Nanomed Res J 3(1): 25-30, Winter 2018

ORIGINAL RESEARCH ARTICLE

Characterization of a new biodegradable edible film based on Sago Starch loaded with Carboxymethyl Cellulose nanoparticles

Mahsa Tabari*

Department of Food Science and Technology, Lahijan Branch, Islamic Azad University, Lahijan, Iran

ARTICLE INFO

Article History:
Received 25 December 2017
Accepted 1 February 2018
Published 15 February 2018

Keywords:
Biodegradable
Carboxymethyl Cellulose (CMC) Nanoparticles
Edible Films
Mechanical Properties
Sago Starch

ABSTRACT

Objective(s): Biodegradable film is widely used because it is free from synthetic substances and does not lead to environment pollution. This study aimed to prepare and characterize biodegradable sago starch films loaded with Carboxymethyl Cellulose nanoparticles.

Methods: Sago starch films were prepared and plasticized with sorbitol/glycerol by the casting method. Nano Carboxymethyl Cellulose with 0%, 1%, 2%, 3%, 4% and 5% (w/w) was added to the films before casting them. The effects of the addition of nanoparticles were measured on mechanical properties, water absorption capacity, density and heat sealability.

Results: In mechanical test of the combined films, by increasing of CMC nanoparticles concentration significantly ($P<0.05$) increased tensile strength and Young Modulus and elongation prameter showed significant ($P<0.05$) reduction from 17.69 to 15.39. The seal strength for the sago film was increased by incorporating a low percentage of nano Carboxymethyl Cellulose and enhanced the physicochemical properties and heat sealability of sago films.

Conclusions: Considering biodegradability of the edible films and improvement of their mechanical properties by CMC nanoparticles, they can be utilized in different industries, particularly in food industry, as an edible coating for packaging food and pharmaceutical products. With regard to its properties such as cost saving, biodegradability and mechanical properties when percentage of CMC nanoparticles increased can found a position among packaging materials.

How to cite this article
Tabari M. Characterization of a new biodegradable edible film based on Sago Starch loaded with Carboxymethyl Cellulose nanoparticles. Nanomed Res J, 2018; 3(1): 25-30. DOI: 10.22034/nmrj.2018.01.004

INTRODUCTION

Most biodegradable polymers exhibit excellent properties that are comparable with petroleum-based plastics, but their applications are limited by certain poor properties, such as brittleness and high permeability. Thus, researchers started to modify and enhance biopolymer properties. Nanotechnology is one of the most recent important technological advancement in the field. In addition to, the low amounts of nanoparticles incorporated to biopolymers improves their mechanical, thermal, and barrier properties, thus it allows the use of polymers to various applications, particularly in food packaging[1].

* Corresponding Author Email: *m_tabari@iau-tnb.ac.ir*

Packaging materials that are made from oil are not deconstructed in the environment and are dangerous for human health. During recent years, finding an alternative for sanitizing plastics which bears less environmental pollution has attracted experts' attention. Using recoverable agricultural resources is recommended for protecting the environment [2-5]. Bio polymers which are a good potential for replacing sanitized packaging materials are called green materials because of being environmentally friendly[2, 5-7]. Films refer to very thin layers that are made of food products and used as food coatings, polysaccharides protein and fat or their combination [6].

Starch is among polysaccharides that are available in nature with very low cost and have thermoplastic feature that could be used in packaging industry[8]. Sago palm is a tropical tree that can also grow in wet lands. This starch can be extracted using both traditional and modern methods. The composition of the starch from this plant is approximately the same as other starch products. Amoles and gelatin temperature is like sorghum starch; but, its fermentation with hot water is like that of potato[8, 9]. Although sago has its unique characteristics, some of its features are like those of cassava and potato. It is a complicated starch grain size with diameter of 30 μm and humidity of 0.32%-0.26%, which can produce an appropriate film[5]. The water friendly feature of starch and weak resistance of the film toward any humidity and weaker mechanical feature compared to synthetic polymers are the most important weaknesses of starch which limit its use[10].

