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Properties and permeability of aroma compounds in food through plasticized cassava films

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Abstract: The properties and permeability of aroma compounds in food through the cassava starch films was investigated. Films were prepared by 5% starch and properties of the films were monitored at different concentration of two plasticizers; glycerol and sorbitol. Sorbitol-cassava starch films showed a better transmission rate (water vapor or/and oxygen), and had a higher mechanical properties; tensile strength and elongation, than those glycerol-cassava starch films. 35% sorbitol-cassava starch films was the best film which had the best mechanical properties, low tensile strength and high elongation. Thus, the 35% sorbitol-cassava starch film was further studied for permeation of aroma compounds in foods (cinnamaldehyde, cis-jasmone, benzyl benzoate, eugenol, 1,8-cineol, limonene, 2,4,6-trimethylpyridine (TMP)). Permeability of aroma compounds was determined by measuring the steady-state flux (J) of both static and dynamic systems. Results showed that benzyl benzoate had the lowest J values demonstrating that the cassava starch films revealed the lowest permeable to this aroma compounds probably due to absorbed, adsorbed, covalently linked, and trapped mechanism.

Keywords: Cassava, starch, film, permeability, aroma compound

Introduction

Biopolymer films have several advantages over polymeric packaging such as mild processing, easily modifiable physical properties, biodegradability and recyclable raw materials. The potential usage of edible film is for coatings or wrapping various kinds of foods, fruits, meats and candies. It has been suggested as a matrix material for controlled release and encapsulation active agent such as flavors, perfumes, essential oils, herbicides, pesticides and pheromones (Dziezak, 1988; Gennadios and Weller, 1990; Shahidi and Han, 1993; Atterholt *et al.*, 1998) which are made available at a desired site, time, and at a specific rate (Pothakamury and Barbosa-Canovas, 1995). The main function of edible film could be to prevent mass transfer of water or other compounds, such as oxygen, carbon dioxide, oil and aroma compounds, between a product and surroundings or between different layers of a product (Huang *et al.*, 2006).

Edible films can be prepared from biomaterials such as polysaccharides and proteins (Banker, 1966; Kester and Fennema, 1986). Starch is a low cost material and edible starch film is frequently used as matrix material which gelatinized starch forms can interact with other molecules (Reineccius, 1991). Edible films can also be plasticized by low molecular weight carbohydrates, such as polyols (Stading *et al.*, 2001; Mathew and Dufresne, 2002; Talja *et al.*, 2007). The addition of a plasticizing agent to edible films is required to overcome film brittleness caused by extensive intermolecular forces. The plasticizers also increase polymer chain mobility, improving flexibility and extenseibilityof the film, and diffusion coefficients and generally lead to increased gas and water vapor permeability (Huang *et al.*, 2006). In films manufactured from whey protein isolate (WPI), increasing levels of glycerol and sorbitol have been reported to increase film permeability and extensibility and reduce film strength (McHugh and Krochta, 1994). In Shaw *et al.* (2002) studied on WPI, they proposed the effects of glycerol, xylitol, and sorbitol to film properties. Increasing glycerol or sorbitol content led to increase in moisture content, water vapor permeability, and % elongation; and decrease in tensile strength, elastic modulus, and glass transition temperatures of films (Laohakunjit

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and Noomhorm, 2004). Although increasing levels of xylitol have no effect on permeability, moisture content, and glass transition temperatures of the films, %elongation, tensile strength, and elastic modulus decreased (Shaw *et al.*, 2002).

Aroma compounds may be dissolved, absorbed or adsorbed, covalently linked, trapped, encapsulated and limited in their diffusion as a result of the presume of food components (Langourieux and Crouzet, 1994). There are several mechanisms explained for the transfer process of small molecule with starch. Many experiments and analytical techniques have been developed to study the interaction of starch with flavor and aroma compounds (Godshall and Solms, 1992). The transfer of compounds within the product and their release from its depends on the functional group of the aroma compound in foods such as alcohol (eugenol, 1,8-cineol), ester (benzyl benzoate), aldehyde (cinnamaldehyde), ketone (cis-jasmone), alkene (limonene), pyridine (2,4,6-trimethylpyridine; TMP), the composition and the structure of the matrix (Seuvre *et al.*, 2006; Habeych *et al.*, 2007). Edible films are mainly hydrophilic, and sorption of aroma compound in foods is reduced compared to that of apolar plastic packaging (Willige, 2002), resulting in smaller permeability of aroma compounds through edible films. Thus, aroma barrier of traditional packaging could be improved with edible coating films. The purposes of these studies were to investigate the properties of cassava starch film and permeability of aroma compounds in foods through plasticized cassava starches films.

