ISSN : 0974 - 7443 Volume 9 Issue 4

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 9(4) 2014 [134-139]

Physical properties of starch–Carboxy methyl cellulose composite films incorporated with Iranian honey propolis extract

Azadeh Sadat Shekarabi[1]*, Abdol Rasool Oroomiehie[2], Ali Vaziri[1], Mahdi Arjmand[3], Ali Akbar Safekordi[1]

[1]Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, (IRAN)
[2]Khatam Polymer Co. Units 9, No.2, Hamsayeghan str. Valiaser Str. Tehran, (IRAN)
[3]Chemical Engineering Department, Islamic Azad Universities Tehran South Branch, Tehran, (IRAN)
E-mail: azadehshekarabi@yahoo.com

ABSTRACT

The aim of this study was to develop and characterize antimicrobial edible films produced from amylose of starch and Carboxy methyl cellulose, Honey propolis extract and plasticized with glycerol. The physical properties of the films were characterized. A water-based coating with desirable barrier properties is important for the environment as well as health. The films obtained were easily manageable and flexible. Carboxy methyl cellulose reduced tensile strength (TS), while starch at concentrations above 60% increased it. The elongation at break values (EAB %) were higher for films containing higher Carboxy methyl cellulose concentrations. Water vapour permeability of films was found to increase as the antimicrobial agents content increased. Glass transition temperatures increased as a result of propolis honey extract content increased. Thus, it was observed that propolis honey extract is a significant factor in the properties of these films and their food technology applications.

KEYWORDS

Antimicrobial film;
Honey propolis extract;
Physical properties;
Starch;
Thermal properties.

INTRODUCTION

The food industry faces challenges related to the protection of the properties of products. Preserving the characteristics of food products by using preservatives or developing protection systems such as packaging, films and coatings, is in progress area of study[1]. One of the most cost effective ways to keep quality and safety of food products is to use edible films. The function of edible films is to provide a barrier to the water vapor, incorporate functional agents such antimicrobials, antioxidants, probiotics to products and improve mechanical-handling propertie[2]. The significant film-forming materials are polysaccharides (i.e. starch, carrageenan, pectin, alginate, carboxy methyl cellulose and chitosan), proteins (i.e. wheat gluten, whey protein isolate, caseinate and soy protein), and lipids (i.e. waxes and fatty acids)[3]. Several studies have reported the use of polysaccharides to prepare coatings and films with different properties, and have shown that these carbohydrates are promising materials[4]. Antimicrobial films and coatings have been used as active packaging developed to reduce, inhibit or delay the growth of microorganisms on the surface of foods in contact with the packaged product[5]. Selection of formulation for edible film or coating largely depends on its desired function such as appearance, biodegradability, edibility, good barrier properties against water vapor which varies based on composition of the coating[6]. Corn starch is used as the base of this formulation because of its characteristic in forming a continuous matrix, renewability and abundance[7]. However, starch exhibits several disadvantages such as poor mechanical properties and strong hydrophilic character (water sensitivity) compared to conventional synthetic polymers, which make it unsatisfactory for some applications such as packaging[8].

Carboxy methyl cellulose (CMC), water-soluble polysaccharides available at various molecular weights and viscosities, is non-toxic and non-allergenic. It is often used with starches to provide a desirable texture and control moisture of pharmaceutical formulations, textiles, paper and food and as filler in bio composite films. In addition, CMC enhances mechanical and barrier properties of starch-based films[9]. Honey propolis extract (HPE) is incorporated in the formula as an antimicrobial, antifungal and antibacterial agent. Propolis, a flavonoid-rich product of honey comb is very powerful natural antibiotic and very useful in fighting upper respiratory infections, such as common cold and influenza viruses[10] Several aspects of its use indicate that it also functions as an antibacterial, antioxidant, antitumor, anti-inflammatory, anti-browning, and antiviral compound[9]. The mechanical, water vapor permeability and thermal properties of edible films can be modified by addition of various materials. For instance addition of plasticizers such as glycerol could modify mechanical properties of edible films. Plasticizers decrease intermolecular attractions between adjacent polymeric chains and increase film flexibility which may also cause significant changes in the barrier properties of the films[11]. This study aims to develop a new antimicrobial edible film based on starch/Carboxy methyl cellulose composite films; to determine the influence of Iranian HPE on the antimicrobial properties of film-forming solutions; and to investigate its impact on the physical properties (water vapour permeability, mechanical and thermal) of films.