In order to enhance its quality, biopolymers were obtained by plasticizers. Bio composite with combined films consist of 2 or more biopolymers. One of the most important polysaccharides that are used in production of edible films is cellulose and its modified forms. Cellulose is the most accessible and frequent natural polymer that forms the most primitive structure of green plants[11].

Cellulose and its modified forms is one of the composites of cellulose than can be dissolved in water and are flexible and firm by it. So, because of its resistance, it can improve strengths of films. It is also non-poisonous and cheap and can be dissolved in both hot and cold water. It can make viscosity in film, has an appropriate feature of elasticity and has many applications in producing food products[11-14]. These films should be resistant to any break or cracks and should have elasticity. Their mechanical feature depends on kind of ingredients and their preparation. The aim of this study was to directly combine nano-biopolymers and produce edible films that were nature-friendly, had appropriate mechanical features and could be used in food industry.

MATERIALS AND METHODS

Materials

Sago starch (with 12% humidity) was purchased from Sim Company ((Penang, Malaysia) and glycerol and liquid sorbitol were purchased from Traco Liang (Penang, Malaysia). Magnesium nitrate for humidity control was obtained from Sigma– ldrich (Kuala Lumpur, Malaysia), and nano CMC was obtained from Sigma Chemical Co. (St. Louis, MO, USA).

Film preparation method

Four grams of sago flour was dispersed in 80 ml of distilled water (according to water or water/ ethanol) at room temperature by simple magnetic stirring, and the pH of the dispersion was adjusted to 8 by using 1M of NaOH. Certain ratios of sago starch and CMC nanoparticles with concentrations of 1%, 2%, 3%, 4% and 5% were mixed with each other using casting method and, after adding sorbitol-glycerol 40% (w/w of starch), the compound was placed on a hot plate for 1 h. Starch suspension was heated up to 90°C and then was maintained for 45 min in order to complete gelatination. A mixture of plasticizer (sorbitol:3 /glycerol:1) that previously reported by Hebeish *et al*. as the best heat seal-ability at 40%, also added. This mixture was cooled to 40–45°C. Film making solution was poured by a pipette on the plates made of poly methyl methacrylate (with trade name of Plexiglass) with dimension of 16×16 and thickness of 2 ml. It was dried within 24 h in laboratory conditions (temperature of 25°C and relative humidity of 50°C) and was isolated from surface of the plates and maintained inside a desiccator at 23±2°C with relative humidity (RH) of 50±5% until tested. The thickness of each film was then measured using a hand-held micrometer (Mitutoyo, Tokyo,Japan), at the nearest ±0.01 mm and eight different locations. All the films (including the control) were prepared in triplicate.

Film density

Films with 2 cm × 3 cm dimensions were conditioned at 55% ± 3% RH and room temperature for 48 h. Film thickness was measured by averaging the eight measurements for each of the three replicates. Nanofilm density is the ratio of film mass to its volume (the product of area and thickness).

Heat seal strength measurement

The heatsealability of bionanocomposite films were determined according to the ASTM F-88-09 standard by using a TA.XT2 texture analyzer equipped with Texture Exponent 32 software V.4.0.5.0 [1].

Mechanical properties

Evaluation of deformation (stretching) at constant speed in a sample of standardized dimensions was used to measure the resultant force required to rupture the material. From the curves of force vs. displacement a number of parameters were determined.

Tensile Stress: (also called tensile strength), σ, expressed in MPa. This corresponds to the measured force (N) needed for the film failure (rupture) the section of the specimen [15]:

$$\sigma = F/A, \quad (1)$$

Where *F* is the force in Newton (N) and *A* is the area of the section of the test piece (thickness width in mm^2).

Elongation (also called strain), ε (unitless). This is the ratio of displacement to length of reference sample:

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l - l_0}{l_0} \quad (2)$$

Where *l* is displacement (mm) and l0 is reference length (mm). Elongation at break is reported as a percentage relative to comparison flexibility of films[15].

