Physical, mechanical, and barrier properties of sodium alginate/gelatin emulsion based-films incorporated with canola oil

Physical, mechanical, and barrier properties of sodium alginate/gelatin emulsion based-films incorporated with canola oil

A Syarifuddin*, Hasmiyani, A Dirpan, M Mahendradatta

Department of Food Science and Technology, Hasanuddin University, Makassar

E-mail address : adiansyah@agri.unhas.ac.id

Abstract. The development of mixed emulsion-based films formed by sodium alginate/gelatin incorporated with canola oil can offer particular properties such as water vapor barrier properties. The different ratios of sodium alginate/gelatin and sodium alginate/gelatin emulsion-based films incorporated with canola oil were developed and their effects on films' physical, mechanical and barrier properties were assessed. Here we set out to examine whether canola oil addition and different ratio of sodium alginate/gelatin modified physical, mechanical, and barrier properties of films. To do so, the films were prepared by vary the ratio of sodium alginate/gelatin (2.5, 1, 0.5). Canola oil addition induced changes in moisture content, thickness, solubility, water vapor transmission rate (WVTR), percent elongation at break ($p<0.05$). In addition, it is apparent that varying ratio of sodium alginate to gelatin induced change the mechanical properties of films. The reduction of sodium alginate to gelatin decreased the tensile strength of both films. Improved values of WVTR, tensile strength and solubility at break were observed when the ratio of sodium alginate/gelatin emulsion film incorporated with canola oil was 2.5. Therefore, different ratio of sodium alginate/gelatin incorporated with canola oil can be used to tailor emulsion films with enhanced water vapor barrier and mechanical properties

1. Introduction

The prevalence of novel techniques to maintain the quality of food without the requirement of food preservatives has encouraged food manufactures to improve edible film properties particularly linked in food preservation. One approach to further improve barrier properties for water vapor transfer is to design composite films by dissolving a lipid or oil into hydrocolloid film-forming solutions to make emulsion based-films. Emulsions are thermodynamically unstable systems and are prone to destabilize (e.g., coalescence, creaming) during food processing, transportation or storage [1] and emulsified films show better mechanical properties in comparison with pure lipid layers [2]. Many of the most important properties of emulsion-based films are determined by the right selection of the components used in the polymer matrix, compatability and preparation techniques [2].

Polysaccharides and proteins are usually applied to form films with good mechanical properties and can impart a barrier properties to the oxygen and carbon dioxide but their inherent hydrophilic nature makes them a poor barrier for moisture loss. In order to have better funcionality properties, most composite films were formed by dissolving hydrophobic compounds into hydrocolloid aqueous

solution. Hydrocolloids (polysaccharides and proteins) form a continuous and cohesive network and hydrophobic compounds provide the moisture barrier properties [3,4]. For example, oil addition over the hydrocolloids matrix forms bilayer films or dispersed oil into the hydrocolloid matrix forms emulsion (emulsified films).

Sodium alginate, a copolymer consisting of D-mannuronic and L-guluronic acid monomers [5], has been known as a pH and electric fiel-responsive polymers. Films prepared with hydrocolloids such as sodium alginate generally provide a strong films but remain exceptionally poor to water because of their hydrophilic nature [6,7]. In addition, film-forming potential of protein such as gelatin is mainly used because edible films made from gelatin are commonly characterized very transparent and form an excellent barrier to oxygen and carbondioxide but the mechanical properties of these films are vulnerable to higher water content. Several researchers have tried to improve the quality of gelatin films by adding corn starch [8], alginate [9], pectin [10]. The use of oils in order to improve moisture barrier properties of films has been well documented [11,12,13]. Canola oil has potential to be incorporated into hydrocolloids matrix since 18 carbon fatty acids account for about 95% of canola's total fatty acids [14].

Sodium alginate and gelatin have been known for their ability to increase viscoelastic of gels [15] and to form good film-forming properties [16]. However film properties of different ratios of sodium alginate/gelatin with added canola oil have not been investigated.

