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Biogradable Starch Film from Cassava, Corn, Potato and Yam

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Abstract

Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules each typically containing several million amylopectin molecules accompanied by a much larger number of smaller amylose molecules. Starch films were prepared from starch extracted from cassava, corn, potato and yam with and without plasticizers to evaluate the effects of the type and quantity of plasticizer on the mechanical properties of the starch films obtained. Ubbelohde viscometer was used to determine the intrinsic viscosity and molecular weight of the prepared films in dimethylsulfoxide (DMSO)/water solution (90%/10% v/v). The molecular weights of the films were found to range from $2.70 \times 10^{13} – 2.14 \times 10^{17}$ for films prepared from corn starch, $2.86 \times 10^{10} – 1.01 \times 10^{17}$ for films prepared from yam starch, 2.69×10^{13} - 3.97×10^{17} for films prepared from potato starch and 4.15×10^{6} - 4.05×10^{8} for films prepared from cassava starch. The molecular weights of the films were found to decrease with increase in the plasticizer content because the bonds between starch-starch molecules were replaced with the bond between starch-water molecules. This led to the reduction in the chain length of both the amylopectin and amylose, and hence reduction in the molecular weight average. Amylose and amylopectin molecules contribute to mechanical properties and hygroscopic properties of starch. The effects of plasticizer on mechanical properties of film prepared from corn starch and yam starch were investigated at six levels of plasticizer content. The tensile strength of the films prepared from corn starch ranged from 0.10MPa - 5.20MPa, 0.05MPa - 5.10MPa for films prepared from yam starch, 0.09MPa - 5.74MPa for films prepared from potato starch and 0.51MPa – 5.33MPa for films prepared from cassava starch. The value of Young's modulus was found to range from 0.39MPa -104.06MPa for films prepared from corn starch, 0.33MPa - 49.32MPa for films prepared from yam starch, 0.36MPa – 191.33MPa and 3.14MPa – 97.5MPa for films prepared from cassava starch. The tensile strength of films was influenced by the type and the content of plasticizer used.Generally, the Young's modulus and the tensile strength of the films decreased with increase in plasticizers content, with concurrent increase in elongation at break and tensile strain of the films due to increase in ductility of the films. Glycerol exhibited more plasticizing effect on both starches than sucrose due to the hygroscopic or hydrophilic nature of glycerol.

Keywords: biodegradable, starch films.

Introduction

Polymers are large molecules produced from the combination of many constitutional repeating units of small molecular weight called monomers. Polymer is characterized by high relative molecular weight which dictates its properties. The properties of polymer also depend on the monomer(s) from which it is formed. Biopolymer films and coatings produced from polysaccharides, protein, and lipids, formulated either with one or more components such as plasticizers, cross-linked agents, salt, lignin etc, have potential to replace non-biodegradable polymers in the market due to their biodegradability (Garcia et al., 1999). The bio-plastics found in the market are made mainly from starch. Starch-based bio-plastics represent about 85%-90% of the market Bio-plastics (Bastioli, 2000). Among starch bio-plastics are those manufactured with native or slightly modified starch, either isolated or blended with natural or synthetic molecules (Oliver and Luc, 2012). The use of starch in the manufacture of bio-plastics began in the 70's (Curvelo et al., 2001). Among its advantages starch is cheap, abundant and renewable. Bio-plastic is found in several forms depending on the origin of its raw materials (Lawter and Fischer, 2001).

Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules each typically containing several million amylopectin molecules accompanied by a much larger number of smaller amylose molecules. By far the largest source of starch is corn (maize) with other commonly used sources being wheat, potato, tapioca and rice. Amylopectin (without amylose) can be isolated from 'waxy' maize starch whereas amylose (without amylopectin) is best isolated after specifically hydrolyzing the amylopectin with pullulanase. Starch is a white, odorless, tasteless, carbohydrate powder. It plays a vital role in the biochemistry of both plants and animals and has important commercial uses. In green plants starch is produced by photosynthesis. By treatment with hot water, starch granules have been shown to consist of at least two components, known as amylopectin and amylose. Amylopectin is a branched glucose polymer; amylose is a linear glucose polymer. Starch is widely used for sizing paper and textiles, for stiffening laundered fabrics, in the manufacture of food products, and in making dextrin. In addition to its other uses, cornstarch is a source of corn syrup, of which large quantities are used in making table syrup, ice cream, and other confectionaries. Corn sugar (glucose) is also derived from cornstarch (Martins, 2012).

The thermoplastic-like starch (TPS) is a relatively new concept. Today, it is one of the main research hints for manufacturing of biodegradable materials (Curvelo et al., 2001).Starch is not a real thermo-plastic, but in the presence of a plasticizer (water, glycerol, sorbitol, etc), high temperatures (90°C-180°C) and shearing, it melts and fluidizes, enabling its use in injection, extrusion and blowing equipment like synthetic plastics (Lourdin et al., 1999).Water in the starch acts as a plasticizer and also as an agent that breaks the structure of the native granules, breaking the bonds of hydrogen chains. Addition of plasticizer such as polyols influences the atmospheric conditions in the sorption and desorption mechanisms and would allow melting at a temperature lower than that of the starch degradation (Averous, 2002).

