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Effects of Plasticizer Type on the Characteristics of Mung-Bean Protein Films and Rice Starch and Chitosan Composite Films

Marija Radojkovic, Z. Zekovic
University of Novi Sad, Faculty of Technology, Department of Biotechnology and Pharmaceutical Engineering, Serbia

T. Bourtoom
Prince of Songkla University, Faculty of Agro-industry, Department of Material Product Technology, Hat Yai, Thailand

D. Tomanek
University of Novi Sad, Faculty of Technology, Department of Biotechnology and Pharmaceutital Engineering, Serbia

Abstract: The effects of different plasticizer types (sorbitol, PEG and glycerol) were tested on the characteristics of two types of films of natural origin: mung-bean protein films and composite films made of rice starch and chitosan. An examination was made of the effect of different concentrations (40%, 50% and 60%) of the above plasticizers on the characteristics of the protein films as well as the effect of different starch to chitosan ratios on those of composite films (1:1; 1:1,5; 1:2; 1,5:1; 1,75:1; 2:1) made up of equal concentrations of the said plasticizers (40%). The identified characteristics included film thickness and water vapour permeability.

The thickness of mung-bean protein and composite films ranged from 60.4 to 256.2 µm, and from 45.4 up to 188.8 µm, respectively. This data shows that the smallest film thickness values were recorded with the protein films containing 50 % of plasticizers, irrespective of the plasticizer type used. Furthermore, the largest composite film thickness was determined with the films with the chitosan to starch ratio of 1:2. The increase in composite film thickness was equal with all plasticizer types used.

The water vapour permeability in protein and composite films varied from 0.4064 to 1.4130 g mm/m^2 day kPa, and from 0.0126 to 0.4592 g mm/m^2 day kPa, respectively. An increase in plasticizer concentration induced higher water vapour permeability i.e. film

flexibility in protein films, whereas the lower chitosan proportion in the composite films resulted in lower permeability of the films.

Key words: mung bean, chitosan, rice starch, plasticizers, biodegradable and edible films, water vapour permeability, film thickness.

Introduction

Biodegradable edible polymer films serve as an alternative to the traditional use of synthetic components in film preparation and packaging and do not without producing any side effects (Kester and Fennema 1986). The components used in the production of biodegradable polymer films can be classified into three categories: hydrocolloids (proteins, polysaccharides and alginates), lipids (fat acids, natural wax and acil glycerol) and composites (Donhowe and Fennema 1993).

Mung bean is used as an alternative substance in biodegradable film production due to a high protein level. It can also be used against quinsy, system infections and hypertension, as an antidote to toxins and poisons, as a nutritive tonic and it is also known for its anti-cancer characteristics (www.iii.edu). Only limited information is currently available on the use of mung bean protein films, their mechanical characteristics and application, due to the lack of standard quality commercial mung bean protein (Thawien 2005). Most protein films provide good water barrier characteristics as compared to the synthetic ones (Nelson and Fennema 1991).

Biodegradable films can have heterogenic structure. It means that they can be made from a mixture of polysaccharides, proteins and/or lipids. This approach enables favourable exploitation of the functional characteristics of each film component (1). The pure-chitosan films are mostly used as gas barriers (Elson and Hayers 1985) and the rice starch ones do not possess any water vapour permeability characteristics (Jokay *et al.*, 1967). Composite films are primarily aimed at increasing permeability or mechanical characteristics in order to meet specific requirements (Guilbert 1986).

The film quality determined by polymer can be improved by plasticizer addition. Plasticizer increases film flexibility and extensibility, thus increasing its persistence (Jovanovic 1990). There is no rule determining the proportion of plasticizers in the coating solution, but they are used at lower concentrations than those of the film-making substances. The plasticizer proportion is estimated from its concentration in the final form of the film. It most generally amounts to 1 to 50% of the film solution, the optimum concentration being determined after the experiment (Zekovic 2004).

