Study on the Comparative Biodegradable Films by Using Different Rice Starch and Plasticizer Effects (Ayar-min, Lone-thwe-hmwe)

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Abstract

In the research work, the rice sample-1 (Ayar-min) and sample-2 (Lone-thwe-hmwe) of two cultivated rice were collected from Kanbalu Township, Sagaing Region. The rice samples were grinded with motor and pestle and then sieved with 80 mesh size and the powder sample was stored in plastic bag for studying. Moisture content of the rice powders was determined by oven drying method. Dry ashing principle was used to determined ash content of the rice powders. The starches were extracted from the starch solutions with 0.01M NaOH solution. These starch samples were characterized by the physical properties such as bulk density, water absorption capacity, and starch solubility, swelling power, viscosity, turbidity and light transmittance respectively. Moreover, the rice starch films were prepared by various amount of water and different amount of plasticizers. These films were characterized by physico-mechanical properties such as thickness, tear strength, tensile strength and elongation at break. And then the morphology of extracted starches were determined by Scanning Electron Microscopy (SEM).

Keywords : Starch, biodegradable film, plasticizers, SEM, physico-mechanical properties

Introduction

Rice is the seed of the monocot plants *Oryza sativa* or *Oryza glaberrima.* Rice starch contains high amylose which is attractive raw materials for use as barriers in packaging materials. Rice starches have been used to produce biodegradable films to partially or entirely replace plastic polymers because of their low cost, renewability and good mechanical properties (Bourtoom and Chinnan, 2008).

Biopolymers from vegetable or animal proteins are new alternative materials for use instead of synthetic polymers in plastic and plastic film manufacturing in the light of environmental problems (Garcia *et al*., 2000). Starches used in industrial applications are usually extracted from cereal seeds (corn, wheat, and rice), tubers (potato), and roots (tapioca) (Chiou *et al*., 2005). Starch has been investigated widely for the potential manufacture of products. Starch granular organization as well as its amylose and amylopectin structure depends on the botanical source. It is an abundant raw material with low cost, and has been applied in the area of degradable plastics. Blend films containing starch are potential materials in the agriculture, medicine, and the packaging industries (Funke *et al.*, 1998; Hulleman *et al.*, 1998; Lu *et al*., 2005; Xiong *et al*., 2008). In the present study the properties of rice starch films were improved by comparing the viscosity, pasting temperature, and mechanical property.

Botanical Description

Botanical name	-	*Oryza sativa* L.
Family	-	Poaceae
English name	-	Rice
Myanmar name	-	Sapar
Part used	-	Rice grain

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(a)

(b)

Figure (1) Paddy plant (a) Ayar-min (b) Lone-thwe-hmwe

Materials and Methods

Sample Collection

Two brands of rice sample-1 and sample-2 (Ayar-min, Lone-thwe-hmwe) were collected from Kanbalu Township, Sagaing region. The rice samples were grinded with motor and pestle and then sieved with 80 mesh size and the powder sample was stored in plastic bag for studying.

Determination of Moisture Content of Rice Powder Samples

1.0g of the rice powder sample was accurately weighed in a pair of watch glass and it was fitted together by mean of a clip and which had been previously dried and cooled in a desiccator. The watch glasses containing the sample were placed in the air oven and dried for 30 minutes at about 100 ℃. They were removed from the oven and cooled in a desiccator to room temperature and weighed. The procedure was repeated until lose in weight does not exceed 0.05 % per minute drying period.

Determination of Ash Content of Rice Powder Samples

1.0 g of the dry sample was accurately weighed in a preheated, cooled and weighed porcelain crucible. The contents were carefully heated over an open flame until the sample was completely carbonized. The partially decomposed sample was then heated in a muffle furnace until the residue was free from carbon. The crucible and residue were cooled in a desiccator prior to weighing.

Confirmation of Rice Powder Samples by Iodine Test

About 0.1 g of rice powders were dissolved in 5 mL of distilled water and it was heated in boiling water bath for 30 minutes. When one drop of iodine solution was added, deep blue color solution was obtained.