The aims of the present work were to assess the effect of different ratios of sodium alginate/gelatin on films's properties. Physical and mechanical properties changes of sodium alginate/gelatin emulsion-based due to canola oil incorporation were also investigated. This evaluation was carried out by measuring the physical, mechanical and barrier properties to films.

2. Materials and Method

2.1. Materials

Sodium alginate (SA) and gelatin (G) purchased from Nura Jaya (Surabaya, Indonesia) were used as film-forming components of the hydrophilic continous phase for emulsion-based films. Canola oil (CO) purchased from local market was used as hydrophobic disperse phase, and glycerol purchased from local chemical store was added as plasticizer. Span 80 and tween 80 employed as emulsifiers were purchased from local chemical store.

2.2. Methods

2.2.1. Film formation

Films were produced by using casting technique in two stages. First, polysaccharides films were produced in different ratios of sodium alginate and gelatin in order to find out the formulation that resulted in films with better performance. This formulation then was used in the second stage of the study along with canola oil. In first stage, the effect of different ratios of sodium alginate/gelatin on physical, mechanical and barrier properties was evaluated. The effect of the canola oil addition was also evaluated in the second stage of the study.

Films were produced by using casting technique. First, polysaccharides films were prepared by mixing amounts of κ-carrageenan and gelatin to achieve a final polysaccharides concentration of 2.25% (w/w).

For sodium alginate/gelatin films-based films (SA/G), sodium alginate, gelatin and glycerol aqueous solutions were prepared (Table 1). Sodium alginate was dissolved in 200 ml of warmed distilled water (60^0C) for 15 min using magnetic stirrer. The gelatin was succesively added under constant stirring for 15 min. Then, glycerol was added under constant stirring for 15 min. After 45 min stirring, the solution was kept in waterbath for 2 h. The obtained film solution were cooled at room temperature. 20 ml of film-forming solutions were spread onto petri dishes and they were

subsequently dried in an oven at 50^0C for 18 h. Finally, dried film were peeled off from the dishes and kept in dessicators at room temperature.

For sodium alginate/gelatin emulsion-based films incorporated with canola oil (SA/G CO), the formulations above were used in addition with canola oil (40% of polysaccharides) (Table 2). After 2 h in waterbath, another step is neccesarry before pouring of film-forming solution in order to incorporate blends of emulsifiers and canola oil. The amount of span 80 and tween 80 required were pre-solubilised in canola oil. Then, all of these components were homogenized with Ultra-Turrax at 24.000 rpm during 2 min. 20 ml of film-forming solutions were poured onto petri dishes and they were dried in an oven at 50^0C for 18 h. Finally, dried film were peeled off from the dishes and kept in dessicators at room temperature.

Table 1. Experimental design of edible films with sodium alginate/gelatin (SA/G)

Ratio Sodium alginate/gelatin	Sodium alginate (% w/w)	Gelatin (% w/w)	Glycerol (% w/w)
2.5	1.61	0.64	30
1	1.125	1.125	30
0.5	0.75	1.5	30

Table 2. Experimental design of sodium alginate/gelatin emulsion-based films incorporated with canola oil (SA/G CO)

Ratio Sodium alginate/gelatin	Sodium alginate (% w/w)	Gelatin (% w/w)	Glycerol (% w/w)	Canola oil (% w/w)
2.5	1.61	0.64	30	40
1	1.125	1.125	30	40
0.5	0.75	1.5	30	40

2.2.2. Film characterization

Thickness

Film thickness was measured by using a digital caliper (KRISBOW KW06-422) with 200 mm x 8" and 0.01 mm accuracy. The values showed represent the means of five measurements randomly taken during each evaluated samples.

Water Vapour Transmisson Rate (WVTR)

The water vapour transmisson rate was determined using gravimetric dessicant method [17] that was modified. Small cups with lids were prepared and filled with silica gel. Then, the films were placed on the mouth of cup then sealed with wax. After sealed, the cups were weighed then placed in dessicator containing NaCl with concentration 70% for interval time 0, 8, 24, 32, 48 h. Then, the weights of cup were recorded. Data obtained then made linear regression equation in order to obtain the slope of weight of cup. Water vapor transmission rate is expressed by the slope of weight of cup (g/h) divided by the area of the film tested (cm^2). The mean value of three measurement replications was reported for each sample.

