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Physicochemical, mechanical and barrier characteristics of biodegradable film from biopolymer (starches) modified by ionic gums and dry heat

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ABSTRACT

In the present study, potato, sweet potato and taro starches were modified by dry heating with ionic gums such as carboxy methyl cellulose (CMC) and Sodium Alginate. The native and modified starches were utilized to produce biodegradable films by casting technique. The films were analyzed for physicochemical, mechanical, barrier and biodegradability characteristics. The thickness of film increased significantly with modification whereas maximum effect was seen in potato starch film. Film solubility was higher in acidic as compared to water medium and least solubility was shown by sweet potato starch films. Modification and starch concentration showed significant effect on tensile strength, deformation force and deformation distance. It was found that the water vapour permeability (WVP) decreased significantly with modification and best results were obtained in film prepared from potato starch modified with CMC and heated for 4h. The biodegradability of modified starch films was comparatively less than native starches films. In conclusion the modification of starch produced film with promising barrier property and mechanical strength.

KEYWORDS

Ionic gums;
Biopolymer;
Barrier properties;
Mechanical properties;
Biodegradable film;
Biodegradability.

INTRODUCTION

Starch being a biodegradable polymer with well-defined chemical properties has huge potential and acts as a versatile renewable resource for various material applications in food and non-food areas[1]. Starch properties mainly depend on physical and chemical characteristics such as mean granule size, granule size distribution, amylose/ amylopectin ratio and mineral content[2]. The root and tuber starches as reported contain significant amounts of monophosphate esters covalently bound to starch[3]. Phosphorus affects starch functional properties such as paste clarity, viscosity consistency and stability[4]. Potato (Solanum tuberosum L.) a tuber crop contains starch up to 85 to 87% of the total dry matter. It is unique in comparison to other cereal starches (corn, wheat, rice, etc) because of its larger granule size, longer amylose and amylopectin chain length, presence of phosphate ester groups on amylopectin, ability to exchange certain cations which correspondingly effects on viscosity behavior[5]. The extent of variation in the granular structure of starches from cultivar to cultivar is significantly higher in potatoes[6]. It has been reported that the sweet potato contain phosphorus content ranging from 0.09 to 0.025%[7] whereas the taro starch have a high proportion of short chains and long average chain length fractions of amylopectin displayed high elasticity and strong gel during heating[8].

Starches in their native form have limited application in industries under extreme conditions like pH, temperature and shear during processing. Native starches have low shear stress resistance, thermal decomposition, high retrogradation, and syneresis. The functionality of starch can be modified through physical, chemical, and biotechnological means. Modification changes starch properties and greatly extends the range of starch applications[1]. Another purpose of starch modification is to stabilize starch granules during processing and make starch suitable for many food and industrial applications[9]. The dry heating process has been reported to be an alternative to chemical modification of starches or flours of various origins. Heating causes the peak viscosity to show noticeable reduction, but the final viscosity does not change[10].

Alginates are widely used to provide viscosity at low concentrations. The addition of gum to starch in food system is known to modify and control the rheological properties of starch. The specific adjustment of the rheological properties of starch is of significance in order to regulate production processes and to optimize applicability, stability, and sensory properties of food products[11]. Gum affects on gelatinization and retrogradation of starch through strong associations of amylose with gum, resulting in decrease in the retrogradation of starch[5].

Edible films and coatings have received considerable attention in recent years because of their advantages over synthetic films. It may be possible to improve food quality and shelf-life by coating low moisture food products with biomaterial based coatings. These coatings prevent or retard water transfer from surrounding atmosphere to the food products[12] and can be used as a barrier for oil uptake in deep fat frying[13]. In food packaging applications low water vapor permeability (WVP) and gas permeability (GP) are often desired[14]. Biodegradable films are known to be effective barrier to gas transport (O_2, CO_2)[15]. Water vapor permeability analysis can be useful to understand possible mass transfer mechanisms and solute and polymer interactions in edible films[16]. Biodegradable films with good mechanical properties can be used in-place of synthetic packaging films to carry food ingredients such as antioxidant, antimicrobial agents and flavors. They can also improve mechanical integrity or handling characteristic of food[17].

Plasticizers are added into polymeric films in order to reduce brittleness, improve flow and impart flexibility. They also increase toughness, strength, tear resistance and the impact resistance. Polysaccharides such as starches, cellulose derivatives and plant gums, have been reported as edible films and coatings in food packaging and preservation[18]. They have been used to produce biopolymer (biodegradable) films, to partially or entirely replace plastic polymers because of its low cost, renewability and good mechanical properties[19]. Presently, edible starch films have been used to extend the shelf life of many of fruits and vegetables, such tomatoes, apple etc. With increasing industrial demand for starches, there is need to explore new and alternative sources of starch. Tropical root and tuber crops could offer this opportunity as these crops are rich in starch[20].