Extraction of Rice Starches from Rice Powders Using Base Solution

50 g of rice powder sample-1 and 2 was weighed placed in each beaker. 250 mL of 0.01M sodium hydroxide solution was added into the weighed sample. The mixture was stirred with magnetic stirrer with a rate of 1600 rpm at room temperature and allowed 30 minutes. The supernatant was decanted off and this starch washes with water for three times until neutral. The supernatant solution was then decanted off and filtered through double layered cotton cloth. Then, the starch obtained was dried at room temperature. The starch lumps were powdered and weighed stored in polyethylene bag.

Preparation of Defatted Starch from Rice Starch by Soxhlet Extraction Method

Rice starch powder sample (100 g) was placed into a thimble. Then, Soxhlet apparatus was set up. Pet- ether (500 mL) was added on to the Soxhlet apparatus and heated at 8 to 24 hours. The extracted solution was distilled with distillation apparatus. The obtained defatted starches and fat were dried at room temperature until the constant weight was obtained.

Confirmation of Rice Starch Powders by Iodine Test

About 0.1 g of rice starch sample-1 and 2 was dissolved in 5 mL of distilled water and it was heated in boiling water bath for 30 minutes. When one drop of iodine solution was added into the starch solution, deep blue color solution was obtained.

Determination of Physical Properties of Rice Starch Samples

Determination of Bulk Density of Rice Starch Samples

The clean and dry specific gravity bottle (25 mL) was weighed. The bottle was filled with the powder sample and weighed.

Determination of Water Absorption Capacity of Rice Starch Samples

Rice starch powder (1 g) was placed in a pre-weighed centrifuge tube and added 10 mL of distilled water. The tube was shaken with shaker for about 2 hours and allowed to stand for 30 minutes. The tube was centrifuged for ten minutes. The supernatant was decanted. The centrifuge was weighed. The gain in weight was used to calculate the water absorption capacity.

Determination of Viscosity of Rice Starch Samples

1 g of rice starch powder sample and a few mL of distilled water were added to make a paste. The pastes were added into 100 mL boiling water and then boiled for 10 minutes to obtain 1% starch solution. Using an Oswald's Viscometer, the viscosity of starch solution was determined.

Determination of Starch Solubility and Swelling Power of Rice Starch Samples

The starch solubility and swelling power of the rice starches were measured at different temperatures according to the method of starch with some modification.

1.0 g of rice starch was weighed and put into the beaker. 100 mL of distilled water was added into the beaker. The suspension was stirred at 1100 rpm and heated at 50 ºC for 1 hour. Then the suspension was cooled for 30 minutes. After 30 minutes, it was poured into pre-weighed centrifuge tubes and centrifuge for 10 minutes. The supernatant was carefully removed using a pasture pipette. The suspension was added again to the centrifuge tube and the procedure was repeated till the suspension was over weighted of sediment was determined. Solubility was measured by pouring supernatant into evaporating dishes and evaporated at 110 ºC and weight of dry solids was determined. Swelling power and solubility of the rice starch powder were determined at 50ºC, 60 ºC, 70 ºC, 80 ºC and 90 ºC by using the similar procedure as above.

Determination of Turbidity of Rice Starch Samples

2.0 g of the rice starch sample was dissolved in 100 mL of distilled water. The starch solution was stirred and heated in a boiling water bath for about 1hour with continuous gentle stirring. It was cooled at room temperature. The absorbance of the starch solution was determined by using spectrophotometer at 640 nm against water as blank. The absorbance of the sample solution was determined after 2 and 3 days.

Determination of Light Transmittance of Rice Starch Samples

Light transmittance provides the information on the behavior of starch paste when the light passed through it. The light transmittance of starch paste is a function of the amount of swollen starch granules in the paste, which refract light. The light transmittance of the rice starch was measured according to the method reported by Singh. 1.0 g of rice starch sample was dissolved in 100 mL of distilled water and it was heated in a boiling water bath for 30minutes with continuous gentle stirring and then cooled for 1 hour in a 25 ℃ water bath. The light transmittances of the starch solution were determined at 620 nm and 680 nm against water as blank. Similarly, the absorbance of the wheat starch sample 1g, 2 g, 3 g, 4 g and 5 g were determined after 1 hour, 2 hours, 3 hours, 4 hours and 5 hours respectively.

