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Mechanical and oxygen barrier properties of sodium caseinate edible film

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Abstract

Petroleum based packaging material wastes have always been associated with negative environment impacts. Hence, the demand for renewable yet environmental friendly packaging materials have been in the rise. Various natural resources such as proteins, polysaccharides, and lipids have been used in developing edible films and coatings. Particularly, caseinate with natural open and flexible chemical structure has excellent film forming ability. The main purpose of the study was to develop edible films from various levels of sodium caseinate, sorbitol and palm olein (cooking oil). The physical properties of the edible films were evaluated and compared with the commercially produced cling film. Edible films were prepared using casting method and dried in an oven for 24 hours. Dried films were conditioned in the storage with relative humidity 55±3% at 23±2ºC for at least 48 hours prior to evaluation. Overall, edible films developed for the study were found to have better oxygen barrier property than the cling film. It was also found that, cling film had higher tensile strength and better elongation properties than the developed edible films. For Young's modulus, edible films with sodium caseinate: sorbitol at 1:0.25 had higher Young's modulus value than cling film. The good oxygen barrier property exhibited by sodium caseinate edible films may prolong the shelf life of food.

Keywords: packaging, edible film, sodium caseinate, sorbitol, palm olein, mechanical properties, oxygen permeability, tensile strength, Young's modulus, elongation, cling film

INTRODUCTION

Food packaging functions as barrier to reduce penetration of moisture, gases, and aroma to protect food from microbial contamination. Besides that, it acts as protective layer to prevent the food from further physicial damage upon handling processes. Various materials such as plastics, paper, metal and glass are commonly used to produce food packaging (Lee et al., 2008). In the past, synthetic polymers especially petroleum based packaging have been commonly used due to the excellent mechanical and barrier properties. Furthermore, synthetic packaging can be easily obtained at relatively low cost, and hence makes it the common choice of the industry as packaging material.

However, high volume of non-biodegradable synthetic packaging waste has led to critical environmental issues. As a result, there has been considerable interest in edible films and coatings research. Furthermore, edible coatings and films were found to have similar functions as the synthetic films and having potential to provide effective moisture and gas barrier to food. On top of that, it is biodegradable (Shaw et al., 2002; Robertson, 2006) which fulfills the current market demand for environmental friendly yet renewable packaging materials.

Various natural resources from both plant and animal, such as proteins, polysaccharides, plasticizer, lipid, and resins (Krochta, 2002; Robertson, 2006) have been

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used in edible packaging development. Protein and polysaccharides are usually the major components used in film and coating formation. Among these materials, particularly caseinate has random coil nature, and the ability to form extensive intermolecular hydrogen, electrostatic and hydrophobic bonds which results in increase of interchain cohesion, hence it can easily form edible film from it aqueous solution (Khwaldia et al., 2004). Although caseinate is good for film formation, however, the nature of the formed films and coatings are stiff and brittle due to the extensive interaction between the protein chains through hydrogen bonding, electrostatic forces, hydrophobic bonding and disulfide cross-linking (Krochta et al., 1990; Avena-Bustillos and Krochta, 1993; McHugh and Krochta, 1994a,b; Arvanitoyannis and Biliaderis, 1998; Kroachta, 2002). Thus, plasticizer is added to reduce the film brittleness and increase the flexibility of film and coating (Chick and Ustunol, 1998; Chen, 2002). On the other hand, addition of lipid into the edible film and coating is to improve moisture barrier property (Kokoszka et al., 2010).

As the composition of proteins, plasticizer and lipids are closely related to one another, proportion of each of the ingredients has to be properly adjusted to produce an optimum film and coating system with optimum barrier properties and mechanical properties. Improper establishment of edible films and coatings will result in increase in cost and food waste in bread and buns manufacturing. Therefore, the main purpose of this study was to evaluate mechanical and barrier properties of edible films developed from combination of sodium caseinate, sorbitol and palm olein and compared with commercially produced cling films.