Keeping in view the above facts, present study was planned to modify starch using natural elements such as ionic gums and utilization of modified starch in the preparation of biodegradable film followed by characterization of the films to study the desirable characteristics as required for its application.

MATERIALS AND METHODS

Sweet potato (Ipomea batatas) and Taro (Colocasia esculenta) are seasonal crops and remain available in the local market during November and December. The availability of the potato (Solanum tuberosum) crop is round the year but the special variety having red skin remains available only in winter season (November- December). The good quality raw materials free of blemishes were procured from the local market of Sangrur, Punjab (India). Carboxy Methyl Cellulose was procured from Central Drug House (CDH) Laboratory Reagents, New Delhi and Sodium Alginate was procured from S. D. Fine Chemicals Ltd, Mumbai, India. All the reagents used in the study were of AR-grade.

Isolation of starch

Starch was isolated from potato, sweet potato and taro by slight modification of the method as described by[21]. The tubers about 2kg were washed peeled and shredded. Shreds were put into plain water (pH 6.8). After that the shreds were put in water solution containing potassium meta-bisulphite (0.25%) containing citric acid (0.12%) in order to improve the colour of starch. The shreds were then ground in a lab blender to a fine paste. Water (1:2 ratios) was added to the paste, mixed and sieved through 80mesh sieve. The filtrate was then allowed to settle down. The starch precipitates thus obtained were transferred to the trays evenly and dried in a cabinet drier at 50°C to a moisture content of 10% (wet basis). After drying starch was ground in lab grinder and passed through 100mesh sieve, stored in air tight containers at 4°C for further use.

Modification of starch

Potato, sweet potato and taro starches were modified using method of[22]. The treatments for starch samples are given in TABLE-1. The Modification of starches was carried out by dry heating of starch with ionic gums such as sodium alginate and carboxy methyl cellulose (CMC). Initially sodium alginate or CMC, (0.4g, 1% on starch basis) was added slowly in distilled water about 70 ml with vigorous stirring using magnetic stirrer. Starch (39.6g) was added to the gum solution and the dispersion was stirred continuously for 30 min at room temperature. The whole dispersion was then transferred to a glass dish and dried at 45°C in an oven to a moisture content of about 10%. The dried starch was ground into powder using lab grinder and passed through 100 mesh sieve. The starch-gum powdered mixture was heated in an aluminum dish in an electric oven at 130°C for 2 h or 4 h. The starch itself was concurrently heat treated without gum under identical conditions.

Analysis of potato, sweet potato and taro starches

The analysis of starches for residual protein (%N×6.25) was carried by the official method[23]. The total starch content was determined by the method of[24] whereas, the amylose content was determined as per the method described by[25].

Preparation of biodegradable films

The starch films were prepared according to the method described by[26]. The films were prepared by the casting technique using a film-forming solution containing 3% or 5% native and modified potato, sweet potato and taro starches. Glycerol at concentrations of (0.25g/g on dry starch basis) was used as plasticizer. The mixture was heated to boiling temperature in boiling water bath for 30 min with con-

TABLE 1 : Treatments for modification of potato, sweet potato and taro starches with ionic gums and dry heating

Samples	Starch (g)	Treatments			
		Sodium Alginate (%w/w)	CMC (% w/w)	Heating Temperature (°C)	Heating (h)
1	50.0	-	-	-	-
2	50-0	-	-	130	2
3	50.0	-	-	130	4
4	39.6	1	-	-	-
5	39.6	1	-	130	2
6	39.6	1	-	130	4
7	39.6	-	1	-	-
8	39.6	-	1	130	2
9	39.6	-	1	130	4

stant stirring initially for 10 min using magnetic stirrer. Mixture was cooled till bubbles got vanished and then poured (hot) about 25 mL homogenously into the plastic trays (9×9×2cm). The trays centering the film forming solution were dried in a cabinet drier at 50°C for 5 h. The dried films were peeled off from the trays and kept in air tight polyethylene bags for further study.

Testing of films

Film thickness

A sheet of film having size (9×9cm^2) was used for thickness measurement with the help of micrometer. The thicknesses of these films were measured at five random locations of the film. Mean thickness values for each sample were then calculated.

Solubility in water or acid

The solubility was measured as percentage of dry matter in the film solubilized after 24 h immersion in water or acid. The percentage of initial dry matter in each film was determined at 105°C for 24 h. Two discs of film (2 cm diameter) were cut, weighed, immersed in 50 mL of distilled water or 1N HCl and slowly and periodically shaken for 24 h at 25°C. The pieces of film were then taken out and dried (105°C for 24 h) to determine the weight of dry matter not solubilized in water. The weight of solubilized dry matter was calculated by subtracting the weight of dry matter not solubilized from the weight of the total dry matter and was reported on an initial dry weight basis.

$$(\%)\ \text{Solubility} = \frac{\text{Initial Weight} - \text{Final Weight}}{\text{Initial Weight}} \times 100$$

Mechanical properties

The prepared starch films were tested for mechanical properties such as puncture strength and tearing strength using texture analyzer (TAXT2i, Stable Micro System, Godalming, and Surrey, U.K.).