Preparation of Starch Films by Various Amount of Water

One gram of each starch was dissolved in 50 ml and 40 mL of distilled water and placed in a beaker. The solution was stirred 800 rpm about 2 hours on the magnetic stirrer while heating. Then it was transferred into the Petridis which placed of ethanol and dried at room temperature to obtain starch film.

Preparation of Starch Films with Various Amount of Different Plasticizers

1.0 g of starch was dissolved in 50 mL of distilled water then 0.4 g and 0.6 g of glycerol were added in a resultant solution and the solution was stirred to 800 rpm about two hours on the magnetic stirred at room temperature. The solution was poured immediately into the petridis and dried for a few days at room temperature to obtain starch-glycerol film. And then starch–polyethylene glycol film was prepared above procedure.

Physico-mechanical Properties of Rice-Starch Films, Starch-Glycerol Films, Starch-Polyethylene Glycol Films

Determination of Thickness

Procedure(A) : Thickness of the prepared starch films and starch-glycerol, starch-polyethylene glycol films were measured by using NKS micrometer. The thickness of the films were measured at 5 locations (centre and four corners) using digital micrometer (Cervera, 2003).

Procedure(B): Thicknesses of samples were measured using slide clipper by reading accurately, changing different area of film thickness and calculated mean value.

Determination of Tensile Strength and Percent Elongation at Break

The prepared starch blended films were cut off according to JISK 7127(1987). The shape and dimension of the test pieces were described. Both ends of the test piece were firmed clamped in the jaws of a testing machine. One jaw was fixed and the other was movable. The movable jaw moved at a rate of 100 mm/min. The recorder of the machine showed the tensile strength in MPa. The percent elongation at break was calculated. The procedure was repeated three times for each result.

Determination of Tear Strength

Testing specimen was cut out by a die from starch blended films. Specimens are cut with a single nick (0.05 mm) at the center of the inner concave edge by a special cutting device using a razor blade. The clamping of the specimen in the jaws

of a testing machine was aligned with travel direction of the grip. The speed of the moving grip is 100 mm/min, the recorder of the machine showed the highest force to tear from a specimen nicked. Tear strength can be calculated.

Characterization of Rice Starch Samples by SEM

The morphology of rice starch powders were characterized by SEM at Universities of Research Center, Yangon.

Biodegradability of Blended Films

The biodegradability of the blended films was investigated by soil burial test. The blended films were introduced into the soil (six inches depth). Total time of biodegradation was one week. The influences of microbial action on the biodegradability were studied 3 days.

Results and Discussion

Results of Moisture and Ash Content of Rice Powders

The moisture and ash content of rice sample-1 and sample-2 were measured and these results were shown in table (1). According to the results, rice powder sample-2 has more moisture and ash contents than sample-1.

Table (1) Results of Moisture and Ash Contents of Rice Powders

Sample	Moisture (%)	Ash (%)
Sample-1 (Ayar-min)	7.00	1.00
Sample-2 (Lone-thwe-hmwe)	9.00	2.00

Confirmation of Rice Powders Samples by Iodine Test

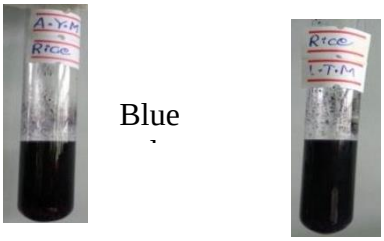


Figure (2) Confirmation of Rice Powder Samples by Iodine Test

Extraction of Starch from Rice Powders Using Base Solution

The rice starch sample-1 and 2 were extracted with 0.01 M NaOH solution from rice powders and the yield percent were calculated. And then the physical properties of the two rice starch samples were determined. These results were expressed in the tables.

Table (2) Yield Percent of Rice Starch Samples

Sample	Weight of rice powder	Time taken (mins)	Concentration of NaOH solution (M)	Weight of starch (g)	Yield (%) of starch
Sample 1	50. 00	30	0.01	42.6	85.2
Sample 2	50. 00	30	0.01	43.6	87.2

According to the table, sample-2 has higher percentage of starch than the sample-1.