According to Levesque, 2001, the use of starch and its derivatives as the only component of biodegradable materials was object of a number of surveys. Techniques on starch plasticization were developed to allow the manufacturing of objects (usually massive objects), which, however, evolve rapidly due to the atmospheric humidity. To plasticize starch, it is necessary to use a large quantity of plasticizers with hydrophilic properties. The plasticizer, such as glycerol and sorbitol with hydrophilic properties, in a ratio ranging from 20% to 40% to the starch weight could be used. The plasticizer content is directly related to the mechanical properties and glass transition of the material (Lourdin et al., 1999).

A key part of the picture of starch functionality includes data on the unassociated molecular structure of all starch polymers. The molecular weight of polymer is commonly determined by size-exclusion chromatography (SEC). However, this measurement for starch is challenging because of calibration standard usually required. High pressure size-exclusion chromatography (HPSEC) instrumentation equipped with both muiti-angle laser light-scattering (MALLS) instrumentation and differential refractometer (RI) have been used routinely to determine the molecular weight of polymers without the use of standards. This technique makes starch molecular weight measurement possible but to obtain the accurate molecular weight of amylopectin or amylose or both by this technique, the complete dissolution of amylopectin and amylose is necessary (Yokoyama et al., 1998). Di-methyl-sulfoxide (DMSO) is the most frequently used polar solvent for size exclusion chromatography analysis (Jackson, 1991). DMSO disperses starch acting as a hydrogen bond acceptor, disrupting inter-molecular and intra-molecular starch-starch and starch-water hydrogen bonds, and replaces hydroxyl-hydroxyl hydrogen bond with DMSO-starch hydrogen bonds (French, 1984). High temperature and high pH increases the solubility of many cereal starches in aqueous solvent, but may result in molecular size reduction resulting from degradation, de-polymerization, or oxidation (Yokoyama et al., 1998). To increase the solubility of starch in DMSO, addition of small amounts of water or low molecular weight electrolytes could be used (Yokoyama et al., 1998; Chang et al., 1987; Erlander et al., 1968 and Meehan, 1995). The objectives of this study were to evaluate the effects of the type and quantity of plasticizer on the mechanical properties of the starch films prepared from cassava, corn, potato and yam.

Experimental

Methods.

1. Extraction of starch.

The peeled yam tubers, potato tubers, cassava tubers and the white maize grains were blended separately into pastes. The pastes were mixed with distilled water and then sieved on sieving cloth to obtain starch slurries of the four starches. The starches were dried to constant weight in the oven at 60°C. The dried starches were grinded to powdery form.

2. Preparation of starch films.

7g each of homogenized starch powder was weighed into 400ml beaker, 10ml of distilled water and 5ml of 0.1M hydrochloric acid were added. The mixture was heated slowly on hot plate to gentle boiling with continuous stirring for 10minutes. 0.1M sodium hydroxide solution was added drop-wise to the hot product to neutralize the added acid, and tested with blue litmus paper until the solution was made basic. The resulting hot liquid was poured on labeled white tiles and left for two days to solidify into thin film. The above procedures were repeated with different mass percent of glycerol (22%, 36%, 46%, 53% and 59%) and different mass percent of sucrose (22%, 36%, 46%, 53% and 59%) for four types of starch used. Each preparation was made in triplicate.

3. Determination of intrinsic viscosity molecular weight of starch films.

Viscometric determination of intrinsic viscosity molecular weight was carried out on each sample film using Ubbelohde viscometer(50ml) after complete dispersion and solubilization of 0.1g of each sample film in dimethysulphoxide (DMSO)/water solvent(90%/10% v/v).The Ubbelohde viscometer used was calibrated using 20% sucrose solution and distilled water. For each sample film, 0.1g of each sample film was dissolved in small volume of 90% DMSO-water solution and then made up to the mark in 50ml standard flask and kept in a constant temperature water bath at 25°C. The polymer solution was poured into the calibrated Ubbelohde viscometer, and sucked up to the upper mark on the viscometer arm. The time taken for the meniscus of the polymer solution of the film to fall from upper mark to lower mark was monitored with the stop watch. Serial dilution was used to obtain other concentrations of each film ranging from 0.01-0.05g/ml from the prepared polymer solution and the diluted solutions of each film were kept in constant temperature water bath at 25°C. The viscosity of each polymer solution was calculated using equation (1). The intrinsic viscosity of each polymer solution was obtained by extrapolating the viscosity (η)/concentration(C) against concentration(C) curve to zero concentration. The intrinsic viscosity of each sample was used in Mark-Houwink equation (2) to obtain weight average molecular weight (M_w).

$$\eta/dt = A + B/t^2 \qquad \text{Equation(1)}$$

Where A and B are constants obtained from calibration, d is the density of the solvent, t is the time of flow and η is the reduced viscosity.

$$[\eta] = K M^{\alpha}_{w} \qquad \text{Equation (2)}$$

Where [η] is the intrinsic viscosity, K is a constant (0.59×10^{-3}), and M_w is weight average molecular weight.