MATERIALS AND METHODS

Materials

Sodium caseinate 180 produced by Fonterra, purchased from VIS Foodtech Ingredient Supplies, Kuala Lumpur, Malaysia was used as the main component in film production. Sorbitol from Sigma Aldrich, Co. was used as the plasticizer and Vesawit brand palm oil was purchased from local mart as the lipid in the study. Sodium hydroxide was used to adjust the pH of the emulsion and magnesium nitrate saturated salt was used to control the relative humidity of the storage chamber.

Film preparation

Edible film was prepared based on the method recommended by Banerjee and Chen (1995) with some modifications. The protein solution was prepared in 6, 7 and 8% (w/w) of sodium caseinate was added into an ice-water mixture in a ratio of 1.0:1.0 respectively. The mixture were blended for 3 seconds, and continued with another 15 seconds blending. Subsequently, the solution was manually mixed for 30 seconds and finally blended for 30 seconds before pH adjustment. pH of the solutions was adjusted to 9.0±0.02 using 2N sodium hydroxide. Sorbitol was dissolved into the protein solutions at 1.0:0.25, 1.0:0.5 and 1.0:0.75 (sodium caseinate: sorbitol), whereas lipid was added into the mixtures with the ratio to protein at 1.0:0.0, 1.0:0.25 and 1.0:0.5 (sodium caseinate: palm olein) after the addition of sorbitol. The composite solutions were then blended for 2 minutes to ensure homogeninity of the solutions. The homogenized solutions were kept in the chiller for 1 hour to eliminate some of the bubbles that were formed upon blending and followed by 1 hour of degassing by using a vacuum oven (BINDER GmbH, model VD53, Germany) until no bubbles were observed. Before casting the emulsion on petri dishes, the emulsions were homogenized with a high pressure homogenizer (APV Homogenizer AS, Albertslund, Denmark) at 180±20 bar for 7 passes.

Film emulsions were casted on disposable polystyrene petri dishes with internal diameter of 150mm. In order to ensure consistency in the film thickness, 8.5ml of solutions was cast on each petri dish. Once casting procedure was done, the solutions were allowed to set under room temperature for 1 hour before drying in the oven (Memmert Universal Oven, Model UF110) at 32ºC for 18 to 24 hours.

Film conditioning

The dried films were peeled off from the petri dishes and were kept in a controlled environment prior to testing. The relative humidity was controlled by using saturated magnesium nitrate hexahydrate salt with relative humidity of 52.89 ± 0.22 at room temperature (25°C) in a desiccator. The relative humidity and temperature was monitored by using hygrometer (Model NT-311, Prokits). The samples were condition for at least 48 hours before using for further testing.

Oxygen permeability

In order to determine the oxygen permeability of the films, Oxygen Permeation Analyser (Model 8000, Illinois Instrument, USA) was used. It was operated at the temperature of 23± 1°C and relative humidity of 50±5% in accordance with the American Society of Testing Materials Standard D3985-05 (ASTM, 2005). Three replicates were examined for each formulation. Oxygen permeability was calculated with the following mathematical equation (1):

$$\text{Oxygen Permeability} = \frac{OTR \times \ell}{\Delta P} \quad (1)$$

where
OTR = Oxygen transmission rate
ℓ = Thickness of film
ΔP = Partial pressure of oxygen

The thicknesses of the films were measured at 4 random places. Three replicates of each film were evaluated.

Mechanical Properties

Tensile properties (tensile strength, elastic modulus (Young's modulus) and % of elongation) of the films were examined in accordance with the ASTM standard method D882 (ASTM, 2002). Instron Universal Testing Machine (Model 5566, Instron Corp. Canton, MA) with Bluehill 2 software was used to examine these mechanical properties of edible films. Prior to testing, the films were cut into 25mm*100mm test strips using a razor blade and stored under controlled environment with 53% relative humidity for at least 48 hours. Film strips were placed between 2 pneumatic-action grips at a separation of 50mm and deformed at a crosshead speed of 50mm/min. At least 10 readings of each film type were tested.