Material and Methods

Material

Mung bean protein samples produced by extraction were used in the experiment. Chitosan samples were isolated from sea crabs. All samples, including commercial rice starch, were produced at the Faculty of Agro-Industry, Prince of

Songkhla University, Thailand. The plasticizers used included glycerol, polyethilen-glycol (PEG) and sorbitol, their purity as requested by laboratory testings.

Film preparation

Mung-bean protein film preparation: The mung bean protein samples that were freeze-dried upon extraction and refrigerated until use (7.5g) were dissolved in distilled water (100ml) at room temperature. A specific plasticizer (sorbitol, PEG or glycerol) was added to the solution at concentrations of 40, 50 or 60%, respectively, of the solid phase. The pH level of the film solution was adjusted to 9.5 by adding NaOH. Then, the film solution was homogenized (10000rpm for 2 minutes). If dissolved air bubbles began to form, they were removed with a spoon. The homogenized solution was heated up to 75°C for 30 minutes, and then it was poured into non-stick trays to set. If the sediment appeared, the solutions were filtered before pouring into non-stick trays. The films were conditioned at 55°C for 18 hours in the heater. Testing of the plasticizer effect was performed in two parallel series of tests. After drying, Teflon plates with films were taken out of the heater and left at room temperature for about half an hour before the films were peeled off the plates.

Composite films made of rice starch and chitosan were prepared by mixing the solutions of these two substances.

Chitosan solution: 1 ml of acetyl salicilyc acid (1g/100ml) and 1g of chitosan were dissolved in 100ml of distilled water and mixed until the solution was fully homogenized.

Rice starch solution: Rice starch (3g) was dissolved in distilled water at room temperature and plasticizer (sorbitol, PEG or glycerol) was added at the concentration of 40% of solid mass. The solution was heated at 85°C for 15 minutes. After the solution was cooled down to 50°C, it was mixed with chitosan solution.

The rice starch and chitosan solutions were mixed at different ratios until uniform, the ratios being 1:1; 1:1.5; 1:2; 1.5:1; 1.75:1; 2:1 (v/v).

Further procedures of pouring the solutions onto plates and conditioning were identical to those in the production of mung bean protein films.

Film conditioning

All films were conditioned prior to being subjected to permeability and mechanical testing, in accordance with the Standard method, D618-61 (ASTM 1993a).

The films were first cut into suitable shapes (3 circles per film with a diameter of 70mm). These films were used to determine the film thickness and WVP (Water Vapor Permeability). They were left in desiccators at room temperature and 60% RH for at least 72 hours.

Film thickness determination

Thickness of the films was measured using a precision digital micrometer to the nearest 0.0001 (±5%) at five random locations on the film.

Water vapor permeability determination

Water vapor permeability was determined by the Modified Cup Method E96-92 (McHugh et *al.*, 1993).

The circles that were prepared and conditioned by the defined procedure were used for the water vapor permeability determination. The test cups were filled with 20g of Silica gel. A sample of film was placed in between the cup and the ring cover of each cup coated with silicone sealant and held with four screws around the cup circumference. After that, cups were placed in the heater at 25°C and 50% RH and measured every two hours (after 2, 4, 6 and 8 hours). The WVP value was calculated using basic equations for relative WVP value determination (McHugh *et al.*, 1993).

Results and Discussion

The plasticizers examined in this work are different chemical compounds, having different molecule sizes and shapes, as well as different relative molecular mass. These facts give us an opportunity to examine the effects of these factors on the water vapor permeability and mechanical characteristics of the films.

Mung bean protein films

Film thickness

Tables 1-3 show the results of film thickness determination (d, mm) in different plasticizers. The values presented are average ones, obtained by measuring thickness at five random places on the circles. These values suggest that the films containing plasticizers at the concentrations of 50% have the lowest film thickness values, irrespective of the plasticizer type.