4. Mechanical properties of prepared starch films.

Tensile strength measurement was used to quantify the mechanical strength of the starch films produced. Thin strip of film was cut out from each solidified film on white tile with razor blade. The width and thickness of each strip were determined using the digital vernier calipers; the dimension of each film was used to calculate the cross-sectional area of each strip of film. The two ends of the strip were secured with two C-clamps, one end was hung on the suspended spring balance supported with retord stand and long ruler. The other clamp was held and pulled gently and slowly (1N per second) to obtain a maximum force required to break the film along its cross-sectional area. The increase in length of the strip (extension) was measured.The value of the maximum force and the cross-sectional area for each strip were used to compute tensile strength (MPa) using equation (3). The tensile strain was determined from the original length of each strip and the extension produced during force application using equation (4). Young's Modulus (MPa) was determined from tensile strength and tensile strain for each film using equation (5).

$$\text{Tensile strength} = \frac{\text{Force}}{\text{Cross sectional area}} \qquad \text{Equation (3)}$$

$$\text{Tensile strain} = \frac{\text{Elongation or extension}}{\text{Original length}} \qquad \text{Equation (4)}$$

$$\text{Young's Modulus} = \frac{\text{Tensile stress}}{\text{Tensile strain.}} \qquad \text{Equation (5)}$$

Results and Discussions

Effect of plasticizers on average molecular weight of starch films.

The results obtained in Tables 1 and 2 show the decrease in viscosity average molecular weight with increase in plasticizer content for the four starches. The films without plasticizer showed the highest molecular weight average values in all the starches. The above observation could be explained based on the effect of plasticizers content. The bonds between starch-starch molecules were replaced by the bond between starch-water molecules. This led to the reduction in the chain length of both the amylopectin and amylose, and hence reduction in the molecular weight average. The starch films without plasticizer showed the highest values of average molecular weight due the presence of longer amylose and amylopectin molecules. However, the presence of plasticizer such as sucrose and glycerol used in this work interrupted with the polymer-polymer chains linkages by forming hydrogen bond between the of polymer thereby reducing the compactness of the plasticized film prepared. Similarly, the molecular weight average values for starch films plasticized with sucrose were higher than that of the corresponding starch films plasticized with glycerol due to hygroscopic nature of glycerol.

According to Fang et al., 2006, the molecular weight average of amylopectin from waxy rice and non-waxy rice were 58.8×10^8 and 26.8×10^8 respectively using high pressure size exclusion chromatography (HPSEC). Using sedimentation field flow fractionation combined with multi-angle laser light-scattering detector (MALLS), Hanselmann et al., 1995 reported apparent average molecular weights for waxy maize amylopectin molecules within a range of $37 – 360 \times 10^6$. The values of molecular weight average obtained in Tables 1 and 2 were almost double of that of amylopectin fraction only. This was due to the fact that the values obtained in this study were for amylose-amylopectin present in the films.

TABLE 1 - Effect of glycerol content on the Viscosity average molecular weight of starch films prepared from cassava, corn, potato and yam.

Glycerol Content (%)	Average Molecular Weight			
	Potato	Corn	Cassava	Yam
0%	3.97 × 10^{17}	2.14 x 10^{17}	3.3 x 10^{8}	1.01 x 10^{17}
22%	4.44 × 10^{16}	2.49 x 10^{16}	2.1 x 10^{8}	2.09 x 10^{15}
36%	1.21 × 10^{16}	6.81 x 10^{15}	7.35 x 10^{7}	1.50 x 10^{14}
46%	1.23 × 10^{15}	7.11 x 10^{14}	1.03 x 10^{7}	5.70 x 10^{12}
53%	5.06 × 10^{13}	2.70 x 10^{13}	-	2.39 x 10^{10}
59%	2.69 × 10^{13}	-	-	-

TABLE 2 - Effect of sucrose content on the Viscosity average molecular weight of starch films prepared from cassava, corn, potato and yam.

Sucrose Content. (%)	Viscosity Average Molecular Weight			
	Potato	Corn	Cassava	Yam
0%	3.97 × 10^{17}	2.14 x 10^{17}	3.3 x 10^{8}	1.01 x 10^{17}
22%	1.44 × 10^{17}	8.09 x 10^{16}	4.05 X 10^{8}	2.12 x 10^{16}
36%	3.37 × 10^{16}	1.51 x 10^{16}	2.54 x 10^{8}	4.23 x 10^{15}
46%	1.94 × 10^{16}	8.46 x 10^{15}	1.7 x 10^{8}	1.27 x 10^{14}
53%	4.89 × 10^{15}	1.79 x 10^{15}	2.39 x 10^{7}	2.05 x10^{14}
59%	5.79 × 10^{14}	1.07 × 10^{14}	4.15 × 10^{6}	2.86 × 10^{10}

2. Effect of plasticizer content and plasticizer type on mechanical properties of starch film.

In Tables 3 and 4, it could be observed that no samples were obtained in solidified forms for cassava starch, corn starch and yam starch for the glycerol content of 59% because of higher content of glycerol used than the amount needed to make the product to solidify. This could be attributed to the hygroscopic nature of glycerol. However, solidified films were obtained for 59% of sucrose, this confirms more plasticizing effect of glycerol than sucrose. The contribution of this to the existing knowledge is that the maximum glycerol content for film formation from 7g of cassava starch, corn starch, and yam starch is 53%, and 46% for cassava starch. Although the films with 53% glycerol were too flexible, a more reliable film could be obtained with a plasticizer content ratio ranging from 20%-40% to the starch weight (Lourdin et al., 1999).