Tensile strength

Starch films were cut into 30 mm length and 15 mm breadth for the determination of tensile strength. The strips were then equilibrated either at 4°C or 25°C where as RH was maintained at 85% and 75% respectively for minimum 4 h period. After equilibration each test piece was removed and placed centrally on the sample platform of Keiffer rig with the extension hook positioned beneath previously. Tensile strength was calculated by dividing the maximum force to the initial specimen cross-sectional area.

Texture analyzer was operated under the following test conditions

Mode: Measure Force in Tension; Pre-test speed: 1.5 mm/s; Test speed: 2.0 mm/s; Post-test speed: 10 mm/s; Rupture test distance: 1.0 mm; Distance: 20 mm; Data acquisition rate: 200 pps; Temperature: ambient (26-28°C).

Puncture strength

Puncture test was performed to determine deformation force (N) and deformation distance (mm). Samples with diameters of 40 mm were fixed on the plate of the equipment having central hole of 20 mm diameter with the help of a sample holder. A cylindrical probe of 5 mm diameter was moved perpendicularly to the film surface at a constant speed of 1 mm/s until the probe passed through the film. Force–deformation curves were recorded at rupture point force and deformation was determined.

The texture analyzer was operated under the following test conditions

Mode: Measure Force in Compression; Pre-test speed: 2.0 mm/s; Test speed: 2.0 mm/s; Post-test speed: 5.0 mm/s; Rupture test distance: 1.0 mm; Distance: 2.0mm; Data acquisition rate: 200pps; Temperature: ambient (26-28°C).

Water vapor permeability (WVP)

Each film sample was sealed over a circular opening in a permeation cell that was stored at 30°C in desiccator. To maintain 75% RH gradient across the film, anhydrous calcium chloride (0%RH) was placed inside the cell and sodium chloride saturated solution 75% RH was used in desiccator. The RH inside the cell was always lower than the outside, and water vapor transport was determined from the weight gain of the permeation cell. After steady state condition were reached (about 2 h), the weight measurement were made after each 2 h intervals upto 24 h duration. Changes in the weight of the cell were recorded to the nearest 0.0001g and plotted as a function of time. The slope of each line was calculated near regression ($r^2 > 0.99$) and the water vapor transmission rate (WVTR) was calculated from slope of straight line (g/s) divided by transfer area (m^2). After the permeation tests, film thickness was measured and WVP ($g\ Pa^{-1}\ s^{-1}\ m^{-1}$) was calculated as:

$$\mathrm{WVP} = \frac{\mathrm{WVTR}}{\mathrm{S}\ (\mathrm{R}_1\text{-}\mathrm{R}_2)\ \mathrm{D}} \times 100$$

Where, S; is the saturated vapor pressure (Pa) of water at test temperature (30°C), $R_{1;}$ the RH in the desiccators, $R_{2;}$ the RH in the permeation cell and D; the film thickness (m). Under these conditions, the driving force [S (R_1-R_2)] was 1753.55Pa.

Biodegradability of films

Biodegradability of films was determined according to the method given by[27]. The film samples with stable weight (W_1) were heated by placing under the soil surface 20 -25 cm deep in a summer average temperature of 32°C. The samples were subsequently taken out and washed with alcohol. Alcohol was evaporated from the washed samples by keeping in hot air oven. The samples were then returned to the soil after recording the stable weight (W_2). The process was repeated with an interval of one week for a total period of nine weeks. Weight loss (%) was calculated and data were used to record the biodegradability of the film samples.

$$\text{Weight loss (\%)} = \frac{\mathrm{W}_1\text{-}\mathrm{W}_2}{\mathrm{W}_1} \times 100$$

Statistical analyses

The statistical analyses were carried out with two ways Analysis of Variance (ANOVA) and means were compared using LSD (Least square Difference) test, with the help of Excel spreadsheets of MS Office 2007 software package and Genstat12 edition.

RESULTS AND DISCUSSIONS

Compositional analysis

The starch content in potato was 84.34% (wb), where as sweet potato and taro contained about 83.60% and 79.92% starch respectively. The residual protein contents in the potato starch were 0.26%, sweet potato (0.35%) and taro starch (0.44%). The amylose contents in isolated potato, sweet potato and taro starches were 24.00%, 25.60% and 20.40% respectively.

