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Raising Lipid Content Improve Moisture Barrier of Soybean Protein-isolation/carboxymethyl Cellulose Composite Films

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Abstract. Three lipids (beeswax, palmitic acid and stearic acid) and a hydrophilic film (soybean protein-isolate/carboxymethyl cellulose film) were selected as a model to inspect the relation between the lipid state and barrier properties. The free-lipid ratio of composite films was the best indicator for the transparency rather than the moisture barrier. The free-lipid content/total-lipid content had the highest negative correlation factor with the moisture barrier. Hence, raising free-lipid ratio was effective to improve the moisture barrier of hydrophilic films.

Introduction

Edible films have attracted more and more interests for being degradable and safe [1-4]. Proteins, or starches, or polysaccharides usually contain a lot of hydroxyl and carboxyl groups which lead them to be highly hydrophilic [4-8]. Hence, the moisture barrier was a barrier for their application [9, 10]

Adding lipids is an effective way to improve the moisture barrier [11-14]. The lipids are distributed as a free state or a bound state in film matrix. The bound lipid has been proved to be positive related to the moisture barrier of films, because the bound lipid is cross-linked with ingredients and raises their hydrophobicity [13, 15-17]. But the conclusion only came from the results of soybean protein-isolate (SPI)-beeswax films. Moreover, the relations between the bound-lipid content/total-lipid content and water vapor permeability (WVP)were neglected.

The effects of beeswax, palmitic acid and stearic acid additions on properties of SPI/carboxymethyl cellulose (CMC) composite films were compared. Correlations between the free-lipid ratio and free-lipid content and other properties were compared to give a deeper insight of the moistures immigration in film matrix.

Materials ad Methods

Preparation of SPI/CMC composite films. The SPI/CMC composite films were fabricated according to the preceding researches [15, 18] with a few modifications. Briefly, SPI (10 g, Gushen Biological Techonology Co., Ltd, Shandong, China), CMC (10 g, Heyi food additive Co., Food grade, degree of substitute x=0.9, Shanghai, China), and glycerol (5 g, Sinopharm Chemical Reagent Co., Beijing, China) were mixed in 1000 ml of deionized water. Lipids (beeswax, palmitic acid and stearic acid, Sinopharm Chemical Reagent Co., Beijing, China), which accounted 4 % (400 mg), 8 % (800 mg), 12 % (1200 mg), and 16 % (1600 mg) of SPI, were added and stirred in the mixture at 90 ^{o}C for 30 min. The resultant mixture was subjected to a high-speed homogenizer (IKA T10 Basic, Werke GmbH & Co. KG, Staufen, Germany) for 5 min. The homogeneous solution was cast on acrylic plates (20 cm×20 cm) and dried at 30 ^{o}C for 48 h. The specimens were stored at 25 ^{o}C and 55 % relative humidity for 24 h at least.

Transparency. The transparency of specimens was determined by following the recent method [19]. The specimen was cut as 40 mm × 10 mm and attached on outside of cuvettes by a double-faced

adhesive tape. The fixed specimen was measured at 600 nm by a spectrophotometer (UV-1800 spectrophotometer, Shimadzu Corporation, Kyoto, Japan) with Air as blank (100 % transmittance).

Mechanical properties. The tensile strength and elongation at break of specimens were determined by a texture analyzer (TA.XT2i Plus, Stable Micro Systems^{TM}, Godalming, Surrey, UK) according to the ASTM Standard Test Method [20].

Barrier properties. Water vapor permeability of specimens was determined by a MOCON tester (Model PERMA TRAN-W 1/50G, MOCON, Minneapolis, USA) at 25 ºC according to ASTM standard method [21]. Water vapor permeability was calculated by dividing the water vapor transmission rate by the difference in relative humidity between the sides of the specimen (0.1 MPa) and multiplying by the average specimen thickness.