Preparation of Defatted Starch from Rice Starch by Soxhlet Extraction Method

Table (3) Percent Defatted Starch from Rice Starch by Soxhlet Extraction Method

Sample	Amount of starch (g)	Defatted starch (%)	Fat (%)
Sample-1	100	99.5	0.5
Sample-2	100	99.87	0.13

From the results, the amount defatted starch 99.5 % in sample-1 and 99.87 % in sample-2 were observed.

Confirmation of Rice Starch Powder Samples by Iodine Test

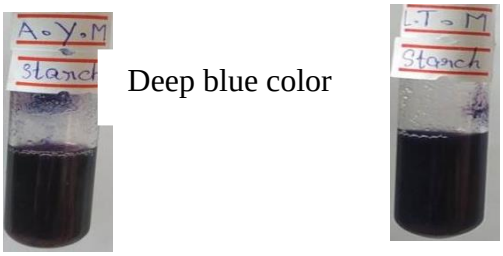


Figure (3) Confirmation of Rice Starch Powder Samples by Iodine Test

Results of Physical Properties of Rice Starch Samples

Physical properties of rice starch sample-1 and 2 were determined such as bulk density, water absorption capacity, viscosity, solubility and swelling power, turbidity and light transmittance. These results were shown in table (4) to table (11).

Table (4) Results of Bulk Density of Rice Starch Samples

Starch Sample	Bulk density (gcm^{-3})
Sample-1 (Ayar-min)	0.558
Sample-2 (Lone-thwe-hmwe)	0.658

From this table, the bulk densities of all rice starches sample have nearly the same values. So, rice cultivars showed the same bulk density.

Table (5) Results of Water Absorption Capacity of Rice Starch Samples

Starch Sample	Water absorption Capacity
Sample-1 (Ayar-min)	1.10
Sample-2 (Lone-thwe-hmwe)	1.03

In this table, sample-1 has more water absorption capacity than sample-2.

Table (6) Results of Water Absorption Capacity of Rice Starch Sample

Starch Sample	Viscosity
Sample-1 (Ayar-min)	1.2
Sample-2 (Lone-thwe-hmwe)	2.1

From this table, sample-2 has higher viscosity value than sample-1. So the sample-2 has higher starchy than the sample-1.

Table (7) Results of Starch solubility of Rice Starch Samples

Starch Sample	Solubility of Rice Starch in water (%)				
	50 ºC	60 ºC	70 ºC	80 ºC	90 ºC
Sample-1	5	9	10	14	17
Sample-2	2	4	7	12	15

According to this table, sample-1 has more solubility than sample-2. Thus, sample-1 has more inter molecular space than sample-2.

Table (8) Results of swelling power of Rice Starch Samples

Starch Sample	Swelling power				
	50 ºC	60 ºC	70 ºC	80 ºC	90 ºC
Sample-1	3.50	6.19	6.79	9.02	10.85
Sample-2	4.01	5.95	8.70	10.17	12.35

When the temperature is raised, the swelling power of samples is higher. So sample-2 has higher water swelling power than sample-1.

Table (9) Results of Turbidity of Rice Starch Samples

Starch Sample	Second day		Third day	
	% transmittance	Absorbance	% transmittance	absorbance
Sample-1	12.5	0.892	24.9	0.605
Sample-2	9.6	1.019	25.1	0.609

According to the table, sample-2 has more turbid than sample-1. Thus, sample-2 has more starchy than sample-1.