Properties of biodegradable films

Physico-chemical properties

Thickness

Thickness of starch films are shown in TABLE-2. Thickness of starch film containing either 3% or 5% starch varied from 0.11 to 0.13 mm and 0.16 to 0.18 mm respectively. It was observed that with increase in the starch concentration the thickness of

TABLE 2 : Thickness of the biodegradable films from native and modified potato, sweet potato and taro starches at 3% and 5% starch levels[a]

Sample	Thickness (mm)		Sample	Thickness (mm)		Sample	Thickness (mm)	
	3% starch	5% starch		3% starch	5% starch		3% starch	5% starch
P_1	0.11^{aA}	0.16^{bA}	SP_1	0.11^{aA}	0.16^{bA}	T_1	0.11^{aA}	0.16^{cA}
P_2	0.11^{aA}	0.17^{dB}	SP_2	0.11^{bA}	0.16^{cA}	T_2	0.11^{bA}	0.16^{dA}
P_3	0.12^{aC}	0.17^{cC}	SP_3	0.11^{aA}	0.16^{bA}	T_3	0.12^{aB}	0.17^{bB}
P_4	0.12^{aB}	0.17^{cB}	SP_4	0.12^{bA}	0.16^{cA}	T_4	0.12^{bB}	0.17^{dB}
P_5	0.13^{bC}	0.17^{eB}	SP_5	0.12^{aB}	0.16^{dA}	T_5	0.12^{cB}	0.18^{bC}
P_6	0.13^{bC}	0.17^{cB}	SP_6	0.12^{aB}	0.18^{dC}	T_6	0.13^{bC}	0.18^{dC}
P_7	0.12^{aB}	0.17^{cB}	SP_7	0.12^{bB}	0.18^{dC}	T_7	0.12^{bB}	0.17^{cB}
P_8	0.12^{aB}	0.18^{dC}	SP_8	0.13^{bC}	0.18^{eC}	T_8	0.13^{aC}	0.18^{aC}
P_9	0.13^{aC}	0.18^{cC}	SP_9	0.13^{aC}	0.18^{bB}	T_9	0.13^{aC}	0.18^{bC}

[a] **Samples in duplicate were taken; Values denoted by different small letters in the row and by the different capital letters in the column differs significant ($P \leq 0.05$); P= Potato, SP= Sweet Potato, T= Taro**

TABLE 3 : Water solubility of biodegradable films from native and modified potato, sweet potato and taro starches at 3% and 5% starch levels[a]

Sample	Water solubility (%)		Sample	Water solubility (%)		Sample	Water solubility (%)	
	3% starch	5% starch		3% starch	5% starch		3% starch	5% starch
P_1	35.62^{fF}	35.28^{dF}	SP_1	29.22^{cE}	24.11^{bF}	T_1	24.50^{bE}	22.23^{aF}
P_2	35.23^{eE}	34.74^{dE}	SP_2	29.09^{cDE}	23.81^{bE}	T_2	24.64^{bF}	21.80^{aE}
P_3	35.26^{dE}	33.67^{dD}	SP_3	28.96^{cD}	23.56^{bD}	T_3	24.69^{bF}	21.67^{aE}
P_4	35.19^{dE}	33.52^{dD}	SP_4	28.52^{cC}	23.28^{bC}	T_4	24.57^{bE}	21.46^{aD}
P_5	34.78^{eD}	32.60^{dC}	SP_5	28.36^{cC}	23.13^{bC}	T_5	24.12^{bC}	20.41^{aD}
P_6	34.38^{dC}	32.58^{dC}	SP_6	27.97^{cB}	22.81^{bB}	T_6	24.34^{bD}	20.32^{aD}
P_7	33.86^{dB}	31.95^{dB}	SP_7	28.33^{cC}	22.76^{bB}	T_7	23.72^{bB}	20.03^{aC}
P_8	33.52^{eA}	31.60^{dB}	SP_8	26.98^{cA}	22.53^{bA}	T_8	22.93^{bA}	19.56^{aB}
P_9	33.33^{eA}	31.15^{dA}	SP_9	27.15^{cA}	22.44^{bA}	T_9	23.00^{bA}	18.85^{aA}

[a]Samples in duplicate were taken; Values denoted by different small letters in the row and by the different capital letters in the column differs significant ($P \leq 0.05$)

TABLE 4 : Acid solubility of the biodegradable films from native and modified potato, sweet potato and taro starches at 3% and 5% starch levels[a]

Sample	Acid solubility (%)		Sample	Acid solubility (%)		Sample	Acid solubility (%)	
	3% starch	5% starch		3% starch	5% starch		3% starch	5% starch
P_1	41.99^{dG}	39.78^{dF}	SP_1	29.08^{aF}	31.32^{bG}	T_1	35.48^{cG}	31.43Bd
P_2	41.39^{eF}	38.44^{dE}	SP_2	28.18^{aD}	30.85^{bF}	T_2	34.99^{cF}	31.88bE
P_3	41.36^{eF}	38.60^{dE}	SP_3	28.44^{aD}	30.46^{bF}	T_3	34.75^{cF}	31.25^{bD}
P_4	38.87^{dE}	37.27^{dD}	SP_4	27.74^{aD}	29.83^{bE}	T_4	33.97^{cD}	30.86^{cC}
P_5	37.06^{eD}	36.10^{dC}	SP_5	27.15^{aC}	29.88^{bE}	T_5	33.166^{cD}	28.29^{bB}
P_6	35.02^{dC}	34.77^{dB}	SP_6	27.19^{aC}	28.57^{bD}	T_6	32.43^{cC}	28.57^{bB}
P_7	36.95^{eD}	35.87^{dC}	SP_7	26.45^{aB}	28.03^{bC}	T_7	32.11^{cB}	28.33^{bB}
P_8	34.34^{dB}	33.70^{dA}	SP_8	25.82^{aA}	26.95^{bA}	T_8	31.00^{cA}	26.67^{aA}
P_9	33.68^{dA}	33.66^{dA}	SP_9	25.47^{aA}	27.47^{bB}	T_9	31.03^{cA}	26.69^{bA}