Materials and methods

Chemicals

Standard substances such as cinnamaldehyde, cis-jasmone, benzyl benzoate, eugenol, 1,8-cineol, limonene, TMP were obtained from Fluka, Switzerland. A starch used was cassava starch, of Thaiwa Company, Thailand, purchased at a local market in Thailand. Starch samples were passed through a 100-mesh sieve. D(-)sorbitol was obtained from Merck, Germany. Glycerol was obtained from AnalaR, U.K.

Preparation of cassava starch films

Cassava starch films were prepared by weighing 5 g of cassava starches, followed by the addition of 100 mL of demineralized water. Glycerol (10, 15, 20, 25, 30% (w/w)) and sorbitol (15, 20, 25, 30, 35% (w/w)) dry starch were added to the water-starch mixtures (Laohakunjit and Noomhorm, 2004). Gelatinization of the starch suspensions was performed by heating the mixtures on a hot plate under continuous mixing with a magnetic stirrer. During the gelatinization procedure, the beaker was covered with watch glass aluminum foil in order to avoid excessive evaporation of water. Films were obtained by casting the gelatinized starch solutions into acrylic blocks (width 17 cm x length 21 cm) and adjusting the thickness (2 mm). Films were subsequently dry overnight at 60°C at over water bath. Properties analysis of cassava starch films were water vapor transmission rate (WVTR) (g.mm/m^2/day) by the dish method ASTM E 96 (ASTM, 1995), oxygen transmission rate (OTR) (cm^3.μm/m^2/d.KPa) by the standard method ASTM D1434-82 (ASTM, 1992), tensile strength (TS) (MPa) and elongation properties (%) by the standard method ASTM D 882-97 (ASTM, 1997).

Determination of the flux of the aroma compounds through the films

The determination of the flux of the aroma compounds through the films was performed using glass beaker as chamber (diameter = 2.3 cm, height = 3.2 cm) equipped with a sample container and a cover, in which the films were fitted. The chamber was filled with around 0.5 g of aroma compounds represented

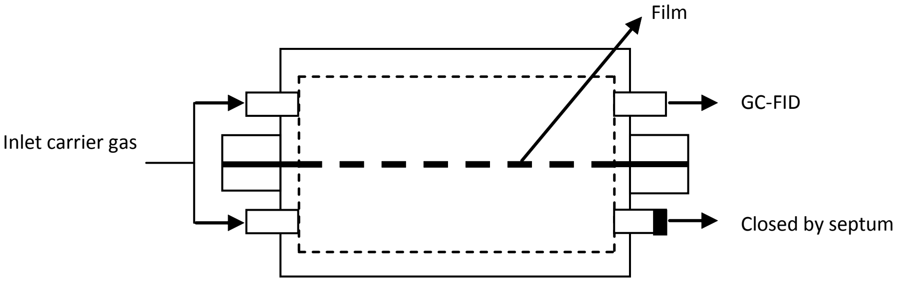

Figure 1. Permeation cell

Table 1. Water vapor transmission rate (WVTR), oxygen transmission rate (OTR), tensile strength (TS) and elongation properties of cassava starch films as affected by plasticizer type (glycerol and sorbitol) and concentration.

plasticizer	concentration of plasticizer (% w/w)	WVTR (g.mm/m^2/ day)	OTR (cm^3.µm/m^2 .d kPa)	TS (MPa)	elongation (%)
cassava starch films	0	1239	27.41	3.62	1.1
glycerol-cassava starch films	10	849	23.84	2.97	1.07
	15	1204	nd	2.84	1.33
	20	1231	24.78	2.60	1.38
	25	1378	nd	2.38	1.52
	30	1577	30.98	2.16	1.70
sorbitol-cassava starch films	15	595	nd	3.88	2.71
	20	638	3.08	2.61	7.22
	25	666	nd	1.43	29.42
	30	785	3.69	1.38	30.07
	35	947	5.23	1.05	30.07

nd means not detect

by 7 chemical compounds; cinnamaldehyde, cis-jasmone, benzyl benzoate, eugenol, 1,8-cineol, limonene, TMP. The chamber was covered with the suitable plasticized cassava starch film (diameter = 2.3 cm). All connection parts were coated by wax. The chambers were subsequently kept in a desiccator which contained silica gel and magnesium sulphate for desicant. The weight of the chamber was determined daily for nine days, and compared with not covered with cassava starch film. From the steady-state flux (J) expressed in mg/cm^2 .h, the diffusion coefficient (D) expressed in cm^2/h of the volatile in the starch matrix was calculated using Fick's first law:

$$J = D.\Delta C/h$$

Where h is the thickness of the film in cm, ΔC (mg/cm^3) is the concentration difference between the two sides of the film (ΔC is equal to the concentration of the aroma compounds at the lower end (receiving side) of the film, since the concentration the upper end (exciting side) is assumed to be zero, and ΔC, therefore, equals the experimentally determined solubility of the volatile in the different films) (Yilmaz *et al.*, 2004).