Table 1. Results on the thickness determination of the mung bean sorbitol-plasticized films

PC*	40		50		60	
Sample	d					
1	0.1682	0.2300	0.1822	0.1052	0.1678	0.1534
2	0.0604	0.1546	0.2562	0.2212	0.1080	0.1778
3	0	0.1518	0.1444	0.1462	0.1526	0.1352

Table 2. Results on the thickness determination of the mung bean PEG-plasticized films

PC*	40		50		60	
Sample	d					
1	0.0952	0	0.1322	0.1514	0.2488	0.1672
2	0.1636	0	0.1482	0.172	0.188	0.106
3	0.0968	0	0.1178	0.171	0.222	0.199

Table 3. Results on the thickness determination of the mung bean glycerol-plasticized films

PC*	40		50		60	
Sample	d					
1	0.103	0.1568	0.2162	0.1892	0.1096	0.1758
2	0.2102	0.176	0.1154	0.1024	0.1198	0.1098
3	0.1452	0.1264	0.1134	0.0986	0.1632	0.1708

**PC-Plasticizer concentration in %*

Water vapor permeability

The effect of sorbitol as a plasticizer was not examined due to the bad texture of the films and their cracking at the RH of 50 %.

Fig. 1 shows the results on water vapor permeability (WVP) with glycerol and PEG used as plasticizers.

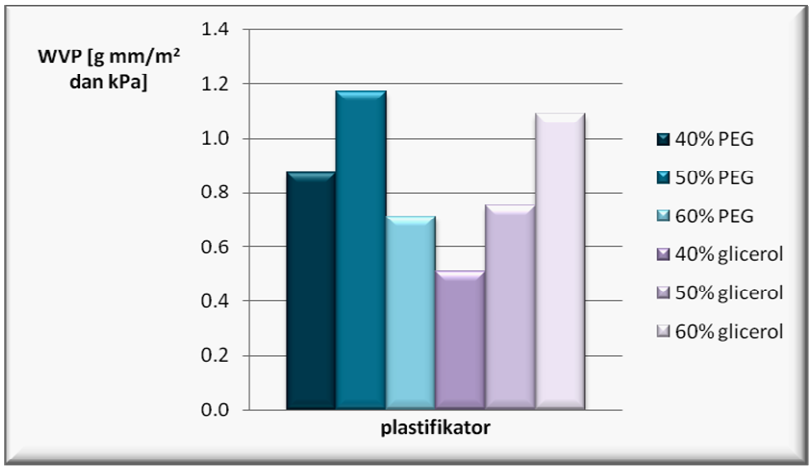

Figure 1. The effect of plasticizer concentration on water vapor permeability of the mung bean protein films

Evidently, an increase in PEG concentration did not induce any linear increase or decrease in the water vapor permeability value, resulting from the fact that measurements were performed during a 10-hour period. If the measurement had been prolonged (for example up to 24 hours), the results would most likely have not deviated, since there would have been sufficient time for big PEG molecules to absorb water vapor. The values of the water vapor permeability of the mung bean films increased with the increasing glycerol concentration. The increasing plasticizer concentration also gave rise to an increase in water vapor permeability. The higher the plasticizer concentration, the more flexible the films, and hence the higher water vapor permeability.

The differences in water vapor permeability values between different plasticizer types (sorbitol and PEG) were brought about by a different number of molecules in equal concentrations of different plasticizer types. Glycerol has smaller molecules and a higher number of them in equal concentration as compared to PEG, inducing higher flexibility and higher water vapor permeability of the films. These results suggest that water molecule binding is highly affected not only by the structure and characteristics of the molecules, but also by plasticizer concentration.

Composite films

Composite films made of rice starch and chitosan with glycerol as a plasticizer were not examined due to the fact that the films produced were too sticky and flexible. The white color of the PEG-plasticized rice-starch and chitosan films came from chemical reaction. These films were oily, because the size of the PEG molecules prevented them from being incorporated into the protein film structure.