Tensile Strength (TS) and Percent Elongation at Break

TS and EB were measured using Universal Testing Machine (Hung Ta, HT-2010). Film strips (10 cm x 2 cm) were prepared and mounted to a separate grip of Universal Testing Machine. Initial grip separation was set at 60 mm and the cross head-speed was set at low speed. The tensile strength of the specimen was calculated by dividing the maximum load to rupture (F) and the area of films (A).

$$TS = \frac{F}{A}$$

Percentage elongation at break was calculated by dividing the film elongation at the moment of rupture of the specimen occured (b) by initial length of the specimen (a) and multiplying by 100.

$$EAB = \frac{b}{a} \times 100$$

Solubility in water [18]

The solubility of samples was expressed as the percentage of the film dry mass which is soluble after 24h immersion in distilled water. First, 3x2 cm of samples were dried in an oven at 105^0C for 24 h and weighed (W1). After 24 h drying, each samples was immersed into a 50 ml tube containing 10 ml of distilled water. After 24 h immersion in distilled water, the solution was filtered using filter paper (Whatman no.1), and finally the samples remained on the filter paper were oven dried at 105^0C during 24 h after which the samples were weighed to determine the dried remnant insoluble mass (W2). Solubilty was then calculated using the formula:

$$\text{Solubility } (\%) = \frac{W1-W2}{W1} \times 100$$

Moisture content (MC)[19]

The moisture content of samples was determined by calculating the loss of film weight after drying in an oven at 105^0C for 24 h.

3. Statistical analysis

Data analyses were performed using R software (R-3.3.1 release). T-test was used to determine significant differences among the mean of physical and mechanical values calculated in SA/G and SA/G CO films. Three replications were used to determine physical and mechanical properties. For all data analyses, the effects were considered significant when $P<0.05$. The relationship between physical, mechanical and barrier properties was studied using explorative principal component analysis (PCA) with R software (R-3.3.1.*release*).

4. Results and Discussion

Table 3. Summaries of mean physical, mechanical and barrier properties of SA/G and SA/G CO films

.

Films	Parameters					
	Moisture Content (%)	Thickness (mm)	Water Solubility (%)	WVTR (g/h.cm^2)	Tensile Strength (MPa)	Elongation at break (%)
SA/G films						
2.5	26.85±1.31	0.12±0.005	27.98±2.27	0.091±0.000	10.68±2.94	24.23±3.26
1	27.91±0.22	0.13±0.003	45.44±18.72	0.090±0.000	9.71±1.79	21.63±3.86
0.5	24.00±0.27	0.13±0.002	36.81±3.08	0.091±0.000	6.79±1.22	20.97±0.42
SA/G CO films						
2.5	22.53±0.86	0.26±0.03	22.66±11.88	0.027±0.006	11.35±1.19	53.60±3.08
1	27.10±0.28	0.25±0.02	30.13±0.23	0.031±0.005	8.99±2.16	103.53±19.08
0.5	16.14±0.97	0.20±0.02	34.76±3.95	0.033±0.004	7.49±1.98	130.22±14.19

Values were mean ± standard deviation

Table 4. Summaries of t-test of physical and mechanical properties between SA/G and SA/G CO films

Films	Moisture Content (%)	Thickness (mm)	Solubility (%)	WVTR ($g/h.cm^2$)	Elongation at break (%)	Tensile Strength (MPa)
SA/G	26.25 ± 1.88^a	0.13 ± 0.00^a	36.74 ± 12.18^a	0.091 ± 0.000^a	22.28 ± 2.94^a	9.06 ± 2.53^a
SA/G CO	$21.93\pm.4.81^b$	0.24 ± 0.03^b	29.185 ± 8.20^b	0.030 ± 0.005^b	95.78 ± 35.75^b	9.27 ± 2.31^a