Determination of aroma compounds vapor permeability

Dynamic measurement method of volatile vapor fluxes through films or membranes was performed. The permeation cell (Figure 1), composed of two chambers which was divided by the film was adapted for the study. Area of cassava starch film exposed to perform was 491.6 cm^2. The two chambers were continuously swept by a 30 ml/min nitrogen gas flow. Aroma in the vapor phase on the down-side of the cell were obtained by mixing two flows: aroma compounds; cinnamaldehyde, cis-jasmone, benzyl benzoate, eugenol, 1,8-cineol, limonene, TMP and nitrogen gas. The upper-side of the cell was obtained by nitrogen gas flow. Two milliliter of outgoing flow from upper-side of the cell was injected at initial time, 4, 6 and 8 hours in a gas chromatography-flame ionizing detector (GC-FID) by using DB-WAX

Table 2. Steady-state flux (J) of various aroma compounds through cassava starch films measured by the static system.

volatile compound	steady-state flux (mg cm^{-2} h^{-1})	
	covered with film	not covered with film
benzyl benzoate	0.011^{e}	0.102^{c}
eugenol	0.015^{e}	0.116^{c}
1,8-cineol	0.041^{de}	0.112^{c}
cis-jasmone	0.074^{cd}	0.247^{b}
cinnamaldehyde	0.100^{c}	0.322^{a}
limonene	0.176^{b}	0.332^{a}
TMP	0.239^{a}	0.342^{a}
F-test	**	**
C.V. (%)	22.614	8.413
LSD	0.050	0.045

^{a,b,c} Means with the same letter are not significantly different at 5%, LSD. Means ± standard deviation.

column. Conditions of GC-FID were helium and nitrogen (both used flow 70 kPa) for carrier gas. Air zero and hydrogen (flow 50 and 60 kPa, respectively) were gas for flame. Injector temperature 200°C, oven temperature 40°C, hold 1 min and increased from 40°C to 240°C by rate 10°C/min hold 1 min and detector temperature 230°C (Debeaufort and Voilley, 1994). The experimental design was set up in Completely Randomized Design (CRD) with 3 replications. All data were analyzed using the SAS General Linear Model, Mean separation was performed by protected LSD method at $P \leq 0.05$.

Results and discussion

Table 1 showed properties of cassava starch films such as water vapor transmission rate (WVTR) (g.mm/m^2/day), oxygen transmission rate (OTR) (cm^3.μm/m^2/d.KPa), tensile strength (TS) (MPa) and elongation properties (%) were similar way of both plasticizers. Glycerol- and sorbitol-cassava starch film at the higher plasticizer content had greater transmission properties. The lower WVTR of plasticized films compared to unplasticized film was due to the hypothesis of hydrogen bonding between hydroxyl groups of polyols and starch which decreases free sorption sites for water in polyol plasticized films (Aurand and Woods, 1973; Le Bot and Gouy, 1995; Talja *et al.*, 2007). WVTR of films was depended on both solubility coefficient and diffusion rate of water in film and they were also depended on partial pressure of water vapor (Kester and Fennema, 1986). The OTR of plasticized films determined at 23ºC, 0% RH had a lower value than unplasticized film because the network micro-structure changed to decrease pore size of plasticized films (Kester and Fennema, 1986). Plasticization of edible films was believed to disrupt intermolecular interactions between polymer molecules with the effect of decreasing brittleness and increasing film flexibility (Lieberman and Guilbert, 1973). Decrease in film strength and increase in ability to elongate with increasing glycerol and sorbitol content, indicated by decreasing tensile strength, and increasing %elongation values, might be attributed to a reduction in the number of intermolecular cross-links between polymerized starch molecules within films (Gontard *et al.*, 1993). The good properties of

Table 3. Steady-state flux (J) of various aroma compounds through cassava starch films measured by the dynamic system using a permeation cell.

volatile compound	steady-state flux (mg cm^{-2} h^{-1})
benzyl benzoate	1.55^{f}
cinnamaldehyde	3.03^{d}
1,8-cineol	4.71^{b}
eugenol	2.16^{e}
cis-jasmone	3.37^{c}
limonene	4.45^{b}
TMP	6.99^{a}
F-test	**
C.V. (%)	5.376
LSD	0.296

