Effect of antimicrobials on mechanical, barrier and optical properties of corn starch based self-supporting edible film

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Abstract

Antimicrobials like potassium sorbate, sodium propionate, and benzoic acid were incorporated in corn starch based formulation to investigate their effect on mechanical, water vapour barrier and optical properties of the developed self-supporting edible film. The film was prepared by casting technique. When incorporated at 1.40% and above, potassium sorbate decreased the tensile strength (about 22%) and increased the elongation (about 55%) of control film; whereas, it increased the water vapour permeability by 15% only when added at 2.66%. At 2.66%, benzoic acid reduced the tensile strength by 24% and sodium propionate increased elongation by 17%. These two antimicrobials did not change the water vapour permeability. However, all the three antimicrobials adversely affected the optical properties by decreasing the whiteness index, increasing yellowness index, and reducing the surface gloss, with potassium sorbate showing the maximum effect. Among the three antimicrobials, sodium propionate appeared to be the best with minimum deterioration of film properties.

Keywords: edible film; antimicrobials; corn starch film
**Nomenclature**

ANOVA  Analysis of variance  
BA      Benzoic acid  
% E     Percent elongation  
HPMC    Hydroxypropylmethylcellulose  
PS      Potassium sorbate  
RH      Relative humidity  
SP      Sodium propionate  
SSEF    Self-supporting edible film  
TS      Tensile strength  
WI      Whiteness index  
WVP     Water vapour permeability  
Z%      Brightness index

**1 Introduction**

Food grade ingredients like carbohydrates, proteins, lipids and plasticizers, in different combinations can be cast into self-supporting edible films (SSEF) aiming for several food quality control purposes to improve shelf-life. The hydrocolloids that have been used for this purpose include polysaccharides like celluloses, starches, and their derivatives, seaweed extracts, pectins, gums, chitosan, and different proteins. Recently starch based SSEF are being considered because of their desirable physical characteristics such as being transparent, odorless, tasteless, semi-permeable to CO$_2$ and resistant to O$_2$ passage (Nisperos-Carriedo, 1994; Vásconez, Flores, Campos, Alvarado, & Gerschenson, 2009). Starch is abundantly available and cheap. SSEF that additionally contains an antimicrobial in its formulation can be used as an active packaging wrapper on fresh/minimally processed fruits and vegetables where the antimicrobial diffuses into the interior and extends the shelf life of the contents (Das & Namitha, 2010; Durango, Soares, & Andrade, 2006; Garcia, Martino, & Zaritzky, 1998). The film can effectively preserve the organoleptic and nutritional qualities of the wrapped food (Campos, Gerschenson, & Flores, 2011). These antimicrobial-containing films can also be layered within fabricated multilayered foods like wafers, cakes, pastries, etc. to retard the growth of microbes at particular sites. Through such techniques, addition of the antimicrobial to the whole of the food mass can be avoided (Salleh, Muhamad, & Khairuddin, 2009; Valencia-Chamorro, Palou, Del Rio, & Perez Gago, 2008).