[a]Samples in duplicate were taken; Values denoted by different small letters in the row and by the different capital letters in the column differs significant ($P \leq 0.05$)

the film increased at constant glycerol concentration of (0.25g/g starch). The general trend is that the hydrocolloid modification significant increased the film thickness as compared to control starch film samples. This is probably due to more water retention and high polymer molecular weight of starch gum interactions[28]. Among gum modified starch films, CMC modification had shown significantly higher film thickness as compared to alginate modified films in both 3% and 5% starch levels. Thickness was reported to have effect on the mechanical and barrier properties (WVP) of the films[29].

Film solubility

Water solubility of the films in water as well as in acid mediums is shown in TABLE-3 and 4 respectively. Water resistance is an important property of biodegradable or edible films for applications as food protection where water activity is high, or when the film must be in contact with water during processing of the coated food[30]. From the results it can be interpreted that the solubility in water was highest in potato starch and least for taro starch containing films. Similarly the films prepared from 3% starch had shown more solubility than the films prepared from 5% starch. This may be due to higher molecular interaction and resistance to solubility for higher starch contacting films as compared to low starch containing films. Moreover dry heating of starch alone also significantly reduced film solubility which can be seen in samples from P_1 to P_3. This may be due to molecular integration of starch polymers during dry heating at high temperature. It has been reported that the hydrophobic nature of wheat starch was enhanced by heating it at 120°C for several hours, a change favorable for cake baking[31].

The acid solubility (TABLE-4) was significantly on higher sides for all starch samples and at all starch concentrations as compared to water. This was probable due to effect of acid which increased hydroxyl groups of polymers due to break down of hydrogen bonds as quoted by[6]. However due to modification and particularly in CMC modified starch samples, the acid solubility was significantly reduced in films for all types of starches. According to[32], starch molecule can interact with hydrocolloids and a network is created which increase starch peak viscosity and hence solubility is decreased. The taro starch films in all modifications and at all starch concentrations had shown significantly least acid solubility where as in the potato starch films, the acid solubility was highest.

Mechanical properties

Tensile strength

Tensile strength of films is shown in TABLE-5. The tensile strength for the films formed from 3% native starch of potato, sweet potato and taro had shown tensile strengths of the order of 6.82N/cm^2, 6.1N/cm^2, and 4.82N/cm^2 respectively. In case of biodegradable films prepared from 5% native potato, sweet potato and taro starch the tensile strengths were 8.14N/cm^2, 7.803N/cm^2 and 7.52N/cm^2 respectively. Among the samples, potato starch had shown the highest ability to stand at normal stress encountered during application at all starch concentrations, followed by sweet potato and then by the taro starch. This may be due to comparatively more phosphate groups present on amylopectin of potato starches and also due to its large granular size[33] which probably enhanced the resistance to tear force. As the film forming ability is governed by the starch amylose content and other constituents such as phosphorous content, amylose/amylopectin ratio, the plasticizer added provides the improved tensile strength[34]. The taro starch film having lower amylose content, phosphorous had shown poor tensile strength.

Modification of starch with dry heating without gums addition had shown significant positive effect on tensile strength for all of the samples studied and at all starch concentrations. The modification of starch for 2 h heating did not show significant effect on the film mechanical strength as compared to starch heated for the 4 h for all starch samples (1 to 3). The alginate modified starches without heating showed higher tensile strength (9.63N/cm^2) for potato starch than those observed in sweet potato (9.47N/cm^2) and taro (8.28N/cm^2) starch films. Modification of the starch with CMC, with or without heating showed

TABLE 5 : Tensile strength of biodegradable films from native and modified potato, sweet potato and taro starch films at 3% & 5% starch levels[a]