Table (10) Results of Light Transmittance of Rice Starch Samples at 620 nm

Starch Sample	Time	Absorbance (620 nm)				
		Sample (1 g)	Sample (2 g)	Sample (3 g)	Sample (4 g)	Sample (5 g)
Sample-1	0-hour	1.369	1.866	1.933	-	-
	1-hour	0.878	1.372	1.462	1.890	-
	2-hour	0.369	0.845	0.935	1.579	-
	3-hour	1.048	1.063	1.262	1.420	0.890
	4-hour	0.815	0.905	1.141	1.183	1.482
	5-hour	0.891	1.074	1.332	1.423	1.446
Sample-2	0-hour	1.330	1.552	1.702	2.301	-
	1-hour	0.852	1.054	1.402	1.876	2.096
	2-hour	0.727	0.933	1.314	1.570	1.827
	3-hour	0.758	0.877	1.173	1.786	2.434
	4-hour	0.745	0.943	1.086	1.639	1.916
	5-hour	0.756	0.878	1.229	1.711	1.864

Table (11) Results of Light Transmittance of Rice Starch Samples at 680 nm

Starch Sample	Time	Absorbance (680 nm)				
		Sample (1 g)	Sample (2 g)	Sample (3 g)	Sample (4 g)	Sample (5 g)
Sample-1	0-hour	1.320	1.820	1.900	2.301	-
	1-hour	0.850	1.346	1.435	1.856	-
	2-hour	0.243	0.850	0.932	1.352	-
	3-hour	0.025	1.030	1.221	1.390	0.860
	4-hour	0.800	0.883	1.097	1.455	1.151
	5-hour	0.864	1.033	1.292	1.377	1.406
Sample-	0-hour	1.273	1.503	1.658	2.221	2.479
	1-hour	0.816	1.016	1.360	1.862	2.096
	2-hour	0.710	0.908	1.277	1.536	1.801
	3-hour	0.745	0.863	1.148	1.766	2.301
	4-hour	0.728	0.917	1.058	1.596	1.886
	5-hour	0.794	0.908	1.254	1.750	1.890

According to table (10) and table (11), the absorbance of rice starch samples increased when the amounts of rice starch samples increased. The decrease in transmittance of starch paste with an increase in storage time was a result of retro gradation of starch.

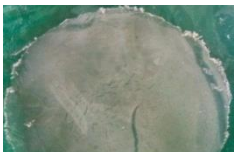
Results of Prepared Starch Films by Various Amount of Water

The effects of various amounts of water were investigated for preparing starch films. The mechanical properties of these films were determined. These results were shown in table (12).

LTM (starch :water) (1g : 50mL)

LTM (starch :water) (1g : 40mL)

AYM (starch :water) (1g : 50mL)



AYM (starch :water) (1g : 40mL)

various a

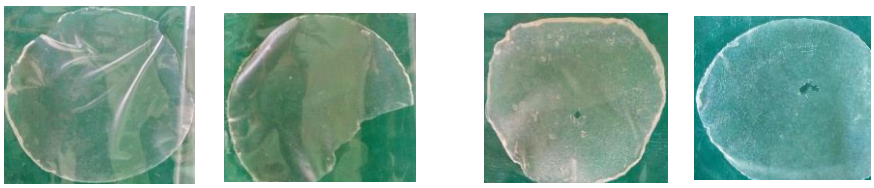
Table (12) Results of Physico-mechanical Properties of Prepared Starch Films

Starch Films	Thickness (mm)	Tensile strength (MPa)	Elongation at Break (%)	Tear Strength (kN/m)
(LTM) (1g : 50mL)	0.10	2.7	5	3.3
(AYM) (1g : 50mL)	0.15	6.8	10	12
(LTM) (1g : 40mL)	0.11	0.76	5	2.7
(AYM) (1g : 40mL)	0.20	0.25	7	9.5

According to the table, starch films of Starch : Water (1g: 50 mL) have higher tensile strength than that of (1g: 40mL). The elongation at break of (LTM) films have the same value. But (AYM) Starch: Water (1g: 50 mL) have higher elongation at break than (LTM) Starch: Water (1g: 40 mL). The starch films with 50mL of water were selected.

Results of Prepared Starch Films with Various Amount of Different Plasticizers

The effects of plasticizers were investigated by using two different plasticizers such as glycerol and polyethylene glycol. Different amount of each plasticizer (0.4 g and 0.6 g) were used for the preparing blended films. The mechanical properties of these blended films were determined. These results were shown in table (13).



