σ), percent elongation at break (ε) and Young's modulus (E) of cassava and tree cassava films, as a function of glycerol content, are summarized in table 4. It is obvious that σ, ε and E of both cassava and tree cassava films are strongly influenced by glycerol content.

While increasing the amount of glycerol, σ and E were decreased. When glycerol was incorporated, some structural modifications occurred in starch network, the film matrix became less dense and under stress, movements of polymers chains were facilitated, improving film flexibility [7]. Considering the percent elongation at break of both films, it was found that the percent elongation values also decreased by

increasing the glycerol content. This observation did not mean that the starch films showed more brittle character. In contrast, the starch films were more ductile resulting in easy breakage [17]. For a given glycerol content, σ and E values were respectively similar for both cassava and tree cassava films while the ε value of tree cassava films was practically twice the ε value of cassava films.

Table 4. Mechanical properties of cassava and tree cassava films, as a function of glycerol content.

	M.Esculenta			*M. Glaziovii*		
Glycerol content	σ (MPa)	ε (%)	E (MPa)	σ (MPa)	ε (%)	E (MPa)
30	2.4 (0.2)*	49.4 (3.4)*	46.3 (4.6)*	2.2 (0.1)*	84.0 (8.6)*	33.0 (3.2)*
35	2.1 (0.2)	41.9 (3.2)	32.2 (3.7)	2.1 (0.1)	72.0 (6.9)	17.0 (1.5)
40	1.4 (0.1)	28.8 (2.4)	14.7 (1.2)	1.6 (0.1)	68.6 (6.4)	14.5 (2.2)
45	1.2 (0.2)	26.8 (4.0)	14.0 (1.1)	1.5 (0.1)	54.8 (3.8)	10.9 (0.5)

*The numbers in parentheses represent the standard deviation

3.6. Conclusion

Some properties of cassava and tree cassava films were studied and compared. Water barrier and mechanical properties of these films were strongly influenced by glycerol content. With increasing glycerol concentration, moisture content, water solubility and water vapor permeability of both cassava and tree cassava films increased while tensile strength, percent elongation and Young's modulus decreased. Tree cassava films presented better WS and WVP values compared to those of cassava films regardless of the glycerol content.

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