Self-supporting edible films have excellent aroma barrier properties (Das & Bal, 1999), and therefore can preserve the quality of aroma-containing materials when packaged with these films. Moreover, the water dispersible character of these films facilitates packaging of specific food additives in separate pouches which can go into the cooking medium, dispersing both additives and pouches together. This helps the addition of pre-measured additives for better quality control in food processing as well as a reduction in conventional petroleum-based synthetic pouch disposal (Das & Bal, 1999; Ninomiya, Suzuki, & Ishii, 1992; Schou et al., 2005; Patel & Thanawala, 2008; Yang, Fuisz, Myers, & Fuisz, 2004). Nonetheless, as they are made from edible materials, on exposure to the open environment SSEF without any antimicrobial additive are susceptible to infection by air-borne microbes, particularly in humid conditions. So, besides providing active packaging, the incorporation of antimicrobial preservatives into the film may become essential for stability of the film itself (Chowdhury & Das, 2010). However, such addition should not bring about any detrimental effects to film properties. Several studies have reported the efficacy of essential oils and other natural antimicrobials in different starch based formulations towards the antimicrobial potency of the film as well.
as the physical properties (Fazilah, Maizura, & Norziah, 2006; Khairuddin, Razi, Radhiah, & Muhamad, 2005; Kechichian, Ditchfield, Veiga-Santos, & Tadini, 2010; Maizura, Fazilah, Norziah, & Karim, 2007; Salleh & Muhamad, 2007). Some low molecular weight synthetic organic acids (acetic, benzoic, lactic, propionic, and sorbic acids) and their salts may also be incorporated for antimicrobial activity in edible films (Valencia-Chamorro et al., 2008); an added advantage is that such antimicrobials are low cost. However, Ofman, Campos, and Gerschenson (2004) observed that such low molecular weight preservatives can form intermolecular complexes and modify film properties, depending on their concentration and chemical characteristics as well as on the type of starch used in film matrix. They reported that even low levels of ionic compounds affect potato starch gel, while cassava starch remains insensitive. Recently, Flores, Fama, Rojas, Goyanes, and Gerschenson (2007) concluded that potassium sorbate at a level of 6% in tapioca starch affected the solubility, colour and mechanical properties of films. Shen, Wu, Chen, and Zhao (2010) studied the effect of up to 15% potassium sorbate on mechanical properties and water vapour permeability of sweet potato starch film. Fama, Rojas, Goyanes, and Gerschenson (2005) indicated a lowering of crystallinity in tapioca starch film with addition of 6% potassium sorbate. However, reports on the addition of potassium sorbate to corn starch films, and addition of sodium propionate and benzoic acid to starch films in general are limited. Such preservatives also modify other polysaccharide based films (Valencia-Chamorro et al., 2008). The objective of the present work was to investigate the effect of incorporation of the antimicrobials benzoic acid (BA), sodium propionate (SP), and potassium sorbate (PS) in corn starch based film formulation on physico-mechanical properties of the final SSEF.

2 Materials and Methods

2.1 Materials

Corn starch (amylose content 21.7%) was procured from local market. Hydroxypropylmethylcellulose (HPMC), BA, SP, and PS, polyethylene glycol (400) and glycerol (87%) were of laboratory or Analar grade. The water used was glass distilled.

2.2 Film preparation

A blend containing corn starch (5.75 g), hydroxypropylmethylcellulose (0.25 g), and plasticizers (glycerol (1.46 ml), polyethylene glycol (1 ml) and water (77.54 ml)), and antimicrobial agents at the levels of 0, 0.1, 0.2, 0.3, 0.4, 0.7, 1.4, 2.0 and 2.66% (w/w, on the basis of wet weight of polymer comprising starch plus HPMC i.e., total polymer weight of 6 g) was gelatinized, spread on a polypropylene plate and dried to obtain the SSEF. Details of film casting have been described elsewhere (Chowdhury & Das, 2010).

2.3 Film conditioning

All films were conditioned at 50% relative humidity (RH) at 25±1 ºC for at least 48 h prior to measurement of different properties. This helped to maintain film water activity (aw) at 0.5 during measurement.

2.4 Film thickness

Thickness of film sample was measured at least at 5 random positions by a hand dial thickness gauge, model 7301 (Mitutoyo Co., Tokyo, Japan) with an accuracy of 0.01 mm. The mean value was calculated.

2.5 Mechanical properties

Peak tensile strength (TS) and percent elongation at break (% E) were estimated according to
ASTM D882-97 using an Instron Universal Testing Machine (model 1011; Instron Corp., Canton, MA, USA). Rectangular pieces of the film were cut both vertically (along the web) and horizontally (perpendicular to the web) (5 replications of each) having a dimension of 100 mm gauge length and breadth of 10 mm. The cut film was conditioned and then pulled apart at a speed of 10 mm/min. TS and % E were obtained directly from the machine, using the average thickness.