Determination of free-lipid ratio/content. The free-lipid ratio/content of specimens was measured by a DSC (Diamond DSC, Perkin-Elmer, USA) analysis [15]. Firstly, a series of stearic acid, palmitic acid, and beeswax, which were ranged from 0.1 mg to 10mg, were sealed in an aluminum pan and transferred to a preheated calorimeter in a nitrogen bath of 40 ml/min. The sealed pan was heated at a rate of 10 ^{o}C /min from 20 to 100 ^{o}C. A working curve was plotted based on the height of endothermic peak and lipid weight with an intercept of 0. And then an aliquot of 5~10 mg of specimens was sealed in the aluminum standard pan and transferred to a preheated calorimeter in a nitrogen bath of 40 ml/min. The sealed pan was heated at a rate of 10 ^{o}C /min from 20 to 100 ^{o}C. The lipid weight in the specimen was calculated followed the working curve and designated as the free lipid. Finally, the free-lipid ratio was the percentage of the free lipid in the total lipid.

Statistical analyses. All experiments were triplicated. The results were expressed as the average ± standard deviation ($n \geq 3$). Analysis of variance was used to compare mean differences of the results. A positive correlation is indentified when the correlation factor is higher than 0.85, while a negative correlation is indentified when that is lower than -0.85. All analysis was conducted by SPSS.

Results and Discussion

Effect of lipid on transparency, mechanical and barrier properties of SPI/CMC composite films. The effect of lipid on transparency, mechanical and barrier properties of SPI/CMC composite films is listed in **Table 1**. The additions of beeswax, stearic acid, and palmitic acid lowered the transparency of composite films significantly, being consistent to recent results [22, 23]. Moreover, the transparency of composite films showed a dosage-dependent manner. This phenomenon resulted from that the number of lipid droplets which blocks light scattering throughout polymer matrix will increase when the lipid content is raised [24].

The stearic acid lowered the tensile strength of composite films compared to the control, while the palmitic acid raised the tensile strength significantly. The tensile strength of beeswax/4 % was significantly higher than that of the control, while that of beeswax/16 % was lower than that. This phenomenon could be explained that the excessive beeswax destroys the integrity of the films matrix [14, 25]. Furthermore, the tensile strength of beeswax/12 %, stearic acid/12 %, and palmitic acid/12 % was compared. The tensile strength of palmitic acid/12 %, beeswax/12 %, and stearic acid/12 % was higher, similar, and lower than that of the control, respectively.

Each lipid lowered the WVP significantly compared to the control. This phenomenon could be explained that the lipids, which are highly hydrophobic substances, act as a predominant barrier anchor against moisture immigration [11]. Moreover, the WVP of composite films showed a dosage-dependent manner with the lipid content. Similar result was also shown on gellan-based films [26]. Remarkably, the WVP of palmitic acid/12 % was significantly lower than that of the beeswax/12 % and stearic acid/12 %. The underlining reason may lie in different structural arrangement of lipid in the polymeric matrix [6, 25].

Effect of lipid on free-lipid ratio/content in SPI/CMC composite films. The free-lipid ratio/content of composite films are listed in **Table 1**. The free-lipid content of each film increased when the content of lipid additions was raised, while the free-lipid ratio did not. The free-lipid content

of palmitic acid/12 % was significantly higher than that of beeswax/12 % and stearic acid/12 %. The free-lipid ratio has been proved to be related to the pressure of high-pressure homogenization and number of small and round particles in the surface of films [15]. However, the free-lipid ratio of each film showed no dosage-dependent manner. When the lipid content was 12 %, the free-lipid ratio of stearic acid/12 % and beeswax/12 % was the highest and the lowest, respectively.