RESULTS AND DISCUSSION

The reduction of oxygen penetration in food packaging is crucial to reduce the development of off-flavours, off-odors, and nutrittonal loss associated with oxidation process (Ozdemir and Floros, 2004). Whereas good mechanical properties are crucial to provide physical protection to food upon handling. Table 1 shows the oxygen permeability and mechanical properties of commercially produced cling film and various sodium caseinate films. The mechanical properties of films are expressed in terms of tensile strength, % elongation and Young's modulus.

As shown in Table 1, oxygen permeability of cling film (LDPE) was significantly higher ($p<0.05$) than all the sodium caseinate films. This indicated that sodium caseinate films had better oxygen barrier property. The linear structure and polar nature of the sodium caseinate leads to higher cohesive energy density and reduce the spacing among the polymer chain, may be the major reason for the low oxygen permeability (Miller and Kroachta, 1997). However, no data could be obtained for all the films with 1.0:0.25 sodium: plasticizer ratios, as the films were too brittle and cracked upon gas purging during oxygen permeability tests.

Table 1. Oxygen permeability and mechanical properties of cling film and sodium caseinate films.

Concentration of sodium caseinate (w/w, %)	Sodium caseinate : sorbitol	Sodium caseinate: palm olein	Oxygen Permeability (*10^{-5} $cm^3.mm.m^{-2}.day^{-1}.KPa^{-1}$)	Tensile strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Cling film	-	-	4.810±0.336[a]	24.360±1.572[a]	89.169±19.768[a]	143.027±12.977[a]
6	1.0:0.5	1.0:0.25	0.160±0.081[b]	2.811±0.613[bc]	48.956±14.486[b]	53.155±10.598[b]
7	1.0:0.5	1.0:0.0	0.045±0.045[b]	6.271±2.231[d]	45.870±1.984[b]	122.384±52.881[a]
8	1.0:0.75	1.0:0.25	0.100±0.031[b]	1.975±0.501[bc]	97.985±27.587[a]	23.519±4.130[b]

** Values in a column followed by different letters are significantly ($p<0.05$) different. Values are mean± standard deviation from 3 replicates for oxygen permeability and at least 10 readings for mechanical properties.

Tensiles strength, which is known as ultimate tensile strength, is defined as the maximum stress that is needed to a film per unit original cross-sectional area before the film breaks (Jooyandeh, 2011). Percentage of elongation is a measurement of the flexibility (Tomasula, 2010), strechablity of the film from its initial length before breaking (Chen, 2002). Whereas, Young modulus (YM) is a common term to use to express the film stiffness (Chen, 2002). These criteria are important in order for packaging to provide physical protection to food upon handling and processing.

In Table 1, it indicates that cling film had significantly ($p<0.05$) higher tensile strength than all the sodium caseinate edible films. Besides that, cling film showed better elongation properties and was significantly different ($p<0.05$) from than most of the edible film except for edible film with 8% of sodium caseinate and with 1.0:0.75 of plasticizer and 1.0:0.25 of palm olein. Young modulus is the term for expressing the stiffness of the film. Table 1 shows that, some of the edible films were more flexible and some of them were stiffer than the cling film.

The effect of content of sodium caseinate, sorbitol, and palm olein on oxygen permeability of the edible films were shown in Figure 1:

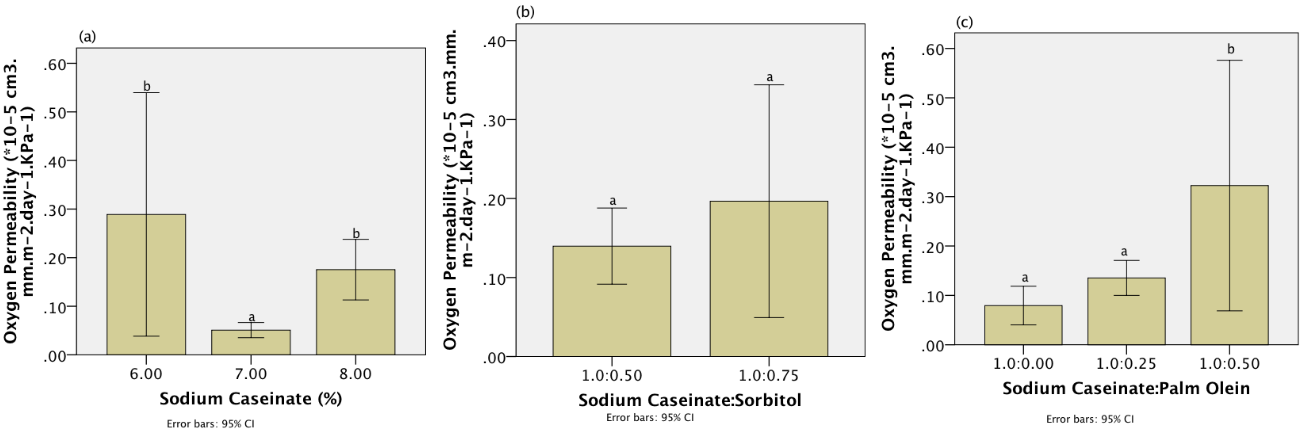

Figure 1. Changes of Oxygen Permeability of Sodium Caseinate Edible Films with (a) sodium caseinate at different concentration, (b) sorbitol at different concentration, and (c) palm olein at different concentration.

Both edible films that contained 7% and 8% of sodium caseinate were found to have lower oxygen permeability than edible films with 6% of sodium caseinate (Figure 1(a)). As in the previous study, it was found that, with the increase in crystallinity, density, orientation, molecular weight or crosslinking there will be a reduction in polymer permeability (Miller and Krochta, 1997). Therefore, edible films that consist of higher protein content serve as a better oxygen barrier (Chen, 1995)

Plasticizers are relatively low-molecular-weight molecules (Talens and Krochta, 2005). They contain more polar groups in each molecule, and cause increasing space between the polar groups within a molecule (Skurtys et al., 2010). As the protein chain-to-chain interactions are being interrupted, it results in higher permeability. Therefore, Figure 1(b) shows that, edible film with sorbitol with the ratio of 0.5 to sodium caseinate had lower permeability.

On the other hand, Figure 1(c) indicates that, among 3 levels of palm olein concentration, palm olein at the ratio of 0.75 to sodium caseinate had the highest oxygen permeability value. According to Gontard et al. (1994), due to lack of cohesive structural integrity, lipid showed poor mechanical properties. Hence, as lipid was added to the edible film, the polymer chain-to-chain interactions were interfered, and hence resulted in plasticizing effect (Talens and Krochta, 2005). Therefore, higher oxygen permeability as the amount of palm olein increased.

The changes of tensile strength of the sodium caseinate films with the sodium caseinate, sorbitol and palm olein at different concentration levels were illustrated in Figure 2:

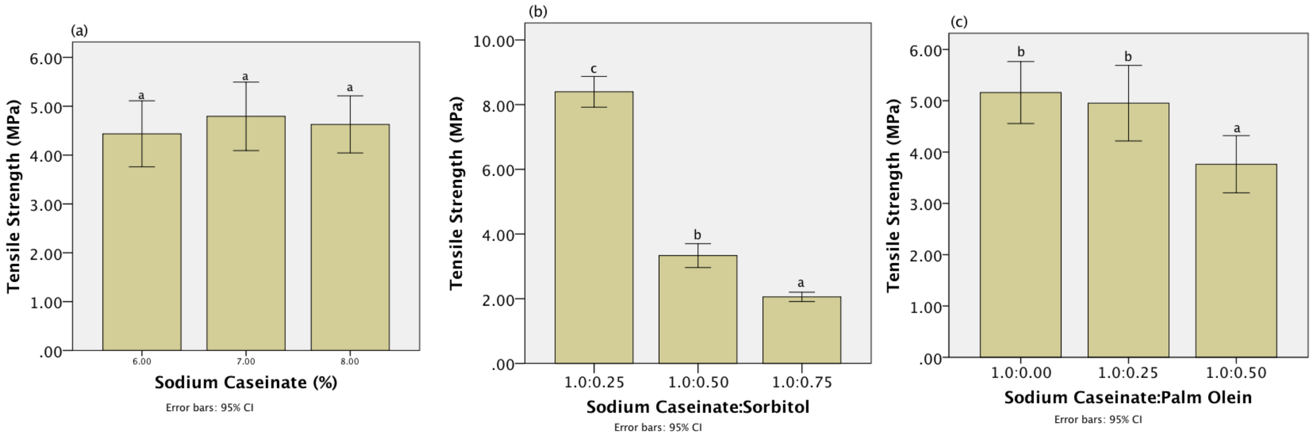

Figure 2. Changes of Tensile Strength of Sodium Caseinate Edible Films with (a) sodium caseinate at different concentration, (b) sorbitol at different concentration, and (c) palm olein at different concentration.

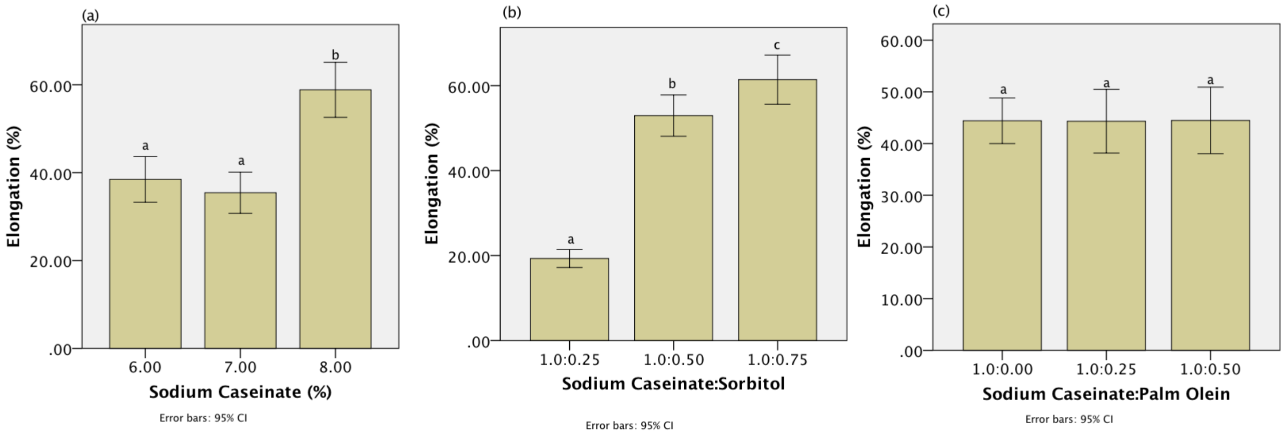

Figure 3. Changes of Percentage of Elongation of Sodium Caseinate Edible Films with (a) sodium caseinate at different concentration, (b) sorbitol at different concentration, and (c) palm olein at different concentration.

Figure 2 (a) shows that, edible films that contained 7% and 8% of sodium caseinate exhibited higher tensile strength than edible films that contained 6% of sodium caseinate. However, there was no significant difference ($p>0.05$) of the tensile strength among these 3

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levels of concentrations. But Figure 2(b) and (c) indicates that, tensile strength of the edible films decreased as the amount of plasticizer and lipid in the film increased. Besides that, it also shows that, the amount of sorbitol added into the edible film had significantly affect ($p<0.05$) the tensile strength of the film. For palm olein content, although a decreasing trend is shown in Figure 2(c) as the content of palm olein increased in edible film, however, edible film that contained palm olein with the ratio of 0.5 to sodium caseinate was significantly lower ($p<0.05$) tensile strength than the other edible films.