Generally, the plasticizing effect of both sucrose and glycerol increased with increase in plasticizer content as observed in tensile strength, tensile strain and Young’s Modulus data in Tables 3 and 4 and Figures 1, 2, 3, and 4. Glycerol is hygroscopic in nature thereby making water molecules available in-between starch polymer chains and reducing the internal hydrogen bonds between the polymer chains. Sucrose acts as plasticizer because of its ability to delay gelatinization by competing for the spaces between polymer chains with water molecules. Both yam starch films and corn starch films without plasticizer were found to have largest tensile strength and Young’s Modulus values but lowest elongation at break and tensile strain, and highest brittleness as observed in the tables. Plasticizers increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains. Young’s Modulus or elastic modulus is the fundamental measure of the film stiffness, the increase in plasticizer content resulted in films with lower Young’s Modulus and high flexibility (Mali et al., 2004, Mali et al., 2002).

The comparison of tensile strength, Young’s Modulus and tensile strain in the Tables 3, 4 showed that glycerol exhibited more plasticizing effect than sucrose on the four starches. This could be as a result of the difference in molecular size of the plasticizers. According to Cuq and Guilbert, 1997, plasticizer with low molecular weight produced more film plasticization than the high molecular weight, at the same mass basis, that is, the number of mole of glycerol(smaller) incorporated in the films were higher than sorbitol (large) and this certainly is more important to the plasticizing effect. The plasticizer type and concentration affected the mechanical properties of cassava starch films; glycerol-containing films showed the lowest values for tensile stress, due to its hygroscopic character that tends to provide additional water molecules in the film matrix (Mali et al., 2004). Monosaccharide-based polyols, such as glycerol and sorbitol, are widely used as plasticizer in edible film applications because of their plasticizing ability and low molecular weights. Plasticizer is added to the film to give better handling properties like flexibility and elasticity. Plasticizer decreases interactions between biopolymer chains, such as amylose and amylopectin, thus preventing their close packing which results in lower degree of crystallinity of the film (García et al., 2000).

The effect of amylose content on the starch-based films has been studied previously. In these studies, films have often been prepared from physical blend of amylose and amylopectin which is plasticized with various polyols. The amylose content affects the crystallinity of the starch film, which is often linked to the mechanical properties (Rindlav-Westling et al., 1998). The Young’s Modulus and tensile strength of the prepared film increase with increase in the crystallinity of amylose and amylopectin in the film with decrease in elongation at break. According to Corbion, 1996, four classes of corn starch exist. Common corn starch has 25% amylose, while waxy maize is almost totally made up of amylopectin.

The remaining corn starches are high amylose corn starches (50 - 55% and 70% - 75% amylose). In the study of the effects of physical, molecular and functional properties of corn, cassava and yam on the film properties of these starches, corn, cassava, and yam starches contained 25%, 19% and 30% amylose, respectively. Amylose from yam starch showed the smallest molecular weight among the starches and amylopectin from corn starch had the smallest molecular weight. Cassava starch presented the highest amylopectin content. Plasticized films of the three starches were less strong, more transparent, and more flexible with higher strain and lower stress at break when the glycerol content increased. Unplasticized films were brittle and had water vapour permeability value ranging from 6.75×10^{-10} to 8.33×10^{-10} g/m/s/Pa (Mali et al., 2004).

The Young’s Modulus and the tensile strength of glycerol plasticized films prepared from cassava starch have been reported to increase with increase in the amount of added amylose due to a denser polymer network (Alves et al., 2007). According to Lourdin et al., 1999, the almost linear increase of breaking forces with respect to the amylose content can be explained through the large agglomeration capacity of linear macromolecules and ramified structures of amylopectin originate nodules. The effect of amylose content is considered a favourable factor when there is no plasticizer. When plasticizers are added, the effect is inverse, since more films with a larger content of amylopectin react more and have a larger plasticity (Lourdin et al., 1995 and 1999).

TABLE 3 - Effect of glycerol content on the Mechanical Properties of starch films prepared from cassava, corn, potato and yam.

Glycerol Content (%)	Tensile Strain				Tensile Strength (Mpa)				Young Modulus(Mpa)			
	potato	Corn	Cassava	Yam	Potato	Corn	Cassava	Yam	Potato	Corn	Cassava	Yam
0%	0.03	0.05	0.08	0.11	5.74	5.20	5.33	5.10	191.33	104.6	97.5	49.3
22%	0.10	0.08	0.13	0.21	1.71	0.94	1.25	0.41	17.10	12.78	7.99	1.92
36%	0.15	0.10	0.25	0.27	1.02	0.25	1.19	0.22	6.80	2.47	4.89	0.86
46%	0.18	0.21	0.39	0.32	0.87	0.11	1.16	0.06	4.80	0.52	3.14	0.20
53%	0.21	0.24	-	0.38	0.35	0.10	-	0.05	1.61	0.39	-	0.12
59%	0.25	-	-	-	0.09	-	-	-	0.36	-	-	-

TABLE 4 - Effect of sucrose content on the Mechanical Properties of starch films prepared from cassava, corn, potato and yam.