Young's modulus E (MPa): This parameter corresponds to the slope in the linear stress-strain curve for low elongations:

$$E = \frac{\sigma}{\varepsilon}, \quad (3)$$

The mechanical properties at each break were characterized[15]. The breaking stress and strain (σ, ε) were calculated for each sample. The test section did not vary significantly during the measurement. The shape of stress-strain curves can be used to define a particular behavior of the material as brittle (breaking in the elastic range) or ductile (failure in plastic).

ASTM D882-10 with some modification was used to determine mechanical properties at standard conditions[15]. Film strips were cut to 100 mm long and 20 mm wide and conditioned for 48 hr in 23°C and 53% relative humidity. Texture analyzer (TA. XT2, Stable Micro System, Survey, UK) equipped with Texture Exponent 32 software was used for measuring mechanical properties of the films. The initial grip separation and crosshead speed were 50 mm and 30 mm/min, respectively. Elongation and tensile strength at break were calculated from the deformation and force data recorded by the software. Eight replicates for every sample were evaluated.

Sorption isotherm

The moisture sorption isotherm at 25°C determined based on the method described by Bertuzzi[16]. Absorption tests at equilibrium were measured in triplicate for each relative humidity and reported as g absorbed water/g dry film. Experimental sorption data were fitted using GAB equation[17]. The GAB model is defined by:

$$w = \frac{w_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}, \quad (4)$$

Where w_m, *K* and C are the GAB parameters, *w* moisture content (dry basis) and a_w water activity. To evaluate accuracy of GAB model for experimental sorption isotherm data for the films the percentage of mean relative deviation modulus (E) was calculated. It is given by the following formula:

$$E = \frac{100}{N} \sum_{i=1}^{N} \frac{|m_i - m_{pi}|}{m_i}, \quad (5)$$

Where *N* is the number of experimental data, m_i and m_{pi}, are the experimental predicted value respectively. The modulus (*E*) value below 10% indicates a good practical fit [18].

RESULTS AND DISCUSSION

Density and thickness

The film density decreased by increasing the percentage of nano CMC and showed small variations (Table 1). The reduction in density might be attributed to the enhanced thickness (and volume) in relation to the increased nano CMC content.

Table 1. Densityand heat seal strength property of sago nanocomposite films

Nano CMC(g/g Sago)	Density(g/cm^3)	Seal strength (N/m)
0	1.433±0.114^a	321±33.5^d
0.01	1.280±0.095^a	395±29.1^a
0.02	1.296±0.082^a	386±44.7^b
0.03	1.248±0.004^a	346±32.5^c
0.04	1.196±0.002^a	338±44.5^{cd}
0.05	1.059±0.019^a	335±22.6^{cd}

Different letters in each column represent significant difference among semolina films at the 5% level of probability

Heat seal strength measurement

Heat sealability is an important factor in the use of films for packaging. The final results on the seal strengths of sago-based nanocomposite films prepared are revealed in Table 1. The seal strength for semolina film was inhanced by incorporating a low percentage of nano CMC. This increscent was probably related to the improvement of hydrogen and other bonds on the surface by nano CMC. However, the sealability of the films decreased with the addition of a great percentage of kaolin, which was likely caused by the reduction in moisture content and the flexibility of the films[2].

Mechanical properties

These results demonstrated that tensile stress of the films increased from 20.2 to 26.99 MPa when concentrations of CMC nanoparticles of these films increased from 0 to 5% and the Young modulus decreased from 1 to 5 % CMC nanoparticles content and slighly increase at 5 % dosage before decreasing again (Table 2). Values of tensile strength of the films containing CMC nanoparticles were significantly higher than those of the control films (P<0.05). Adding CMC nanoparticles did not have a significant effect on reduction of film elongation compared with the control film. Elongation percent significantly decreased from 17.70 to 15.40 (P<0.05) with increasing concentration of CMC nanoparticles (from 0 to 5%).