Values were mean ± standard deviation. Different superscripts within the same column indicate significant differences ($P<0.05$)

Moisture content

Table 3 showed the water content of SA/G films and SA/G CO films at different ratios (2.5, 1, 0.5). Results show that the reduction of sodium alginate (and the corresponding increase of gelatin) lead to a decrease of water content on both films. Possibly, the different ratios of SA/G presented the moisture content values (24.00-27.91%) higher than SA/G CO (16.14-27.10%). In this study we also did t-test to determine significant differences among moisture content values calculated in SA/G and SA/G CO. T-test revealed that SA/G CO films showed lower moisture content in comparing with SA/G films. From these results, it is apparent that varying the concentration of gelatin and canola oil addition can result in modification of the network of structure of the films, which is reflected in the moisture content.

Thickness

Thickness of both films (SA/G and SA/G CO) at different ratios was shown in Table 3. Films made with SA/G particularly with the highest ratio (ratio 2.5) showed the lowest thickness. Conversely, the highest thickness (ratio 2.5) was observed from films made with SA/G CO (ratio 2.5). The possible reasoning for this may be because of the sodium alginate increased. Increasing the amount of sodium alginate used leading to increased immiscibility of the blend resulting in increasing thickness obtained. These results was also supported by t-test on thickness values calculated in SA/G and SA/G CO films incorporated with canola oil. T-test revealed that SA/G CO showed a thicker films in comparing with SA/G. The fact that thickness of that SA/G CO were higher than that of SA/G allowed us to postulate that thickness is inversely related to canola oil addition. Some authors reported that edible films containing hydrophobic substances such as waxes and oils can form thicker films [7,20].

Water Solubility

The water solubility of both films at different ratio was shown in Table 3. Addition of canola oil to films containing different ratio of sodium alginate/gelatin (SA/G CO) resulted in a lower water solubility than those observed for films containing SA/G only. Both ratio 1 of film SA/G and ratio 0.5 of SA/G CO showed the highest values of water solubility indicating influence of gelatin used. These results similar with observed by some authors who found that the addition of gelatin significantly increased solubility in water [8]. The addition of canola oil at different ratios of sodium alginate/gelatin was also observed. T-test revealed that the presence of canola oil within the lowest sodium alginate and the highest gelatin concentration (ratio SA/G 0.5) led to blocking of leaching out these polysaccharides into water.

Water vapor transmission rate

The WVTR of both films at different ratio was shown in Table 3. The WVTR values were lower for all ratio of SA/G CO (0.027-0.033 g/h.cm^2) compared with SA/G films (0.090-0.091 g/h.cm^2). T-test results showed that the presence of canola oil reduced the WVTR values by 30% relative to the values of sodium alginate/gelatin films. Incorporations of canola oil at different ratios of sodium alginate/gelatin showed lower the WVTR values due to the formation of an inter-connecting lipid network within the film matrix, which provides hydrophobicity and thus reduces the adsorption of water molecules, as has been observed in emulsified films by other authors [21,22]. As a result, the water vapor transmission through the SA/G CO would be different with SA/G films.