Film thickness

Tables 4 and 5 show results on composite film thickness (d, μm). The values shown are average ones, obtained by measuring film thickness at five random portions of the circles.

Table 4. Results on composite sorbitol-plasticized film thickness

Ch : S	1:1	1:1	1:1.5	1:1.5	1:2	1:2	1.5:1	1.5:1	1.75:1	1.75:1	2:1	2:1
Sample							d					
1	54.6	62.6	69.2	67	76.6	65.8	67.2	60	70.4	56.2	56.8	82.6
2	67.6	73.8	60.6	75.6	188.8	52.2	78.6	52.2	57.4	63.4	52.4	45.4
3	75.6	58.8	70.8	76	58	76.6	61	62.8	56.6	49.8	49.6	0

Table 5. Results on composite PEG-plasticized film thickness

Ch : S	1:1	1:1	1:1.5	1:1.5	1:2	1:2	1.5:1	1.5:1	1.75:1	1.75:1	2:1	2:1
Sample							d					
1	56,2	52.4	103.4	93.2	69	72.8	90	69.4	71.8	62.2	102.2	86
2	67	60.8	69.2	79.8	77.4	98.2	69.8	79.2	71.8	56.6	67.6	61.2
3	71,4	81.2	89.2	90.6	95.2	119.6	54.2	80.6	70.8	79	57.6	86.8

The results obtained suggest that higher film thickness values were recorded in the films with the chitosan to starch ratio of 1:2. The said increase in composite film thickness was not dependent on the type of plasticizer used.

Water vapor permeability

Fig. 2. presents the water vapor permeability values obtained for the films with PEG and sorbitol used as plasticizers.

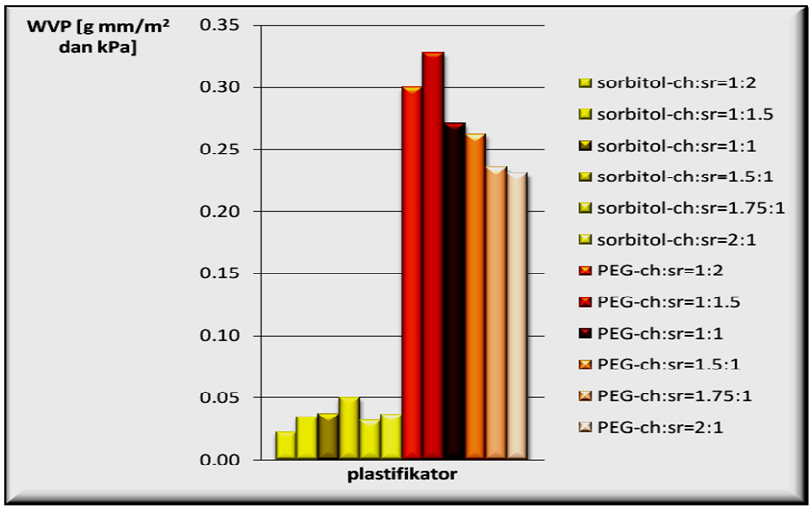

Figure 2. Water vapor permeability of composite films with different plasticizers added and different rice starch proportion

These values obtained with composite sorbitol-plasticized films of rice starch and chitosan vary around optimal concentration. The highest values of water vapor permeability were attained at the chitosan to starch ratio of 1.5:1. The higher chitosan rate induced the presence of a higher number of $-NH_2$ groups, which coupled with water molecules gave NH_3 molecules. PEG used as a plasticizer in composite films of rice starch and chitosan also caused the WVP value to vary around the optimum.

The values obtained were highly affected by the size of PEG molecules, considering the fact that PEG has big polymer chains which are very hard to incorporate into the composite film structure, the values produced being, therefore, constant.

Different plasticizer molecules, their shape, size and relative molecular mass, yield great differences in water vapor permeability values. Small molecules capable of entering the protein chain structure induce considerable reduction in water vapor permeability. This is the reason why optimum chitosan and starch proportions in the mixture differ among different plasticizers.