Figure 3 presented the results of the percentage of film elongation at various level of sodium caseinate, sorbitol and palm olein

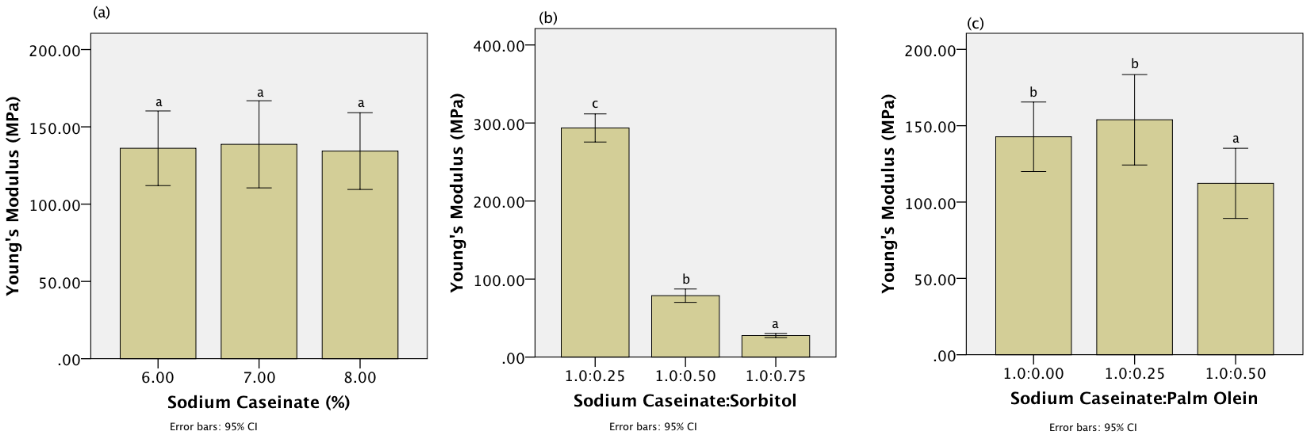

Figure 4. Changes of Young's Modulus of Sodium Caseinate Edible Films with (a) sodium caseinate at different concentration, (b) sorbitol at different concentration, and (c) palm olein at different concentration.

Figure 4 (a) shows that concentration of sodium caseinate had no significant effect ($p>0.05$) on the Young's modulus value. 7% of sodium caseinate edible films had highest Young's modulus value, whereas 6% and 8% of sodium caseinate edible films had similar Young's modulus mean value. As in Figure 4(b) , Young's modulus value shows a decreasing trend as the amount of plasticizer increases. In other words, the incorporatio of plasticizer had improved the film flexibility. In Figure 4 (c), edible films with sodium caseinate: lipid 1.0:0.25 showed highest value of Young's modulus value, whereas films with lipid content of 0.5 to sodium caseinate had lowest Young's modulus value.

As the content of protein content of film increases, there is an increase in protein-protein interaction in the film matrix, which will lead to a higher tensile strength (Tomasula, 2010). According to Chen (1995), mechanical properties of edible films are influenced by the interactions between proteins and other compositions in the films such as water, plasticizers, lipids and other additives which are found in the space of film matrix. Plasticizer is known to contain high polarity molecules and have relatively small molecular weight (Kroachta, 2002; Skurtys et al., 2010). As a result, the dispersion and addition of plasticizer molecules disturbs the protein chain-to-chain interaction in the film matrix as it competes for hydrogen bonding and electrocstatic interactions with the protein chains. Hence, as the content of plasticizer increases, it reduces the mechanical strength of the edible films. As mentioned earlier, besides acting as a moisture barrier enhancer, lipid was found to have plasticizing effect as well. Therefore, the addition of plasticizer and lipid resulted in better elongation, reduced stiffness, but lower tensile strength.

CONCLUSIONS

The following conclusions can be drawn from the study:

– Sodium caseinate edible films provided better oxygen barrier to food than cling film. Hence sodium caseinate films may provide better protection to food from lipid oxidation, microbial contamination.

– Although sodium caseinate edible films did not have mechanical properties that are better than cling film, but some of the sodium caseinate films showed comparable mechanical properties to cling films. In other words, sodium caseinate films are able to provide physical protective layers as commercially produced cling film.

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