The Young modulus decrease seems to be much more realistic. Increased tensile strength was due to surface interaction between starch matrix and fillers due to chemical similarity between structures of polysaccharides. Other researchers investigated effect of calcium chloride on physical and mechanical properties of alginate-sago edible films. Increased concentration of calcium chloride increased tensile strength of alginate-sago edible films but increased elongation percent of these films [5, 7, 10, 13]. In some cases, reported that adding CMC nanoparticles to soy protein film could improve mechanical properties of these films due to reaction and connection between polymeric chains of protein[12, 19].

Parra *et al* conducted studies on mechanical properties of edible films caused by cassava starch. They produced transparent and flexible films from cassava starch, in which glycerol and polyethylene glycol were used as softener and glutaraldehyde was used as cross-linking. In the resulting films at 1% level of glycerol, tensile strength and elongation percent increased with increase of glutaraldehyde rate while these properties were reduced at glycerol level of above 1%. Also, at levels of above 1% glycerol, increase in rate of polyethylene glycol considerably increased elongation percent [20].

Table 2. Results of mechanical properties sago starch with adding CMC

Concentration	Tensile Stress (N/m^2)	Percent Elongation (%)	Young's modulus (N/m^2)
Control Sago	20.2926±0.024^a	1372.65±23.7^a	17.6973±0.322^a
Control CMC	28.4622±0.020^b	2020.82±12.1^b	12.0974±0.054^b
1%	22.5714±0.015^{ab}	1464.53±14.2^a	17.4840±0.052^a
2%	25.0014±0.012^a	1571.62±17.2^{ab}	16.8735±0.062^a
3%	26.4696±0.027^b	1722.24±11.6^b	15.9645±0.030^{ab}
4%	26.9993±0.033^{ab}	1842.32±10.9^{ab}	15.0352±0.045^{ab}
5%	27.3451±0.013^b	1844.23±21.1^{ab}	15.0161±0.026^{ab}

Different letters in each column represent significant difference among semolina films at the 5% level of probability

Table 3. GAB equation parameters for sago starch films containing CMC at 20°C

Concentration	M_0	C_G	K	E (%)
Nano CMC Control	0.084	848.682	0.842	7.91
Sago Control	0.103	104.180	0.846	7.13
1% CMC nanoparticle	0.099	133.754	0.844	7.99
2% CMC nanoparticle	0.096	233.641	0.843	6.49
3% CMC nanoparticle	0.094	657.544	0.842	6.67
4% CMC nanoparticle	0.089	677.000	0.858	6.34
5% CMC nanoparticle	0.088	678.043	0.869	6.44

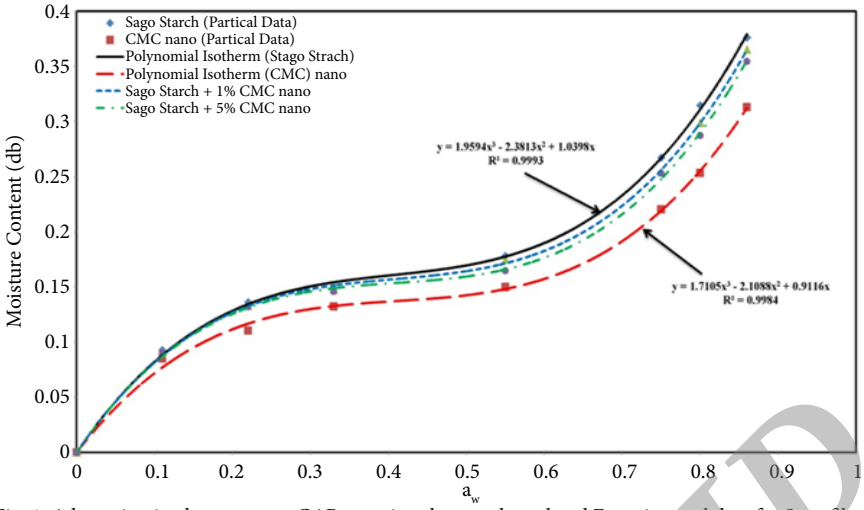

Fig. 1. Adsorption isotherm curves GAB equation theory adapted and Experimental data for Sago films in

Equilibrium adsorption diagrams

Adsorption isotherm curves GAB equation theory adapted and Experimental data for sago starch films in 20°C are presented in Fig. 1 and GAB equation parameters are presented in Table 3.