MATERIALS AND METHODS

Materials

Corn starch was provided from Glucosan Industry (Ghazvin, Iran). Carboxy methyl cellulose (CMC) with average molecular weight of 41,000 (food grade) was purchased from Caragum Parsian Corporation (Tehran, Iran). Glycerol (LR grade) which was used as plasticizer obtained from MojallaliCompany (Tehran, Iran) and propolis honey sample were purchased from Iranian honeybees located on Karaj farms.

Film preparation

Films with composition of 70% corn starch and varying amounts of glycerol (plasticizer), CMC and antimicrobial agents were produced. The 70% amylose content was chosen as mechanical properties tests showed this ratio to be the optimum, as indicated later in the results section of this paper in TABLE 1. Corn starch (1 g) was mixed (25 °C for 5 min) with distilled water (100 mL). These suspensions were agitated by a magnetic stirrer (500 rpm) for 30 min in a water bath (90 °C); then, the suspension was cooled to 10° to separate amylose solution. From these dispersions, water was removed by filtration on the next day and then glycerol (5 ml/100 g starch) was added to the dispersions and Carboxy methyl cellulose (1% W/W) was solubilized in 75 ml of distilled water at 75°C for 20 min. The CMC and amylose solutions were mixed together and stirred at 45 °C for 10 min (PH=5.5). HPE as an antimicrobial agents was added to solutions in 0%, 0.50%, 1.50%, 3% and 5%(w/w) concentrations. These solutions were homogenized under aseptic conditions at 500 rpm for 1 min. Dispersions were then cooled at 25 °C and mixed gently for 20 min to release all air bubbles. Then, about 70 mL of the sample was poured into a Teflon casting tray resulting in films with 0.08±0.01 mm thickness, measured by an Alton M820-25 hand-held micrometer (China) with sensitivity of 0.01 mm; then, they were dried at 35 °C in an oven to cast the films.

Water vapor permeability rate (WVP)

WVP properties of the films were studied using the standard ASTM E 96 with some modifications[12]. Special cups with average diameter of 1 cm and depth

TABLE 1 : Formulation of edible films

Film's Type	Amylose solution (%w/w)	CMC Solution (%w/w)	Propolis Honey (%w/w)	Glycerol (%w/w)
Starch +CMC (PHE 0%)	70.0	29.5	0.0	0.5
PHE 5%	70.0	24.5	5.0	0.5
PHE 3%	70.0	26.5	3.0	0.5
PHE 1.5%	70.0	28.5	1.5	0.5
PHE 0.5%	70.0	29.5	0.5	0.5

of 2.5 cm were utilized to determine WVP of films. The films were cut by a diameter slightly larger than diameter of the cup into discs; then, they were covered by edible films with varying compositions. Each cup was placed in a desiccator containing saturated $Mg(NO_3)_2.6H_2O$solution, which provides a Constant RH of 52% and 25°C. Then cups were weighed every 24 h and water vapor transport was determined by the weight loss of the cup. Changes in the weight of the cup were recorded as a function of time. Slopes were calculated by linear regression (weight change versus time) and water vapor transmission rate (WVTR) was calculated by dividing slope of the curve by the transfer area (m^2) WVP ($g\ m^{-1}\ h^{-1}\ Pa^{-1}$) was calculated as[13]:

$$WVP = \frac{WVTR}{P(R_1 - R_2)} \quad (1)$$

Where P is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R1 is the RH in the desiccator, R_2, the RH in the cup and X is the film thickness (m). All measurements were performed in three replicates.

Mechanical properties

Ultimate tensile strength (UTS) and strain to break (SB) of the films were determined at 24 °C±1 °C using a tensile tester (Elma, Tehran, Iran) according to ASTM standard method D882-ASTM, Three dumbbell forms (10 cm×1 cm) were cut from each of the samples and mounted between grips of the machine. The initial grip separation and cross-head speed were set to 50 mm and 2 $mm.min^{-1}$, respectively[14].