Mechanical properties

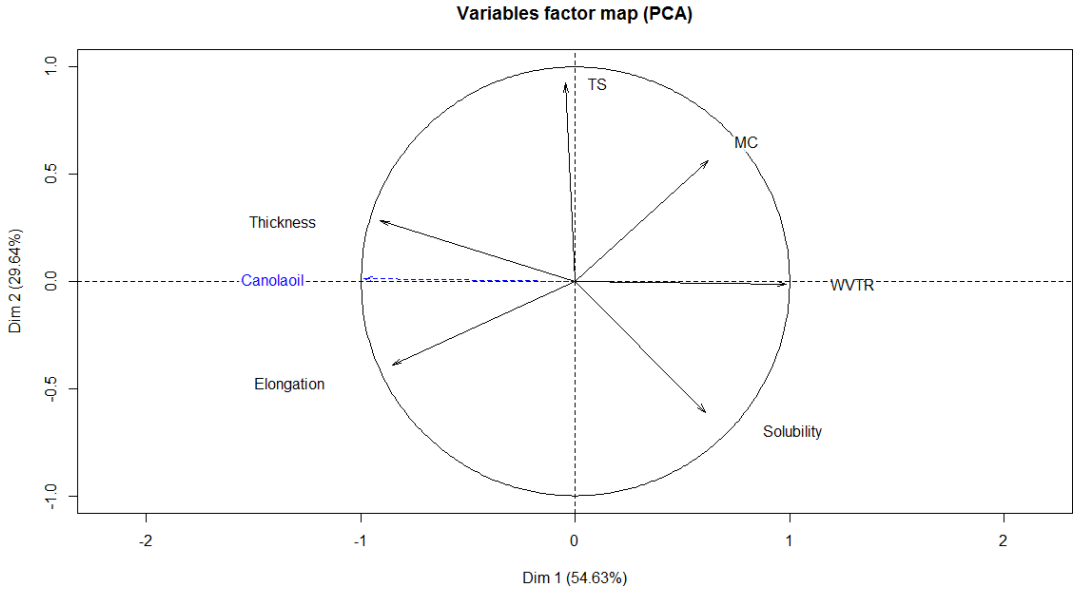
In our study, the properties of tensile strength and elongation at break of both films at different ratio can be seen in Table 3. In this study, a higher amount of sodium alginate used (and the corresponding decrease of gelatin), the highest tensile strength values obtained. It may be due to the presence of intermolecular interactions between polymers. These results were similar with results obtained by some authors who found that high tensile strength were observed for films produced with low gelatin and high starch concentration [23].
On the other hand, the elongation at break of SA/G films demonstrated an intense decrease from 24.23% to 20.97%. In films made with SA/G only the elongation values decreased as gelatin concentration increased (and the corresponding decrease of sodium alginate). A similar results were also observed by some authors [24]. Conversely, an intense increase were observed on SA/G CO. This could be due to the plasticizing effect of canola oil. By t-test we found that the elongation values of SA/G CO significant increased.

PCA analysis

In our study, a PCA was carried out to select the best ratio of films among SA/G and SA/G CO with respect to their physical, mechanical and barrier properties. Fig. 1 showed the PCA of the first two principal components of both films and also showed how the different ratios of sodium alginate/gelatin affected physical, mechanical and barrier properties. The first two components (PC1 and PC2) together explained 84.27% of the variance, with PC1 and PC2 explaining 54.63% and 29,64% of the variance, respectively (Fig.1A). It was clearly separate between SA/G films and SA/G CO films (Fig.1B). PCA1 reflects the effect of film solubility and WVTR and showed mainly a positive correlation with solubility and WVTR and negative correlation with elongation. PCA2 is positive correlated with thickness, TS and MC and negative correlated with elongation and solubility.
PCA showed that thickness and TS of SA/G CO ratio 2.5 and SA/G CO ratio 1films (Fig.1B) were correlated since they are plotted to each other. This is in accordance to the previous results where films containing hydrophobic substances such as waxes and oils can form thicker films. In addition, a higher sodium alginate with the presence canola oil (SA/G CO ratio 2.5) make a strong intermolecular interactions between polymers (and the corresponding higher TS). Whereas MC of SA/G films ratio 2.5 versus elongation of SA/G CO films ratio 0.5 loadings, plotted on opposite side of the PC vector, were negatively correlated between each other. Solubility of SA/G film ratio 0.5 loading which is placed orthogonally against elongation of SA/G CO films ratio 0.5 do not correlate: in fact, it is known that increasing amount of gelatin used, higher values of elongation were obtained.

PCA showed that films composed of ratio 2.5 or 1 of SA/G CO were the best ratio due to good combination of tensile strength, thickness and WVTR. However, when the properties of those two ratios (2.5 and 1) were compared, ratio 2.5 present better mechanical and barrier properties (higher TS, low solubility and low WVTR). Thus, the films composed of sodium alginate/gelatin incorporated with canola oil with ratio 2.5 (SA/G CO 2.5) were elected as a better films.