Conclusion

The study results obtained suggest several conclusions on the use of films of natural origin in the form of edible biodegradable packaging material and pharmaceutical coatings:

- The values of protein film thickness do not depend on plasticizer type, but on the concentration. Composite film thickness is dependent on the ratio of components in the solution the films are made of;

- The higher the plasticizer concentration, the higher the flexibility of mung bean protein films and, hence, water vapor permeability. The effect of molecule size and shape and relative molecular mass is significantly expressed with bigger molecules which slowly absorb water vapor;
- The effect of different plasticizer types used in composite films is equal to that in pure protein films, being dependent on the size and shape of molecules and relative molecular mass of the plasticizer;
- The chitosan and rice starch combination gives stronger but fragile films. Higher chitosan proportion in the composite solution yields lower water vapor permeability and lower film flexibility;
- Different optimal ratios of composite film components are obtained for different parameters. This is of great importance in the use of these films both in pharmaceutical coating and as packaging materials. The ratio of composite film components to be used is dependent on the characteristics and the specific use of the material being filmed.

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UTICAJ PLASTIFIKATORA NA KARAKTERISTIKE PROTEINSKIH FILMOVA MUNG BEAN-A I KOMPOZITNIH FILMOVA PIRINČANOG SKROBA I HITOZINA

- originalni naučni rad -

Marija Radojković, Z. Zeković
Univerzitet u Novom Sadu, Tehnološki fakultet, Katedra za biotehnologiju i farmaceutsko inženjerstvo

T. Bourtoom
Princ of Songkla University, Faculty of Agro-industry, Department of material product techology, Hat Yai, Tajland

D. Tomanek
Univerzitet u Novom Sadu, Tehnološki fakultet, Katedra za biotehnologiju i farmaceutsko inženjerstvo

Rezime

Praćen je uticaj različitih vrsta plastifikatora (sorbitola, polietilenglikola i glicerola) na karakteristike dve vrste filmova prirodnog porekla, proteinskih filmova pripremljenih od mung bean-a i kompozitnih filmova, smeše pirinčanog skroba i hitozina. Kod filmova koji u svom sastavu imaju proteine mung bean-a je analiziran uticaja različitih koncentracija (40%, 50% i 60 %) plastifikatora na ispitivane karakteristike filmova. Kod kompozitnog filma ispitan je uticaj različitih odnosa hitozina i skroba na karakteristike filmova sa istim koncentracijama pomenutih plastifikatora (40%). Karakteristike koje su određene i na osnovu kojih su praćeni pomenuti uticaji su de-bljina i propustljivost vodene pare filma.

Na osnovu ispitivanja dobijene su vrednosti debljine filmova u intervalima 60,4-256,2 µm kod proteinskih filmova mung bean-a i u intervalima 45,4-188,8 µm kod kompozitnih filmova. Dobijeni rezultati pokazuju da debljine ispitanih filmova mung bean-a koji sadrže plastifikatore u koncentraciji od 50%, imaju najmanje vrednosti debljine filma, bez obzira na vrstu dodatog plastifikatora. Takođe, određivanjem debljine kompozitnih filmova, može se zaključiti da filmovi u kojima je odnos hitozina i skroba 1:2 daju filmove najveće debljine. Ovaj porast debljine kompozitnih filmova je isti bez obzira na vrstu dodatog plastifikatora.

Propustljivost vodene pare kod filmova proteinske prirode je od 0,4064 do 1,4130 g mm/m^2 dan kPa, dok je kod kompozitnih filmova od 0,0126 do 0,4592 g mm/m^2 dan kPa. Povećanjem koncentracije ispitivanih plastifikatora kod proteinskih filmova dolazi do veće propustljivosti vodene pare tj. fleksibilnosti filmova, dok manji udeo hitozina u smeši kompozitnih filmova daje filmove sa manjom propustljivosti vodene pare.