2.6 Water vapour permeability

Water vapour permeability (WVP) of the film was determined by the gravimetric method using a cup (Shen et al., 2010). The cup contained distilled water occupying ≈50% of its volume. The film, cut in the form of circular disc, was completely sealed to mouth of the cup covering the aperture. This maintained 100% RH inside the cup. The cup was then placed inside a desiccator maintained at 50% RH. The desiccator was kept at 25±1°C in an incubator. Thus a fixed RH gradient 100%/50% was maintained across the film. Initial weight of the cup and the weight after 24 h were recorded, and WVP value was calculated using Eq. 1.

\[
WVP(\text{g.mm/kPa.m}^2\text{.h}) = \frac{(W_1 - W_2)X}{(P_{A1} - P_{A2})At} \tag{1}
\]

where \(W_1\) is the initial weight of the cup (g), \(W_2\) is the final weight of the cup (g), \(X\) is the film thickness (mm), \(P_{A1}\) is the partial pressure at 100% RH (kPa), \(P_{A2}\) is the partial pressure at 50% RH (kPa), \(A\) is the area of the exposed film (m\(^2\)) and \(t\) is the time (h) during which the change in weight had taken place. The measurement was done in three replications.

2.7 Optical properties

Whiteness index (WI), an estimate of the degree of whiteness, yellowness index (YI), an estimate of yellowness usually arising from product degradation by light, chemical changes etc., brightness index (Z%) measuring brightness of a colour, that is the amount of light it reflects (the more it reflects the brighter it will be), and opacity, indicating the cloudiness of material, were all measured in a Hunter Lab Color Flex®EZ (Reston, Virginia, United States) using D65 illuminant and 10° observer angle. The film cut in the form of circular disc, after conditioning, was placed on a white plate for measuring WI, YI, and Z%; for opacity, the sample was placed consecutively on white and black plates. Five replications were performed following the standard methods as suggested in the manual.

2.8 Statistical analysis

The treatment effect of the concentration of antimicrobials on film properties was determined by analysis of variance (ANOVA) (Gomez & Gomez, 1984) for single factor experiment with completely randomized design with equal replications. Least significant differences (LSD; confidence level \(P<0.05\) and \(P<0.01\)) were also evaluated (Gomez & Gomez, 1984). All the statistical calculations were done using Microsoft Excel (Microsoft Inc., 2007).

3 Results and Discussion

3.1 Mechanical properties

The mechanical properties (TS and % E) of the films were almost similar for the horizontally and vertically cut samples. Hence, irrespective of the direction of cut the average of all 10 replications was considered for analysis. Figure 1 shows the effect of antimicrobial concentrations in percent (w/w) of the polymer that comprised corn starch and HPMC, on the tensile strength of the prepared SSEF. It was observed that incorporation of BA up to 2.00% did not show (\(P>0.05\)) any effect on TS of the control film (19.580±0.004 MPa), however, when increased to 2.66%, TS decreased significantly (\(P<0.01\)) to 14.845±1.760 MPa (24.18% decrease). For the entire range of concentration, SP did not change (\(P>0.05\)) the TS. A similar lack of effect of SP on the TS was also observed for HPMC-lipid film at a\(_w\) of 0.5 by Valencia-Chamorro et al. (2008). When PS was added at 1.40%, a significant (\(P<0.01\)) decrease in TS from that of control was obtained; with higher concentrations, however, there was no further
change (mean of 15.247±0.025 MPa, ≈22.13% decrease from control). The lowering of TS in case of BA and PS, at 2.66% and 1.40% respectively, may indicate an interaction of these antimicrobials with corn starch-HPMC-plasticizer network which probably decreases the cohesive force of the film. According to Shen et al. (2010), the TS (at αω ≈ 0.5) of sweet potato starch film decreases progressively when addition of PS is over 5% of the polymer. Flores et al. (2007) observed that addition of PS to 6% of tapioca starch significantly reduced the TS (at αω of 0.5) of the film and such reduction in TS is described as a plasticizing effect of sorbate on the starch molecule. However, Ofman et al. (2004) observed that PS and sodium benzoate at 2.85% of tapioca starch does not interact with starch at αω less than 0.5. Fama et al. (2005) indicated that tapioca starch film without PS has 36% crystallinity whereas film with 6% PS of starch has 12% crystallinity, indicating an interaction of PS with tapioca starch. Thus, the response of corn starch film towards the reduction of the TS occurs at much lower concentration of PS than that of other starches. It is also pertinent to mention that TS values as shown in Figure 1 of the corn starch based films are comparable to the tensile strength of edible films developed from other polymers as reported by Campos et al. (2011).