(A)



(B)

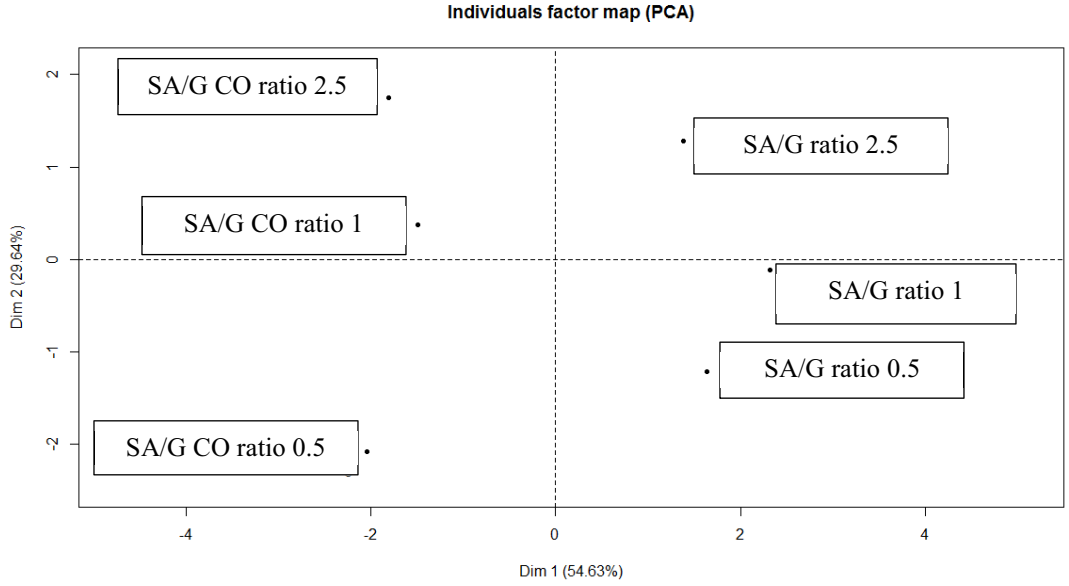


Fig.1A and B. PCA of different ratio of SA/G and SA/G CO films.

5. Conclusions

The incorporation of canola oil into films composed with sodium alginate and gelatin affects theirs basic functional properties. Canola oil incorporation significantly affect moisture content, thickness, WVTR, solubility in water and elongation at break. For all sodium alginate/gelatin emulsion film incorporated with canola oil, the 2.5 ratio films showed the higher tensile strength, lower solubility and lower WVTR.

Acknowledgments

We gratefully acknowledge support of Hasanuddin University via PPI-WCU 2016.