Sucrose Content. (%)	Tensile Strain				Tensile Strength (Mpa)				Young Modulus (Mpa)			
	Potato	Corn	Cassava	Yam	Potato	Corn	Cassava	Yam	potato	Corn	Cassava	Yam
0%	0.03	0.05	0.08	0.11	5.74	5.20	5.33	5.10	191.33	104.06	97.5	49.32
22%	0.15	0.05	0.08	0.12	1.97	0.98	4.31	0.79	13.13	19.6	29.82	6.58
36%	0.20	0.12	0.14	0.21	1.76	0.83	1.42	0.49	8.80	6.91	11.11	2.33
46%	0.22	0.20	0.15	0.33	1.52	0.70	1.02	0.44	6.90	3.50	10.04	1.33
53%	0.25	0.21	0.17	0.38	0.99	0.53	0.89	0.37	3.96	2.52	8.67	0.97
59%	0.30	0.24	0.19	0.42	0.72	0.25	0.51	0.14	2.40	1.04	5.05	0.33

FIGURE 1 - Effect of glycerol content on the Tensile Strength of starch films prepared from Cassava, corn, potato and yam.

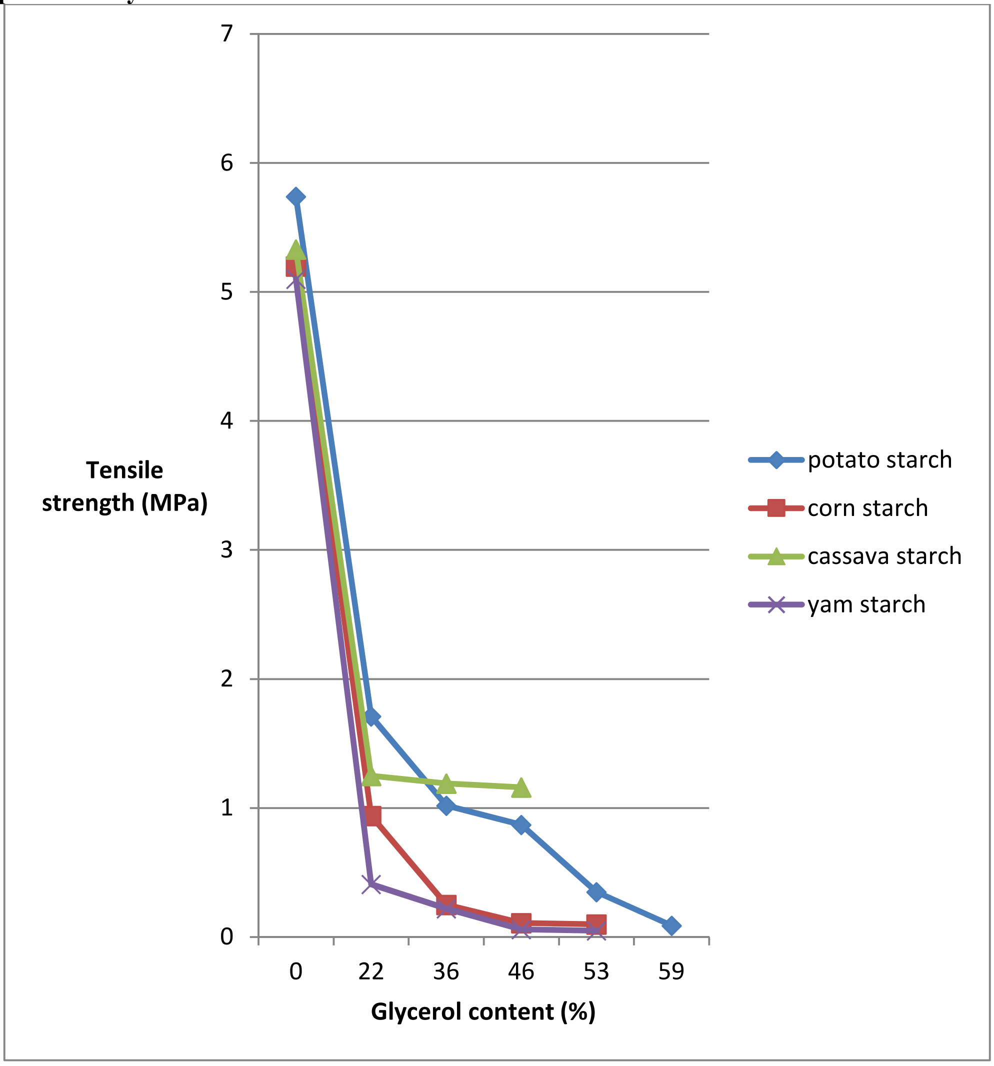


FIGURE 2 - Effect of glycerol content on the Young's Modulus of starch films prepared from cassava, corn, potato and yam.