Figure 2 shows the changes in elongation at break (% E) of the films versus the antimicrobial concentration. For the whole range of concentrations, BA did not affect (P>0.05) elongation value of the control film (2.390±0.493%). For SP, significant (P<0.05) change to 2.810±0.762% (=17.57% increase) was noticed only at 2.66%. Addition of 1.40% PS increased % E of control film to a significantly higher (P<0.01) value, with no significant changes thereafter. Thus, PS at a level of 1.40% and higher caused an increase in the elongation to an average value of 3.716±0.335% i.e., 55.48% increase compared to that of control. According to Valencia-Chamorro et al. (2008), the benzene ring of sodium benzoate adversely affects the flexibility of polymeric film, whereas PS can penetrate more easily because of its straight chain structure so lowering TS and increasing % E in their study of whey protein isolate films containing stearic acid (straight chain structure) and p-aminobenzoic acid (benzene ring).

3.2 Water vapour permeability

The effect of antimicrobials on WVP of the films is shown in Figure 3. The incorporation of BA and SP over the whole range of concentration did not affect (P>0.05) the WVP of corn starch films. However, addition of PS only at 2.66% significantly (P<0.05) increased the WVP value from 0.841±0.005 g.mm/m².kPa.h (control film) to 0.968±0.183 g.mm/m².kPa.h (≈15.1% increase); below this level of PS, the WVP remained unaffected. These results indicated that the addition of PS (2.66%) modified the film structure to such an extent that it could facilitate the permeation of water vapour. Loosening the compactness of the starch film structure due to PS vis-à-vis enhanced moisture permeation has also been described by Fama et al. (2005). Shen et al. (2010) and Flores et al. (2007) reported that with addition of less than 5% PS (w/w of starch), no significant changes in WVP were observed for sweet potato starch or tapioca starch films; however, when PS content was increased from 5% to 10%, WVP for the former film increased considerably from 2.535x10⁻¹⁰ g/(s.m.Pa) to 3.769x10⁻¹⁰ g/(s.m.Pa). Besides starch, PS at different concentration levels has also been reported to increase the WVP of other polymeric films and coatings. Pranoto, Rakshit, and Salokhe (2005) and Park, Stan, Daeschel, and Zhao (2005) incorporated 15% PS (w/w of chitosan) in chitosan film, Valencia-Chamorro et al. (2008) incorporated about 2% PS in HPMC-lipid film solution, Park et al. (2005) included 30% PS (w/w of HPMC) in HPMC coating, and Vásconez et al. (2009) added 1.66% PS (w/w of starch-chitosan mixture) in a starch–chitosan film. All these reported increased WVP which could be attributed to a disruption of the crystalline structure of the homogeneous polymer network.
Figure 1: Effect of antimicrobials on tensile strength of starch films. Means with the same letter are not significantly different ($p > 0.05$ or $0.01$).

Figure 2: Effect of antimicrobials on elongation at break of starch films. Means with the same letter are not significantly different ($p > 0.05$ or $0.01$).
3.3 Optical properties

Whiteness index (WI) of the films is shown in Figure 4. Irrespective of concentration, benzoic acid and sodium propionate decreased (P<0.01) the WI of the control film (72.76±0.03). It was lowered to an average of 69.47±0.59 (4.52%) for BA and 68.68±1.66 (5.60%) for SP. For PS on the other hand, a significant decrease (P<0.01) from the control was observed to a mean of 65.79±0.72 (9.58%) for up to 0.40%, followed by significant changes for each successive addition up to a value of 48.57±1.85 at 2.66%. This indicated that BA and SP exert small and comparable effects on the WI of corn starch film, while PS showed the highest reduction.

Antimicrobials were found to increase the YI of the treated samples compared with the control film (2.36±0.23) (Figure 5). The YI increased significantly (P<0.01) to an average of 3.23±0.38 (∼37% increase) for BA and 4.04±0.43 (∼72% increase) for SP over the entire range of concentrations. On the contrary, there was no significant change in YI value up to 0.40% PS. However, beyond this level, the YI increased significantly (P<0.01) with increasing concentration of PS. This reached a maximum of 7.49±0.49 for 2.66% addition. The starch and HPMC in the film might have undergone interaction with antimicrobials (Ofman et al., 2004; Valencia-Chamorro et al., 2008), and possibly such interaction was responsible for development of yellow colour. The development of substantial YI due to interaction of citric acid and corn starch has been reported by Reddy and Yang (2010) whilst curing the citric acid crosslinked corn starch film. In addition to interaction, oxidative degradation of PS leading to development of polymerized product might be the reason for development of excessive yellow colour in the film (Jager, 2003; Schmidt, 2002).