LTM (1g : 50mL : 0.4g) LTM (1g : 50mL : 0.6g) AYM (1g : 50mL : 0.4g) AYM (1g : 50mL : 0.6g)

Figure (5) Prepared starch films with various amount of different plasticizers

Table (13) Results of Physico-mechanical Properties of Prepared Starch Films

Starch Films	Thickness (mm)	Tensile strength (MPa)	Elongation at Break (%)	Tear Strength (kN/m)
(LTM) (1 g : 50 mL : 0.4 g)	0.14	1.60	14	20.7
(AYM) (1 g : 50mL : 0.4 g)	0.2	0.33	5	4
(LTM) (1 g : 40mL : 0.6 g)	0.25	1.60	9	8.4
(AYM) (1 g : 40mL : 0.6 g)	0.25	0.20	5	2.3

According to the table, the prepared blended films of (LTM) Starches gave the higher tensile strength, elongation at break and tear strength.

Characterization of Rice Starch Powders by Scanning Electron Microscopy

The morphology of rice starch powders were characterized by SEM images. The results were shown in figure (6).

(a) (b)

Figure (6) SEM micrographs of rice starch samples (a) AYM and (b) LTM

According to SEM micrographs, the rice starch sample granules showed polyhedral shape with well-defined edges and surfaces.

Biodegradability of Prepared Blended Films

The biodegradability of prepared blended films was investigated by soil burial test. The prepared blended films were introduced into the soil (six inches depth). The results were shown in the following figure.

Figure (7) The films buried in the soil

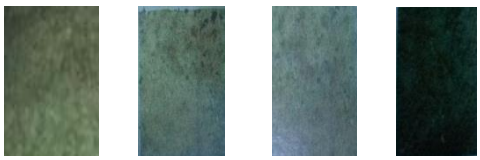


Figure (8) Before sinking the films into the soil

The biodegradable blended film may be disappeared after a short time duration by using burial method.

Conclusion

From the rice samples, the rice starches were extracted by using 0.01 M NaOH solution. The yield percent of rice starch samples were calculated and tested by iodine solution. From the results, the yield percent of extracted starch samples were 85% sample-1 and 87.2% sample-2. These extracted rice starches were defatted by Soxhlet apparatus. In physical analysis, the bulk density and viscosity of sample-2 were higher than the sample-1 but the water absorption capacity and solubility of sample-1 were higher than the sample-2. The higher the temperature, the more solubility of defatted starches was obtained. Increasing the temperature can also increase the swelling power of the rice starches. The morphology of rice starch powder samples were characterized by SEM (Scanning Electron Microscopy) images. From the SEM micrographs, the granular size of rice starch samples showed polyhedral shape with well-defined edges and surfaces.

Starch films were prepared with various amounts of water and with different amounts of plasticizers. The mechanical properties of the films were determined. Among them, prepared blended films of (LTM), starch : water : glycerol (1 g : 50 mL : 0.4 g) and (1 g : 50 mL : 0.6 g) gave the highest tensile strength, elongation at break and tear strength. By using soil burial test, the deformation and biodegradation of films were increased with increase in time.

References

Bourtoom, T. and Chinnan, M. S, (2008). "Preparation and properties of rice starch-chitosan blend biodegradable film". LWT-Food Science and Technology 41: 1633-1641

El-Tahlawy, K., Venditti, R. A. and Pawlak, J. J, (2007). "Aspects of the preparation of starch microcellular foam particles crosslinked with glutaraldehyde using a solvent exchange technique". Carbohydrate Polymers 67(13): 319-331.

Funke. U., Bergthaller, W. and Lindhauer, M. G, (1998). "Processing and characterization of biodegradable products based on starch". Polymer Degradation and Stability 59: 293-296.

Garcia, M. A., Martino, M. N. and Zaritzky, N. E, (2000). "Microstructural characterization of plasticized starch-based films". Starch/Starke 52: 118–124.

Hulleman, S. H. D., Janssen, F. H. P. and Feil, H, (1998). "The role of water during plasticization of native starches". Polymer 39(10): 2043-2048.

Xiong, H. G., Tang, S. W., Tang, H. L. and Zou, P, (2008). "The structure and properties of a starch-based biodegradable film". Carbohydrate Polymers 71: 263–268.