^{a,b,c} Means with the same letter are not significantly different at 5%, LSD. Means ±standard deviation.

plasticized cassava starch films were low WVTR, OTR value, and tensile strength but high %elongation values. The results of comparison between glycerol- and sorbitol-cassava starch films were shown that transmission properties of sorbitol were greater than glycerol. Because sorbitol consists of high hydroxy groups compared to glycerol, greater transmission properties were originating from hydrogen bonding between hydroxyl groups of sorbitol starch films than those glycerol films. At low concentration of sorbitol, transmission properties were good but mechanical properties (TS and elongation) were poor. The best propertiy of films (good transmission properties and flexibility) were found in cassava starch film added with 35% sorbitol, which WVTR (947 g.mm/m^2/day), OTR (5.23 cm^3.µm/m^2/d.KPa), tensile strength (10.29 MPa) and elongation (30.07%). In agreement with Krochta and de Mulder (1997), they disclosed that good properties of edible films were WVTR at 10-100 g.mm/m^2/day, OTR at 1-10 cm^3.µm/m^2/d.KPa, tensile strength at 10-100 MPa and high elongation. Thus, cassava starch film with 35% sorbitol was used for permeation of aroma compounds in the next study of permeation of aroma.

Permeation of aroma compounds through cassava starch film was shown in Table 2. Permeation of benzyl benzoate, 1,8-cineol, eugenol, cis-jasmone, cinnamaldehyde, limonene and TMP was found from low to high, respectively. Cassava starch film could decreased permeation of aroma compounds because the amylose network of cassava starch film could prevent diffusion of aroma compounds, reduce pore size of film, and make aroma compounds difficult to permeation (McHugh and Krochta, 1994). Permeation properties of aroma compounds were depended on the molecule weight, boiling point and structure that could make the rate of volatilization of aroma compounds (Gallo *et al.,* 1998). Benzyl benzoate showed the lowest J values demonstrating that the cassava starch films was lowest permeable to this aroma compounds probably due to high molecule weight (212.25), high boiling point of the compound (323°C), absorbed, adsorbed, covalently linked, and trapped mechanism. Moreover, the most important factor in a polymer film was the forces between the permeated molecule (Piringer, 2000; Nestorson *et al.*, 2007). Fornasiero *et al.* (2005) reported that the rate of permeation of small compounds through a polymeric matrix was affected by the size and their physical-chemical affinity to the polymer. A common approach used to describe the diffusion through matrices was the solution-diffusion model (Fornasiero *et al.*, 2005), where the polymeric-matrix/solute system was considered to be a molecular solution in which solute transport is through diffusion only (Habeych *et al.*, 2007). Other factors affected the permeability were the volatility and molar volume of the aroma compounds (Nestorson *et al.*, 2007). Table 3 showed that the steady-state fluxes of particular the compounds through the cassava starch film utilizing the vapor permeability measurements method. Permeability of TMP by dynamic system was highest at 6.99 mg/cm^2.h but permeability of 1,8-cineol, limonene, cis-jasmone, cinnamaldehyde, eugenol and benzyl benzoate were lower at 4.71, 4.45, 3.37, 3.03, 2.16, and 1.55 mg/ cm^2. h, respectively. Permeation of 7 compounds in dynamic system showed similar pattern as the static system which TMP resulted in the highest permeation and benzyl benzoate showed the lowest permeation. This finding indicated that there was no different between permeability by static and dynamic systems of aroma compounds through plasticized cassava films. From the above data it could also be seen that the permeation of aroma compounds through cassava starch film depended on film properties (good transmission properties and flexibility), physicochemical characteristics of aroma compounds (volatility, molecule weight, and boiling point) and interaction between aroma compounds, and cassava starch films (absorbed, adsorbed, covalently linked, and trapped mechanism).

Conclusion

The study of plasticizer-cassava starch film properties were found that higher plasticizer contents increased transmission properties, the film structure was soften and sticky, low tensile strength and high elongation. 35% sorbitol-cassava starch films showed that 35% sorbitol had greater properties in low WVTR, OTR, and low tensile strength, but high %elongation compared with 30% glycerol-cassava starch films.

The permeation of aroma compounds (cinnamaldehyde, cis-jasmone, benzyl benzoate, eugenol, 1,8-cineol, limonene, TMP) through sorbitol-cassava starch films was found that permeability of aroma compounds was determined by measuring the steady-state flux (J) by the static and dynamic systems. Permeation of benzyl benzoate showed the lowest J values. On the other hand, cassava starch film decreased the permeation of aroma compounds. Permeation ability varied due apparently to differences in properties of the aroma compounds. The improvement of flavor and edible film interaction would be the subject of continuing studies.

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