Film solubility in water

For this study, solubility in water was determined as the ratio of the water soluble dry matter of film that is dissolved after immersion in distilled water[15]. A circular film sample was cut from each film, dried at 100 ± 2 °C for 24 h in a laboratory oven, and weighed to determine the initial dry weight. The solubility in water of the different composite films was measured from immersion test in 50 ml of distilled water with stirring for five hours at 25°C. After that period, the remaining pieces of films were taken out and dried at 100 ± 2 °C until constant weight (final dry weight). The percentage of the total soluble matter TSM of the films was calculated using Equation 2.TSM tests for each type of film were carried out in three replicates.

$$\%\ TSM = \frac{[\text{initial dry weight}] - [\text{final dry weight}]}{[\text{initial dry weight}]} \times 100 \quad (2)$$

Differential scanning calorimetry (DSC)

The thermal properties of the films were carried out using DSC equipment (Setaram, France). The sample weight ranged between 10 and 15 mg. was cut as small pieces and placed into a sample pan of DSC equipment. Samples were scanned at a heating rate of 10°C/min between temperature ranges of -50°C and 150 °C. Nitrogen was used as the purge gas at a flow rate of 20 ml/min. An empty aluminum pan was used as reference. All these properties were determined in duplicates and the results were averaged.

Statistical analysis

The data of physical, chemical, microbiological and sensory parameters were performed and analyzed statistically by ANOVA procedure in SPSS (version 20, Chicago, IL USA) software. Duncan's multiple range test ($p<0.05$) was used to detect differences among mean values of film properties.

RESULTS AND DISCUSSION

Water vapor permeability

Figure 1 shows the water vapour permeability (WVP) values of different composite films. The control film showed higher permeability values than other filmscontaining antimicrobial substances. In fact, WVP declined with the increase of antimicrobial substances. HPE significantly declined WVP of composite films, according to Figure 1. WVP of the control films was 3.0129×10-7g/m.h.Pa and decreased to 1.3072×10-7g/m.h.Pa for 3% HPE containing films. The film containing 3% HPE had significantly ($p<0.05$) the lowest WVP value. Reduction of WVP with increasing HPE resulted in improvement of the hydrophilic characteristics of the antimicrobial agent's matrix; thus, resulting in decreased diffusivity of water vapor through the film matrix. Decreased WVP by incorporation of antimicrobial substances was in agreement with the results usually reported for polymer blends which are studied for packaging applications[16].

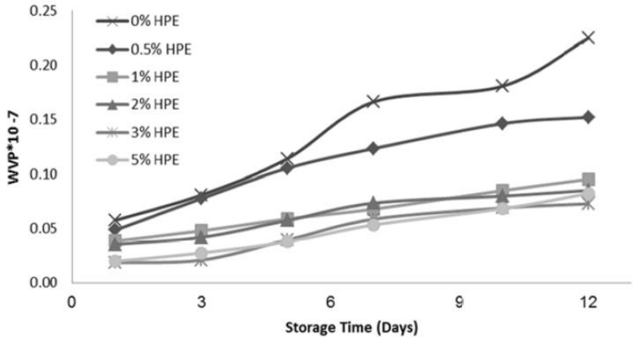

Figure 1 : Effect of HPE concentration on WVP of composite films (p<0.05)

Mechanical properties

Figures 2 and 3 compare tensile strength and elongation of the control film (amylose and CMC blend) and composite films containing HPE. Improvement was seen by addition of antimicrobial agents. The results show improvement of mechanical strength with the increase of antimicrobial agents. This issue was in agreement with the results in which addition of cinnamon essential oil in films of chitosan significantly increased tensile strength of the films. It could be attributed to the strong interaction between polymer and oil with a crosslinking effect, which could reduce free volume of the polymer[17]. According to figures with increasing antimicrobial substance concentration from (0.5% to 5% w/w), UTS increased significantly ($p<0.05$) compared to the control films. The films which do not contain any additives had poor result, which indicates that HPE would probably protect the food from loss of firmness. In general, the HPE films (3%) had higher ($P<0.05$) values of this parameter. It seems that HPE could improve films' strength due to the strong interaction between polymer and extraction oil which reduced free volume and molecular mobility of the polymer[18]. Adding bioactive agent did not significantly affect tensile strength and elastic modulus of the films based on hydroxyl propyl methylcellulose (HPMC) containing propolis extract at different concentrations (0 to 1.5%). However, the elongation at break of these films diminished with increasing concentration of the propolis extracts[17]. Regarding another study, by increasing thyme oil in chitosan films, significant reduction of the tensile strength of the films and decreased percentage of elongation were resulted as a consequence of the increase in film porosity[19].