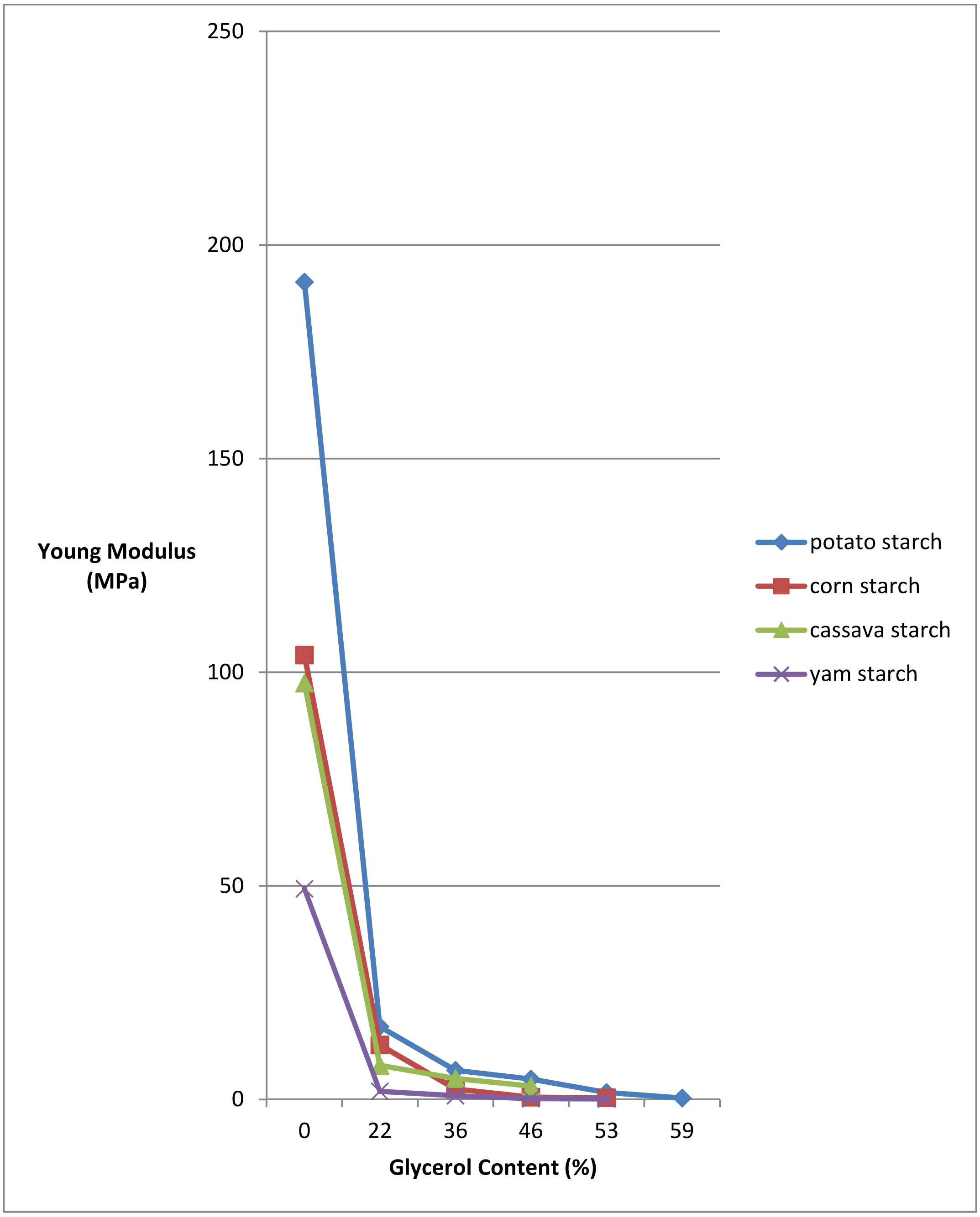


FIGURE 3 - Effect of sucrose content on the Tensile Strength of starch films prepared from cassava, corn, potato and yam.