Table 1 Effect of lipid additions on mechanical properties, barrier properties, and free-lipids content of SPI/CMC composite films

Films	Transparency (%)	Tensile strength (MPa)	WVP (g m/m^2 d)	Free-lipid content (mg)	Free-lipid ratio (%)
Control	13.2±0.11^{a}	6.71±0.978^{c}	167±12.4^{a}	0	0
Stearic acid/4 %	10.2±1.67^{b}	4.48±0.202^{e}	146±10.3^{ab}	72.6	18.2
Stearic acid/8 %	10.9±0.385^{b}	5.41±0.908^{de}	148±11.7^{ab}	103.3	12.9
Stearic acid/12 %	7.50±0.753^{de}	4.50±0.833^{e}	126±5.33^{bcd}	254.6	21.2
Stearic acid/16 %	8.26±1.01^{cde}	4.96±0.669^{e}	101±11.1^{d}	342.3	21.4
Palmitic acid/4 %	9.77±0.418^{bcd}	6.46±0.950^{cd}	150±26. 1^{ab}	64.2	16.0
Palmitic acid/8 %	9.75±0.417^{bcd}	17.1±0.203^{a}	114±12.8^{cd}	128.5	16.0
Palmitic acid/12 %	6.60±0.892^{e}	16.5±0. 818^{a}	66.5±4.32^{e}	286.3	23.8
Palmitic acid/16 %	6.47±0.715^{e}	16.7±0.391^{a}	49.8±5.25^{f}	455.3	28.4
Beeswax/4 %	11.5±1.23^{b}	10.9±1.86^{b}	169±23.5^{a}	0.19	0.0475
Beeswax/8 %	11.4±2.88^{b}	7.84±1.28^{c}	148±5.44^{ab}	0.29	0.0363
Beeswax/12 %	9.62±1.95^{bcd}	7.29±0.315^{c}	135±17.8^{bc}	0.50	0.0417
Beeswax/16 %	9.31±0.363^{bcd}	5.60±0.163^{de}	118±21.7^{cd}	0.72	0.0450

Values are means ± standard deviation (n≥3), calues with different letters as a superscript within a column are significant differences (p<0.05).

Correlation analysis. The correclation factors between the free-lipid ratio/content and the transparency, tensile sthength, and WVP are listed in **Table 2**. Only the transparency and WVP of composite films showed a highly negetive correclation with the free-lipid content and free-lipid ratio, whose absolute value was higher than 0.85. The absolute value of correclation factor between the transparency and free-lipid ratio was significantly higher than that between the transparency and free-lipid content/total-lipid content significantly. Consequently, the free-lipid ratio of composite films could be the best indicator for their transparency rather than the WVP.

The absolute value of correclation factor between WVP and free-lipid ratio was significant lower than that between WVP and free-lipid content. Our previous result proved the free-lipid ratio is highly negative related to the WVP [15]. Combining the current results, the free-lipid content showed a higher negative relation with the WVP. Therefore, raising free-lipid ratio was effective to improve the moisture barrier of hydrophilic films.

Table 2 Correclation between the free lipid content and free-lipid ratio and the related properties

Correlation factor	Free-lipid content				Free-lipid ratio			
	Stearic acid	Palmitic acid	Beeswax	Average	Stearic acid	Palmitic acid	Beeswax	Average
Transparency	-0.769	-0.918	-0.946	-(0.877± 0.095)^{a}	-0.876	-0.960	-0.958	-(0.932± 0.048)^{b}
Tensile strength	0.114	0.621	-0.933	-(0.066± 0.792)	-0.031	0.518	-0.746	-(0.086± 0.634)
WVP	-0.937	-0.955	-0.984	-(0.958± 0.024)^{a}	-0.870	-0.936	-0.859	-(0.888± 0.042)^{b}

Averages are means ± standard deviation (n≥3), averages with different letters within a row are significant differences (p<0.05).

Conclusion

The free-lipid ratio of composite films was the best indicator for the transparency rather than the moisture barrier. The free-lipid content had the highest negative correlation factor with the moisture barrier. Therefore, raising free-lipid ratio was effective to improve the moisture barrier of hydrophilic films.

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