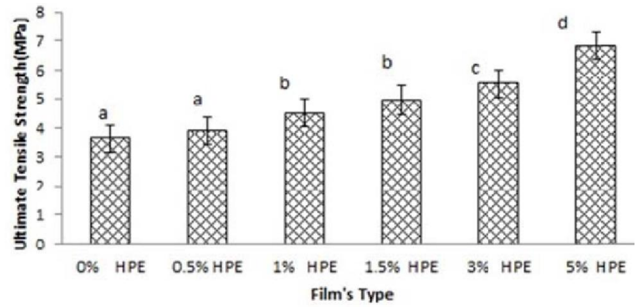

Figure 2 : Effect of HPE concentration on ultimate tensile stress response (p<0.05)

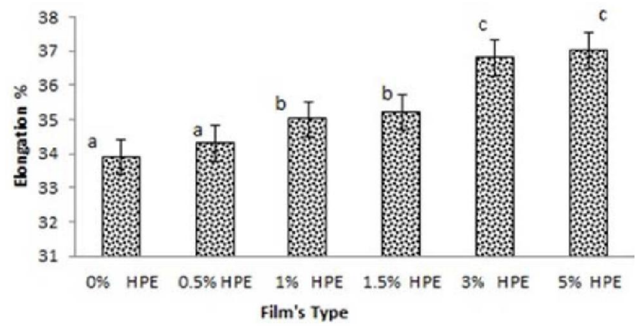

Figure 3 : Elongation at break of composite films based on different HPE concentration (p<0.05)

Film solubility in water

Solubility in water is major property of edible films, since potential applications may require water insolubility to enhance product integrity and water resistance. TABLE 2 shows the effects of incorporating HPE on the physical properties of composite films. Thickness of films varied between 0.065 and 0.079 mm, as shown in TABLE 2.The amount of water present in composite films provides an indication of the films hydrophilicity, being the more hydrophilic films those that present the highest values of moisture content At the same pH, all films with greater HPE content exhibited a higher solubility in water ($p<0.05$). As can be seen in TABLE 2 the water solubility of control film isrelatively around 19.5%, the addition of HPE drastically improved the

TABLE 2 : Film solubility and moisture content of films obtained with different Iranian HPE concentration

HPE Concentration (%w/w)	Thickness (mm)	Moisture Content (%)	Solubility in water (%)
0	0.065	13.83	19.48
0.5	0.069	15.53	23.41
1.5	0.076	19.08	39.51
3	0.071	23.32	45.82
5	0.079	28.50	56.48

water resistance of composite films in the mixtures, solubility in water in the film with 5% HPE is about 56.5%.

Thermal properties

The effect of HPE concentration in composite films on the thermal properties was studied by DSC. The initial temperature of degradation, temperature at maximum degradation rate and apparent enthalpy were measured using the first DSC scan for all the films. TABLE 3 shows the glass transition temperatures (Tg) and melting temperatures (Tm).The glass transition temperature (Tg) is the temperature at which the material undergoes a structural transition from a glassy state to a more viscous rubbery state[20]. The findings of this study exhibited that control films (amylose +carboxy methyl cellulose) had a Tg value of about (70.4±4°C), Tm (127± 0.8°C) and Δ*H* of (119.23). Incorporating honey propolis honey (0.5% to 5%) into the composite films significantly decreased T_g, T_m and Δ*H*. Antimicrobial substances in amylose based films makes films more hydrophilic and keep higher moisture compared to control films when conditioned at the same humidity (RH %) and temperature. Composite film contain 5% HPE had a Tg value of about (60.4±0°C), Tm (102± 0.5°C) and of (89.48).