Absorption isotherm

The moisture sorption isotherm at 25°C determined and shows that increased concentration of CMC nanoparticles reduced humidity absorption of composite films. This could be explained by the presence of CMC nanoparticles, hydrophobic character improved the hygroscopic characteristics of sago starch films.

Studies showed that increased concentration of CMC reduced humidity content due to hydrophobicity property of CMC nanoparticles. Adding CMC improved starch network so that starch could form hydrogenous bond with hydroxyl and carboxyl groups of CMC, leading to reinforcement of structure and reduction in diffusion of water molecules through starch network.

Similar results were also obtained by other researchers who observed reduction of water absorption by polymeric mixtures and bio-composites via adding cellulose–hemicellulose fibers[5, 7, 13, 15]. Ghanbarzadeh *et al* also produced films from corn starch with different amounts of citric acid and CMC, in which increased concentration of citric acid and CMC reduced humidity absorption of composite films[10].This result might be related to the interactions between CMC and Sago in the film structure. The final experimental results demonstrated that when the nanoparticle content of semolina films was high, considerable hydrogen bonds formed between the CMC and matrix components[21]. Free water molecules do not interact as strongly with nanocomposite films as with composite films alone. This result is consistent with the results obtained by other researchers on nanobiocomposites[21-22].

Equilibrium adsorption diagrams

Increased concentration of carboxymethyl cellulose reduced humidity absorption of composite films. Blahov reported for $0 \leq K \leq 1$ and $CG > 2$ films are type II from classification of Brunauer Emmett, and Teller. So this sago starch film is type II of Brunauer classification[23, 24]. Due to the presence of more hydroxyl groups in the molecule, sago starch interacted with water by hydrogen bonding. The results show that adding and changing concentration of sago starch is effective in reducing the equilibrium moisture absorption. These results were consistent with the results of other researchers that with the addition of carboxymethyl cellulose to soy protein isolate decreased the equilibrium moisture absorption [2, 15, 18].

CONCLUSION

This study on composite films of sago starch and CMC showed that:

Increased concentration of CMC reduced equilibrium moisture in composite films and improved mechanical properties of films which

included increased tensile stress and hardness of the composite films compared with the control film. These films, unlike synthetic polymers, were biodegradable in the environment.

Considering the obtained results, the composite films showed better physical and mechanical properties than the control film and they could be used in packaging industry and the composite films were economically cost effective.