Sample	Tensile Strength (N/m^2)		Sample	Tensile Strength (N/m^2)		Sample	Tensile Strength (N/m^2)	
	3% starch	5% starch		3% starch	5% starch		3% starch	5% starch
P_1	6.82^{cA}	8.14^{eA}	SP_1	6.11^{bA}	7.80^{dA}	T_1	4.82^{aA}	7.52^{dA}
P_2	7.32^{cA}	8.58^{dA}	SP_2	6.24^{bA}	8.07^{bA}	T_2	4.89^{aA}	7.60^{cA}
P_3	7.50^{cB}	9.40^{fB}	SP_3	6.86^{bB}	9.00^{eB}	T_3	5.47^{aB}	8.11^{dB}
P_4	7.87^{cB}	9.63^{eB}	SP_4	7.53^{bB}	9.47^{eB}	T_4	5.847^{aB}	8.28^{dB}
P_5	8.13^{cC}	10.59^{fC}	SP_5	7.70^{bB}	10.05^{eC}	T_5	6.08^{aB}	8.71^{dB}
P_6	8.15^{cD}	11.18^{fD}	SP_6	7.84^{bC}	10.65^{eD}	T_6	6.49^{aB}	9.20^{dB}
P_7	8.27^{bD}	11.67^{eD}	SP_7	7.90^{bD}	10.97^{dD}	T_7	6.37^{aB}	9.36^{cB}
P_8	8.83^{aE}	13.62^{eE}	SP_8	8.20^{bE}	11.78^{dE}	T_8	6.65^{aC}	10.01^{cC}
P_9	9.15^{cF}	14.28^{fF}	SP_9	8.53^{bF}	12.63^{eF}	T_9	6.74^{aC}	10.37^{dC}

[a]Samples in duplicate were taken; Values denoted by different small letters in the row and by the different capital letters in the column differs significant ($P \leq 0.05$)

TABLE 6 : Deformation force and deformation distance of biodegradable films from potato, sweet potato and taro starches at 3% & 5% starch levels[a]

Sample	Force (N)		Distance (mm)		Sample	Force (N)		Distance (mm)		Sample	Force (N)		Distance (mm)	
	3% starch	5% starch	3% starch	5% starch		3% starch	5% starch	3% starch	5% starch		3% starch	5% starch	3% starch	5% starch
P_1	35.23^{cA}	45.05^{eA}	0.64^{bA}	0.75^{cA}	SP_1	31.73^{bA}	41.76^{dA}	0.61^{bA}	0.71^{cA}	T_1	20.80^{aA}	36.79^{cA}	0.50^{aA}	0.65^{bA}
P_2	36.13^{cB}	46.90^{eB}	0.64^{bA}	0.78^{cA}	SP_2	32.22^{bA}	42.24^{dA}	0.63^{bA}	0.72^{cA}	T_2	22.42^{aB}	38.13^{cB}	0.53^{aB}	0.66^{bA}
P_3	37.67^{cC}	47.039^{eB}	0.65^{bB}	0.76^{cA}	SP_3	33.28^{bB}	44.81^{dB}	0.63^{bA}	0.76^{cA}	T_3	24.16^{aC}	38.51^{cB}	0.55^{aC}	0.66^{bA}
P_4	39.08^{cD}	52.13^{eC}	0.66^{bB}	0.82^{dA}	SP_4	34.63^{bC}	46.13^{dB}	0.63^{bA}	0.77^{cA}	T_4	25.01^{aD}	39.97^{cC}	0.55^{aC}	0.67^{bA}
P_5	40.65^{cE}	55.75^{eC}	0.69^{bC}	0.86^{dA}	SP_5	35.06^{bC}	47.67^{dC}	0.63^{bA}	0.79^{cA}	T_5	25.04^{aD}	40.52^{cC}	0.56^{aC}	0.69^{bA}
P_6	41.03^{cF}	58.06^{eD}	0.70^{bD}	0.99^{dB}	SP_6	36.09^{bD}	48.09^{dC}	0.65^{bB}	0.79^{cA}	T_6	26.89^{aE}	41.96^{cD}	0.58^{aD}	0.71^{bA}
P_7	42.24^{cF}	62.32^{eE}	0.71^{cF}	1.22^{dC}	SP_7	37.86^{bE}	50.56^{dD}	0.66^{bC}	0.81^{bA}	T_7	29.41^{aF}	42.04^{cD}	0.59^{aE}	0.72^{cA}
P_8	43.19^{cG}	65.61^{eF}	0.72^{bF}	1.23^{dC}	SP_8	38.08^{bE}	53.95^{dE}	0.67^{aD}	0.83^{cA}	T_8	30.92^{aG}	42.33^{cD}	0.61^{aF}	0.72^{bA}
P_9	43.33^{cH}	66.74^{eF}	0.72^{bE}	1.25^{dC}	SP_9	40.41^{bF}	55.52^{dF}	0.68^{aE}	0.87^{cA}	T_9	32.32^{aH}	43.54^{cE}	0.62^{aG}	0.73^{bA}

[a]Samples in duplicate were taken; Values denoted by different small letters in the row for specific characteristics and by the different capital letters in the column differs significant ($P \leq 0.05$)

more significant increase in tensile strength for all starches films as compared to alginate modified starches under similar process conditions. It has been reported that ester bond could be formed between the starch and CMC when the starch and gum mixture were dry-heated. The linking of the starch with gums caused increase in resistance to normal force which further got enhanced due to heating of starches with gums and addition of the plasticizer[35].