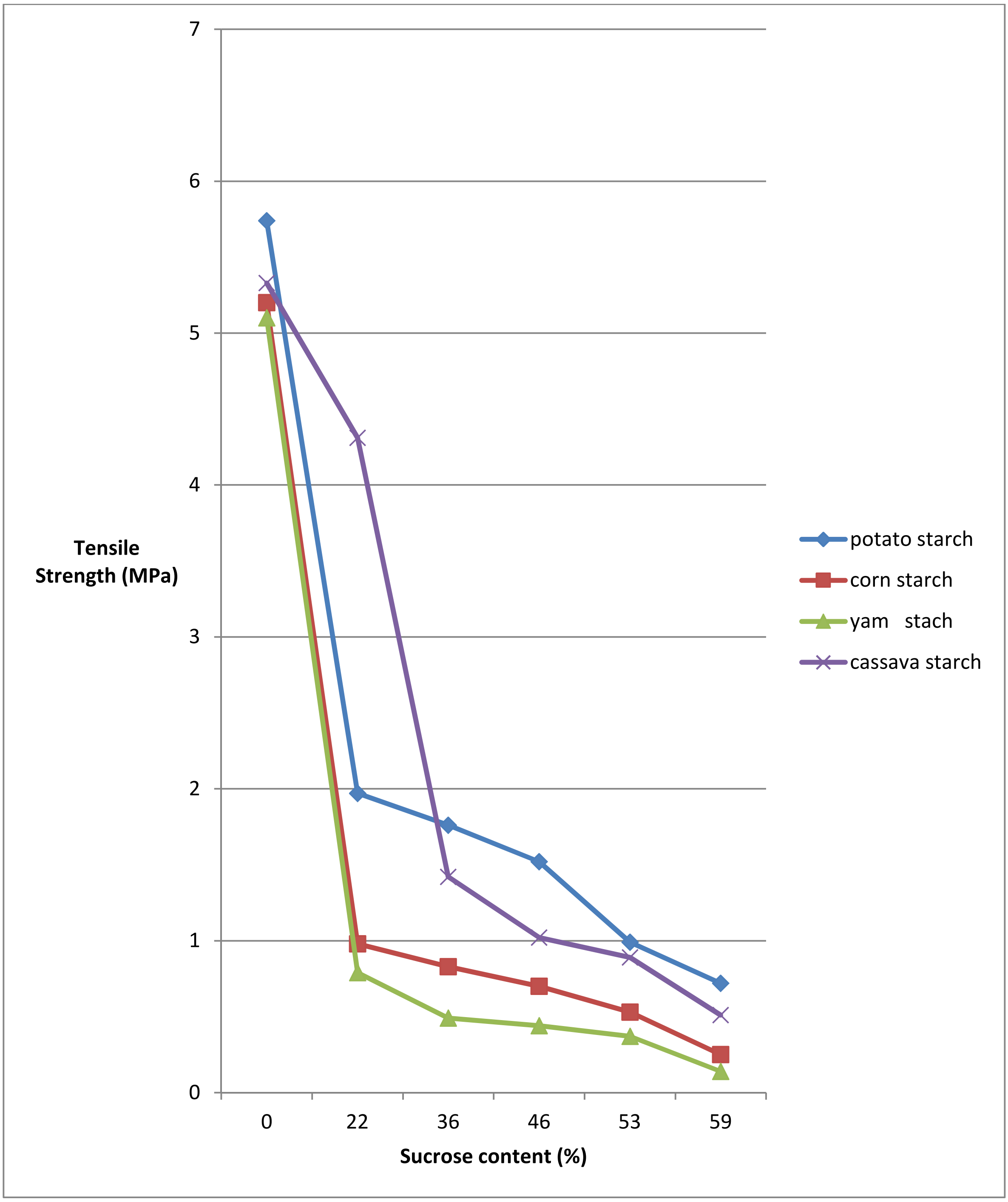
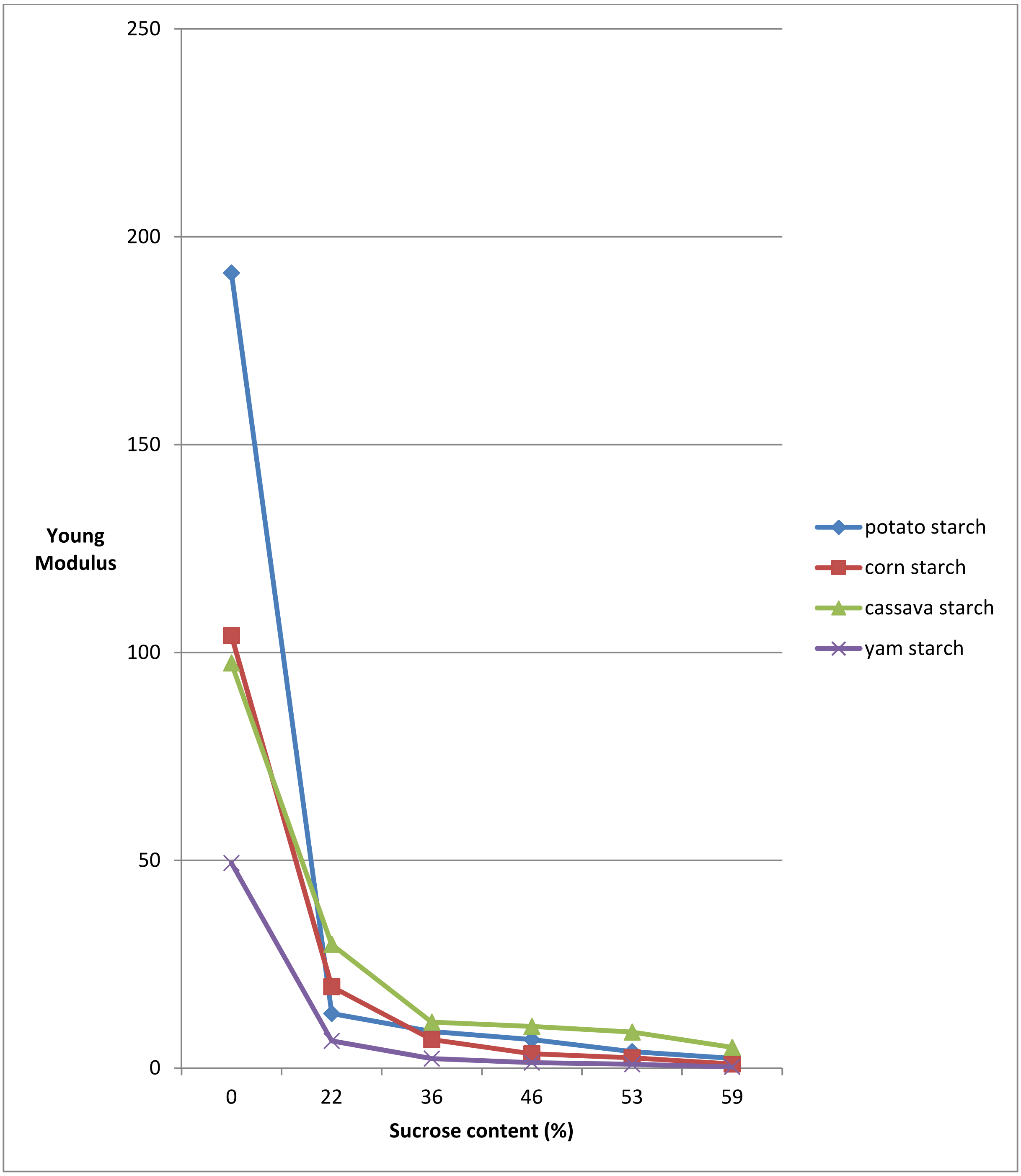


FIGURE 4 - Effect of sucrose content on the Young's Modulus of starch films prepared from Cassava, corn, potato and yam.