Opacity of the films (Figure 6) was found to be unaffected (P>0.05) by BA incorporation up to 1.40%; for 2%, however, there was an increase (P<0.01) from 5.72±0.59 (control) to 6.27±0.14 i.e., about 9.60% increase. The subsequent increase for up to 2.66% was insignificant (P>0.05). For films with SP incorporated, the first significant increase (P<0.01) in opacity was seen for 0.30% addition. Between 0.30 and 2.66%, it averaged 6.72±0.38 (approximately 17.48% increase from the value of the control). Incorporation of PS on the other hand showed a significant decrease in opacity to an average of 5.09±0.20, about an 11% decrease compared with the control film, for the entire range of concentrations.
concentration. The decrease in opacity meant an increase in transparency, which is desirable when the film is to be used as packaging material (Chen, Kuo, & Lai, 2009). According to Chen et al. (2009) the transparency arises from the amorphous character of the film. The reduction in opacity in the present case due to the incorporation of PS might therefore be due to interaction with the biopolymers, producing a modified network structure. Film opacity has also been reported to be affected by interaction of starch with glycerol, which modifies the starch network (Mali, Grossmann, García, Martino, & Zaritzky, 2004). Dehghan, Badiei, and Behmadi (2009) indicated that although glycerol addition reduces the opacity of soy protein isolate films, its concentration does not have a significant correlation with this optical property.

Over the range of concentrations tested, the brightness index, Z%, was reduced significantly ($P < 0.01$) to mean of 76.93±0.16 (≈1.46% decrease) for BA and 75.84±0.35 (≈2.86% decrease) for SP compared with the control film (78.07±0.16) (Figure 7). For PS, the results were a bit different. Compared with the control, the Z% lowered to an average value of 75.75±0.17 for up to 0.70%; up to this concentration, the trend was exactly similar to that of SP. However, at higher levels, the Z% reduced ($P < 0.01$) significantly at each successive level. Brightness index is a measure of surface brightness, and therefore all the antimicrobials reduce the brightness of the films. Among the three, PS when added more than 0.7% in the blend caused the highest reduction in surface brightness. Thus, it was evident that if the amount of PS in film was ≥ 1.40% it lowered the TS and increased % E, but WVP was increased when the amount was increased to 2.66%. When added at 2.66%, BA reduced the TS but did not affect % E, whilst SP increased % E but did not affect TS. Individually, these changes led to the reduction of some cohesive force in the film; this type of mismatch of TS and % E has also been reported elsewhere (Das, 2008). It is worth mentioning that reports of film properties as affected by BA and SP are limited.

Regarding optical properties, all the three antimicrobials adversely affected the corn starch film by decreasing the WI, increasing YI, and reducing the surface gloss. Among these, PS most adversely affected the optical properties. However, PS reduced the opacity of the films by 11%.

4 Conclusions

Depending on concentration, the antimicrobials benzoic acid, sodium propionate and potassium sorbate affected different parameters of the physico-mechanical properties of corn starch-based self-supporting edible film. Sodium propionate did not decrease the tensile strength and water vapour permeability but rather caused an improvement in elongation. Nonetheless, all of them showed undesirable effects by decreasing the whiteness index and surface gloss while increasing the yellowness index with potassium sorbate having the most adverse effect. Overall, sodium propionate appeared to be the best with minimum deterioration of film properties and, therefore, can be recommended for inclusion in film formulations as an antimicrobial agent.

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References


Figure 4: Effect of antimicrobials on whiteness index of starch films. Means with the same letter are not significantly different ($p > 0.05$ or $0.01$).

Figure 5: Effect of antimicrobials on yellowness index of starch films. Means with the same letter are not significantly different ($p > 0.05$ or $0.01$).
Figure 6: Effect of antimicrobials on opacity of starch films. Means with the same letter are not significantly different ($p > 0.05$ or $0.01$).

Figure 7: Effect of antimicrobials on brightness index of starch films. Means with the same letter are not significantly different ($p > 0.05$ or $0.01$).


Effect of antimicrobial on properties of SSEF