TABLE 3 : Differential scanning calorimetry (DSC) measurement results of composite films with different Iranian HPE concentration

Film's Type	T_G (°C)	T_{max} (°C)	ΔH_f (J g^{-1})
o% HPE	74	127.5	119.23
0.5% HPE	73	125	116.61
1.5% HPE	70	120	101.23
3% HPE	63	113	95.45
5% HPE	60.5	1.2.3	89.48

CONCLUSION

Honey propolis extract presence in composite edible films formulated with amylose, carboxymethyl cellulose and glycerol increased flexibility of films. The addition of HPE could improve mechanical properties of composite films made from amylose and carboxy methyl cellulose and decreasing permeability. Hence, it is possible to replace HPE in some applications. HPE revealed higher antibacterial activity against yeast and mold. Moreover, the concentration of the antimicrobial substance in the film affected the physical and mechanical properties of the films to various extents. In this case, The film prepared with the 5% w/w HPE was found to be the best as it had lower water vapour permeability and film solubility. These results suggest a high potential of these films to be used as active packaging materials, and further studies would be required to determine the use of these films in commercial food systems.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to Khatam polymer Institute. Author Shekarabi expresses her thanks and appreciation for this support.

REFERENCES

[1] A.L.Fadini, F.S.Rocha, I.D.Alvim, M.S.Sadahira, M.B.Queiroz, R.M.V.Alves, L.B.Silva; Food Hydrocoll, **30**, 625-631 **(2013)**

[2] F.Tihminlioglu, I.Dogan, A.Banu Ozen; J.Food.Eng., **96**, 342–347 **(2010)**.

[3] F.Falguera, J.P.Quintero, A.Jimenez, J.A.Munoz, A.Ibarz; Trends Food Sci.Tech., **22(6)**, 292–303 **(2011)**.

[4] M.Ghasemlou, F.Khodaiyan, A.R.Oroomiehie, M.Yarmand; Int.J.Biol.Macromol, **49**, 378–384 **(2011)**.

[5] A.M.Durango, N.F.F.Soares, N.J.Andrade; Food Contrl., **17**, 336–341 **(2006)**.

[6] M.S.Chinnan, D.S.Cha; Crit.Rev.Food.Sci.Nut., **44**, 223-237 **(2005)**.

[7] B.Ghanbarzadeh, H.Almasi, A.Entezami; Innov Food Sci.Emerg.Technol., **11**, 697–702 **(2010)**.

[8] H.Dureja; Int.J.Pharm.Sci.Drug.Res., **(2011)**.

[9] P.Delaquis, K.Stanich, B.Girard, G.Mazza; Int.J.Food Microb., **74**, 101-109**(2002)**

[10] M.Motior Rahman, A.Richardson, M.Sofian Azirun; Microbiol.Res., **4(16)**, 1872-1878 **(2010)**.

[11] E.Rezvani, G.Schleining, G.AhSumen, A.R.Taherian; J.Food Eng., **116**, 598–605 **(2013)**.

[12] ASTM E96-95, Annual book of ASTM, Philadelphia, PA: American Society for Testing and Materials, **(1995)**.

[13] H.Saderi, P.Owlia, A.Hosseini, H.Semiyari; WOCMAP III, Traditional Medicine & Nutraceuticals, **6**, **(2006)**.

[14] ASTM D 882-91, Annual book of ASTM. Philadelphia, PA: American Society for Testing and Materials, **(1996)**.

[15] N.Gontard, C.Duchez, B.Cuq, S.Guilbert; Food Sci.Technol., **29**, 39–50 **(1994)**.

[16] L.Fama, L.Gerschenson, S.Goyanes; Carbohydr.Polym., **75**, 230-235 **(2009)**.

[17] S.M.Ojagh, M.Rezaei, S.H.Razavi, S.M.H.Osseini; Food Chem., **122**, 161-166 **(2010)**.

[18] C.Pastor, L.Sanchez-Gonzalez, M.Chafer, A.Chiralt, C.Gonzaez-Martinez; Carbohydr Polym., **82(4)**, 1174-1183 **(2010)**.

[19] D.Altiok, E.Altiok, F.Tihminlioglu; Mater.Sci., **21**, 2227-2236 **(2010)**.

[20] E.Ibanoglu; Food Chem., **90**, 621–626 **(2005)**.