References

Alves, V.D., Mali, S., Beleia, A.,Grossmann, M.V.E. (2007). Effect of glycerol and amylose enrichment on cassava starch film properties. Journal of Food Engineering, Vol. 78(3). Pages 941-946.

Averous, L. (2002). Etude de systems polymers multiphases: approche des relation materiaux-procedes-properties.Habilitatan a diriger des recherché,Universite de Reims Champagne-Ardenne. Page 46.

Bastioli, C. (1998). Biodegradable materials – present situation and future perspectives. Symposium on Macromolecules. Vol. 135. Pages 193-204.

Chang, J.Y., Sydor, R.J. (1987). High performance size exclusion chromatography of starch with dimethyl sulfoxide as mobile phase. Journal of Applied Polymer Science Vol. 34. Pages 1739-1748.

Corbion, C. (1996). Understanding Starch Functionality. Food Product and Design.Scott Hegenbart(Ed). Week publishing company. U.S.A. Pages 54-87.

Cuq, B., Gontard, N., Cuq, J.L. and Guilbert, S. (1997). Selected functional properties of fish myofibrillar protein-based films as affected by hydrophilic plasticizers. Journal of Agricultural and Food Chemistry, Vol. 45 (3). Pages 622-626.

Curvelo, A.A., De Carvalho, A.J.F., Agnelli, J.A.M (2001). Thermoplastic starch-cellulose fibres composite: preliminary results. Journal of Carbohydrate Polymers Barking, Vol.45. Pages 183-188.

Erlander, S.R., Tobin,R .(1968). The stability of the helix of amylase and amylopectin in DMSO and water solution. Journal of Macromol Chemistry Vol. 1. Pages 194-211.

Fang, Zhong, Wallace, Yokoyama, Qian,Wan, Charles, Shoemaker (2006). Rice starch, amylopectin, and amylose: molecular weight and solubility in Dimethyl Sulfoxide-Based Solvents. Journal of Agricultural and Food Chemistry.Vol. 54. Pages 2320-2326.

French, D. (1984). Organization of starch granules. Starch Chemistry and Technology (2nd Edition). Whistler,R.L., Bemiller,J.N., Paschell,E.F. (Eds). Academic Press, Orlando. Pages 184-247.

Garcia, M.A., Martino, M.N., and Zaritzky, N.E. (1999). Edible starch films and coatings characterization: scanning electron microscopy, water vapour transmission and gas permeabilities.Scanning, Vol 21(5).Pages 348-353.

Garcia, M.A., Martino, M.N., and Zaritzky, N.E. (2000). Micro-structural characterization of plasticized starch-based films. Starch/ Starke, Vol 52(4). Pages 118-124.

Hanselmann, R., Ehrat, M., Widmer, H.M. (1995). Sedimentation field flow fractionation combined with multi angle laser light scattering applied for characterization of starch polymers. Starch/Starke, Vol.46. Pages 345-349.

Jackson, D.S. (1991). Solubility behavior of granular corn starches in dimethyl sulfoxide(DMSO) as measured by high performance size exclusion chromatography. Journal of Cereal Chemistry Vol.44. Pages 422- 427.

Lawter, M., Fischer, G. (2001). Potential of starch-based packaging for the food industry. In: The Food Bio-pack Conference, Copenhagen Proceedings. Pages 8-11.

Levesque, G. (2001). Utilization des derives de l'amidon dans les biomateriaux .In: Colloque Biomateriaux, Auray,Proceedings. 1 CD-ROM.

Lourdin, N., Della Valle, G.,Colonna, P., Poussin, P. (1999). Polymeres biodegradables: mise en oeuvre et proprieties de l amidon. Caoutchoues et plastiques. Page 780.

Mali, S., Grossmann, M. V. E., Garcı´a, M. A., Martino, M. M., & Zaritzky, N. E. (2002). Microstructural characterization of yam starch films. Carbohydrate Polymers, 50, 379–386.

Mali, S., Karam, L.B., Ranios, L.P., Grossmann, M.V. (2004). Physicochemical properties of starches with the characteristics of their films. Journal of Agricultural and Food Chemistry, Vol.15. Pages 25-52.

Martins Carplin (2012). Starch Functionality and Structure. Water Structure and Science. Pages 330-1345, Retrieved in Februrary, 2014, from hppt: www/Isbu.ac./ water/hysta.html.

Meehan, E. (1995). Semi-rigid polymer gel for size exclusion chromatography. Handbook for Size Exclusion Chromatography. Wu,Chi-San(Ed).Marcel Dekker Publisher, New York. Pages 25-44.

Oliver V. and Luc A. (2012). Starch-based Plastics. Technology, use and potentialities of Latin American starch tubers. Pages 521 – 553. Retrieved in februrary 2014, from https:vilpoux@raizes-ong.org.br.html.

Rindlaav-Westling, A.,Stadin, M., Hermanson, A., Gatenholm, P. (1998). Structure, mechanical and barrier properties of amylase and amylopectin films. Journal of Carbohydrate Polymer, Vol.36(2-3). Pages 217-224.

Yokoyama, W., Renner-Nantz, J.J., Shoemaker, C.F. (1998). Starch molecular mass and size exclusion chromatography in DMSO-LiBr coupled with multiple angle laser light scattering. Journal of cereal chemistry, Vol.1. Pages 530-535.