Puncture strength

Puncture strength of films in terms of deformation force (N) and deformation distance (mm) are shown in TABLE-6. The native starch films prepared from 3% starch had shown puncture force of 35.23N, 31.73N and 20.80N for potato, sweet potato and taro starches respectively, whereas at 5% starch levels of potato, sweet potato and taro starches the puncture forces were 45.05N, 41.76N and 36.79N respectively. This higher puncture strength at high starch levels and also in potato starch containing films may be due to reasons given above for enhanced mechanical properties for potato starch as compared to other starches. Among all of the starch film studied heat modification produced significant positive effect on puncture strength as compared to native starches. The films formed from the starches dry heated either for 2h or 4h had shown significant positive effect on puncture strength at all starch concentrations except for taro starch samples where the significant effect is seen after 4h of starch dry heating only.

Modification of starch with alginate without heating improved the puncture strength significantly as compare to heat modified starches alone. The 52.13N, 46.13N and 39.97N were the forces required to puncture the film prepared from alginate (without heating) modified starches of potato, sweet potato and taro respectively. CMC exerted stronger plasticizing effect as compared to alginate and goes on increasing as heating advanced from 2 h to 4 h. It has been reported[35] that the ester bond could be formed between the starch and CMC when the starch and gum mixture were dry-heated. Thus, CMC modified potato starches showed highest puncture resistance as compared to other modified starches. The films containing 5% potato starch modified with CMC and heated for 4 h showed 1.25mm deformation distance with respect to deformation force of 66.74N. The taro starches had shown least deformation in the film due to their brittleness. In all the cases modification of starch with gums especially CMC produce beneficial effect on puncture resistance.

It has been observed that the film prepared form 3% native starches being lower in thickness as compared to 5% starch didn’t stand at normal pressure applied during packing of commodities but the modification using ionic gums with or without heating was the way to make the films to withstand the de-

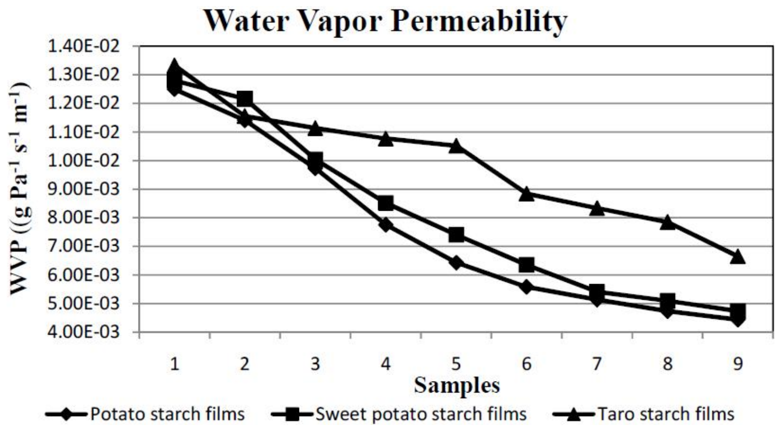

Figure 1 : Effect of modification on the water vapor permeability (WVP) of the films prepared from potato, sweet potato and taro starches

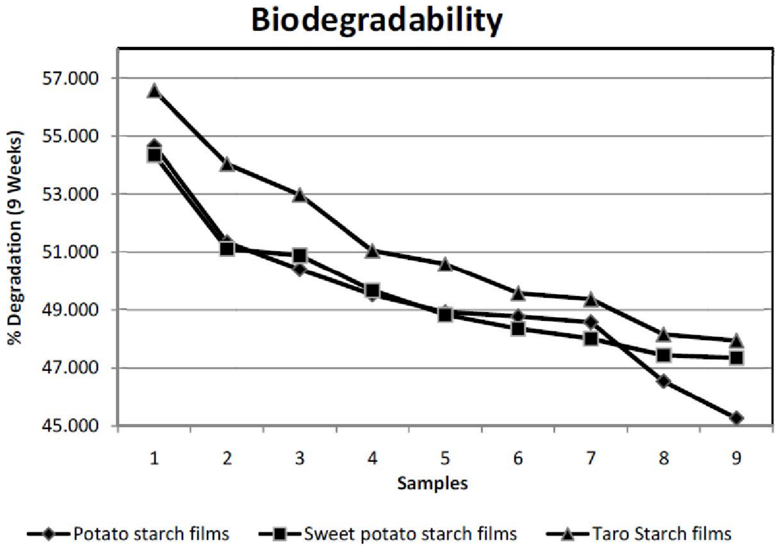

Figure 2 : Biodegradation of the films prepared form native and modified potato, sweet potato and taro starches after 9-weeks soil burial

formation force during application. As CMC modified potato film with 3% starch solution produced equal puncture strength to that produced by modified taro starch film with 5% starch, however 3% starch containing films showed less deformation force as compared to the 5% starch containing films due to less film thickness. It has been indicated that the starch based films have numerous food application and promising mechanical properties which can be improved by modification of starch[19].