ACKNOWLEDGMENTS

The author wish to sincerely thank all who assisted in preparation of this work.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Rhim, J.-W., J.-H. Lee, and H.-S. Kwak, Mechanical and water barrier properties of soy protein and clay mineral composite films. Food Science and Biotechnology, 2005. 14(1): p. 112-116.
2. Abdolahi A, Hamzah E, Ibrahim Z, Hashim S. Synthesis of Uniform Polyaniline Nanofibers through Interfacial Polymerization. Materials. 2012;5(8):1487-94.
3. Mariño M, Lopes da Silva L, Durán N, Tasic L. Enhanced Materials from Nature: Nanocellulose from Citrus Waste. Molecules. 2015;20(4):5908-23.
4. Razak N, Ibrahim N, Zainuddin N, Rayung M, Saad W. The Influence of Chemical Surface Modification of Kenaf Fiber using Hydrogen Peroxide on the Mechanical Properties of Biodegradable Kenaf Fiber/Poly(Lactic Acid) Composites. Molecules. 2014;19(3):2957-68.
5. Veeramachineni A, Sathasivam T, Muniyandy S, Janarthanan P, Langford S, Yan L. Optimizing Extraction of Cellulose and Synthesizing Pharmaceutical Grade Carboxymethyl Sago Cellulose from Malaysian Sago Pulp. Applied Sciences. 2016;6(6):170.
6. McHugh TH, Krochta JM. Sorbitol- vs Glycerol-Plasticized Whey Protein Edible Films: Integrated Oxygen Permeability and Tensile Property Evaluation. Journal of Agricultural and Food Chemistry. 1994;42(4):841-5.
7. Park SK, Hettiarachchy NS, Were L. Degradation Behavior of Soy Protein−Wheat Gluten Films in Simulated Soil Conditions. Journal of Agricultural and Food Chemistry. 2000;48(7):3027-31.
8. Ačkar Đ, Babić J, Jozinović A, Miličević B, Jokić S, Miličević R, et al. Starch Modification by Organic Acids and Their Derivatives: A Review. Molecules. 2015;20(10):19554-70.
9. Lemlioglu-Austin D, Turner ND, McDonough CM, Rooney LW. Effects of Sorghum [Sorghum bicolor (L.) Moench] Crude Extracts on Starch Digestibility, Estimated Glycemic Index (EGI), and Resistant Starch (RS) Contents of Porridges. Molecules. 2012;17(9):11124-38.
10. Ghanbarzadeh B, Almasi H, Entezami AA. Physical properties of edible modified starch/carboxymethyl cellulose films. Innovative Food Science & Emerging Technologies. 2010;11(4):697-702.
11. Jahit, I., et al., Preparation and physical properties of gelatin/CMC/chitosan composite films as affected by drying temperature. International Food Research Journal, 2016. 23(3).
12. Tabari M. Investigation of Carboxymethyl Cellulose (CMC) on Mechanical Properties of Cold Water Fish Gelatin Biodegradable Edible Films. Foods. 2017;6(6):41.
13. Hu D, Wang H, Wang L. Physical properties and antibacterial activity of quaternized chitosan/carboxymethyl cellulose blend films. LWT - Food Science and Technology. 2016;65:398-405.
14. Li H, Wu B, Mu C, Lin W. Concomitant degradation in periodate oxidation of carboxymethyl cellulose. Carbohydrate Polymers. 2011;84(3):881-6.
15. Bertuzzi MA, Castro Vidaurre EF, Armada M, Gottifredi JC. Water vapor permeability of edible starch based films. Journal of Food Engineering. 2007;80(3):972-8.
16. Van den Berg, C., Water activity in concentration and drying of foods, in Concentration and drying of foods. 1986. p. 11-36.
17. Masclaux-Daubresse C, Daniel-Vedele F, Dechorgnat J, Chardon F, Gaufichon L, Suzuki A. Nitrogen uptake, assimilation and remobilization in plants: challenges for sustainable and productive agriculture. Annals of Botany. 2010;105(7):1141-57.
18. Parra D, Tadini C, Ponce P, Lugao A. Mechanical properties and water vapor transmission in some blends of cassava starch edible films. Carbohydrate Polymers. 2004;58(4):475-81.
19. Qi X-M, Liu S-Y, Chu F-B, Pang S, Liang Y-R, Guan Y, et al. Preparation and Characterization of Blended Films from Quaternized Hemicelluloses and Carboxymethyl Cellulose. Materials. 2015;9(1):4.
20. Blahovec J. Sorption isotherms in materials of biological origin mathematical and physical approach. Journal of Food Engineering. 2004;65(4):489-95.
21. Tunç S, Duman O. Preparation and characterization of biodegradable methyl cellulose/montmorillonite nanocomposite films. Applied Clay Science. 2010;48(3):414-24.
22. Kim SJ, Ustunol Z. Thermal Properties, Heat Sealability and Seal Attributes of Whey Protein Isolate/ Lipid Emulsion Edible Films. Journal of Food Science. 2001;66(7):985-90.
23. Zeppa C, Gouanvé F, Espuche E. Effect of a plasticizer on the structure of biodegradable starch/clay nanocomposites: Thermal, water-sorption, and oxygen-barrier properties. Journal of Applied Polymer Science. 2009;112(4):2044-56.
24. Hebeish A, Higazy A, El-Shafei A, Sharaf S. Synthesis of carboxymethyl cellulose (CMC) and starch-based hybrids and their applications in flocculation and sizing. Carbohydrate Polymers. 2010;79(1):60-9.