Barrier properties

Water permeability pattern of different starch films is shown in Figure-1. The main function of a food packaging film is to avoid or at least decrease moisture transfer between the food and the surrounding atmosphere, or between two components of a heterogeneous food product[30]. Water vapor permeability shown by the native potato starch film was 0.0125 (g Pa^{-1} s^{-1} m^{-1}), for sweet potato 0.0128 (g Pa^{-1} s^{-1} m^{-1}) and that of taro starch film WVP was 0.0133 (g Pa^{-1} s^{-1} m^{-1}). Thus the film obtained from the potato starch showed maximum barrier property as compared to sweet or taro starch films.

For all the starch based films with increase in heating time resulted in decrease in WVP. The film obtained from the potato starch heated for 2 h had WVP of 0.0114 (g Pa^{-1} s^{-1} m^{-1}) and after 4 h heating, WVP was reduced to 0.0097 (g Pa^{-1} s^{-1} m^{-1}) which was much lower as compared to the native potato starch film. Similar was the trend for the sweet potato and taro starch films. Higher WVP of the taro starch may be due to fact that film formed possessed low crystallinity, more starch solubility and least swelling power thus facilitated permeation of water through amorphous region of the film.

The alginate modification of the starches had shown positive result with respect to the barrier property of the film as compared to film obtained from native starch and dry heat modified starches. As heating advanced, the starch-gum interaction strength increased which provided the crystallinity to films and sealed pores, cracks present on the films, resulted in decreased WVP of the films[36]. In case of films obtained from the starches modified with CMC showed further decrease in the WVP. The resultant interaction between CMC and phosphate group, CMC and hydroxyl group were stronger than that of alginate phosphate group and hydroxyl group interaction. The addition of CMC probably introduced a tortuous path for water molecule to pass through[37]. The film formed from the potato starch modified with CMC and heated at 130°C for 4 h possessed lowest WVP (0.00444 g Pa^{-1} s^{-1} m^{-1}) among all the films, followed by the CMC and heat modified sweet potato starch film (0.00473 g Pa^{-1} s^{-1} m^{-1}), thus making them suitable for packaging application[14].

Biodegradability

The biodegradability of different starch films after nine weeks of soil burial is shown in Figure-2. Among all the native starch films, the taro starch film showed the highest degradation rate of 56.57%, followed by the potato starch film (54.67%) and least by sweet potato starch films (54.33%). The degradation rate of the taro starch film was highest due to more exposed amorphous region. A semi crystalline polymer, such as granular starch, tends to limit the accessibility of the hydrophilic nature confining the degradation to the amorphous regions of the polymer[38]. The sweet potato and potato starch films were considered to be crystalline as compared to the taro starch film thus showed resistance to the degradation.

The dry heat modification of the starch exhibited reduced rate of biodegradation as compared to the native starches films in all the cases. The heating of the starch might had induced the association reaction i.e. promoted the crystallinity of the starch films hence reduced the biodegradation. The film formed from the modification of the starch with alginate showed reduced degradation rate as compared to native and dry heat modified starch films. The alginate bounded with the starch hydroxyl and phosphate group in the starch thus produced the association reaction which caused increase in the crystalline region. The CMC modified starch film showed highest resistance to the degradation as compared to the alginate modified starches. The ester bonding by CMC replaced the amorphous region present in the film formed from the native starches to the crystalline region, thus further reduced the biodegradability. The film formed from potato starch modified with CMC and dry heated for 4h showed biodegradation of 45.27% after 9 weeks of soil burial, followed by sweet potato (47.35%) and taro starch film (47.94%) under similar modification and process conditions. The results obtained were somewhat similar to those of[27].

SUMMARY AND CONCLUSION

The isolated starches from the potato, sweet potato and taro were dry modified with ionic gums such as sodium alginate and carboxy methyl cellulose followed by dry heating at 130°C for 2h and 4h duration. The modified starches were used to prepare biodegradable film. The prepared films were characterized for physicochemical, barrier, mechanical, and biodegradability properties. It was found that the WVP decreased significantly with modification and best results were obtained for film prepared from potato starch modified with CMC and heated for 4h. Though the film produced were having low barrier properties as compared to plastic packaging films as has been reported in the literature, but still lower enough to be used as a packaging material. The film formed with gum modification showed good resistance to normal forces encountered during handling of the packaging films. The biodegradability of the films formed was excellent compared to plastic films which are non-biodegradable. Conclusively the film produced from the potato starch modified with CMC and dry heated at 130°C for 4h had shown excellent mechanical, barrier and biodegradability property which has its potential in intrinsic food application

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