References

[1] Mao, L., Roos, Y.H., O'Callaghan, D.J. and Miao, S. 2013. Volatile release from whey protein isolate-pectin multilayer stabilized emulsions: Effect of pH, salt and artificial salivas. Journal of Agricultural and Food Chemistry **61**(26): 6231-6239..
[2] Galus, S. and Kadzinska, J. 2015. Food applications of emulsion-based edible films and coatings. Trends in Food Science & Technology **45**(2): 273-283.
[3] Kamper, S.L. and Fennema, O. (1984a) Water vapor permeability of an edible, fatty acid, bilayer film. Journal of Food Science, **49**(6), 1482-5.
[4] Kamper, S.L. and Fennema, O. (1984b) Water vapor permeability of edible bilayer films. Journal of Food Science, **49**(6), 1478-81.
[5] Borchard, W., Kenning A., Kapp A., Mayer C. 2005. Phase diagram of the system sodium alginate/water: a model for biofilms. Inte J Biol Macromol **35**(5): 247-56
[6] Guilbert, S. (1986) Technology and application of edible protective films. In:Food packaging and preservation, M. Mathlouthi (ed.), Elsevier Applied Science Publishers, New York, pp. 371-94.
[7] Kester, J. J. and Fennema, O. R. 1986. Edible films and coatings: A review. Food Technology **40** (12): 47-59.
[8] Fakhouri, F.M., Martelli, S.M., Caon, T., Velasco, J.I. and Mei, L.H.I. 2015. Edible films and coatings based on starch/gelatin: Film properties and effect of coatings on quality of refrigerated Red Crimson grapes. Postharvest Biology and Technology, **109**: 57-64.
[9] Dong, Z., Wang, Q and Du, Y. 2006. Alginate/gelatin blend films and their properties for drug controlled released. Journal of Membran Science, **280**(1-2): 37-44.
[10] Rezvanian, M., Ahmad, N., Amin, M.C.I.M., Shiow-Fern, Ng. Optimization, characterization, and in vitro assesment of alginate-pectin ionic cross-linked hydrogel film for wound dressing applications. International Journal of Biological Macromolecules **97**: 131-140.
[11] Cerquira, M.A., Souza, B.W.S., Teixera, J.A., Vicente, A.A. 2012. Effect of glycerol and corn oil on physicochemical properties of polysaccharides films-A comparative study. Food Hydrocolloids **27**:175-184.
[12] Ghasemlou, M., Aliheidadri, N., Fahmi, R., Shojaee-Aliabadi, S., Keshavarz, B., Cran, M.J., Khaksar, R. 2013. Physical, mechanical and barrier properties of corn starch films incorporated with plant essential oils. Carbohydrate Polymers, **98**(1): 1117-1126.
[13] Zukas, B.G. and Gupta, N.R. 2016. Improved water barrier properties of calcium alginate capsules modified by silicone oil. Gels, **2**, 14.
[14] Ackman, R.G. 1990. Canola fatty acids-an ideal mixturefor health, nutrition, and food use, in Canola and Rapeseed. Production, Chemistry, Nutrition and Processing Technology (ed F. Sahidi). Avi Book, Van Nostrand Reinhold, New York.pp. 81-98.
[15] Derkach, S.R., Ilyin, S.O., Maklakova, A.A., Kulichikhin, A.G. and Malki, A.Y. 2015. The rheology of gelatin hydrogels modified by κ-carrageenan. LWT-Food Science and Technology **63** (1): 612-619.
[16] Pranoto, Y., Lee, C.M. and Park, H.J. 2006. Characterizations of fish gelatin films added with gellan and κ-carrageenan. LWT-Food Science and Technology **40** (5): 766-774.
[17] Poeloengasih, C.D., dan Marseno, D.W. 2003. Karakterisasi edible film komposit protein biji kecipir dan tapioka. Jurnal Teknologi dan Industri Pangan **XIV**(3): 224-232.
[18] Ahmad, M., Benjakul, S., Prodpran, T. and Agustini, T.W. 2012. Physico-mechanical and antimicrobial properties of gelatin film from the skin of unicorn leatherjacket incorporated with essentials oils. Food Hydrocolloids **28**: 189-199.

[19] Zahedi, Y., Ghanbarzadeh, B. and Sedaghat, N. 2010. Physical properties of edible emulsified films based on pistachio globulin protein and fatty acids. Journal of Food Engineering **100** (1): 102-108.
[20] Greener, I. K. and Fennema, O. 1989. Evaluation of edible, bilayer films for use as moisture barrier for food. Journal of Food Science **54**(6): 1400-1406.
[21] Fabra, M., Pérez-Masiá, R., Talens, P., & Chiralt, A. (2011). Influence of the homogenization conditions and lipid self-association on properties of sodium caseinate based films containing oleic and stearic acids. Food Hydrocolloids, **25**, 1112-1121
[22] Shellhammer, T., & Krochta, J. (1997). Whey protein emulsion film performance as affected by lipid type and amount. Journal of Food Science, **62** (2), 390-394.
[23] Zhong, Q-P.; Xia, W-S. 2008. Physicochemical properties of edible and preservative films from chitosan/cassava starch/gelatin blend plasticized with glycerol. Food Technology and Biotechnology, **46**, p. 262-269
[24] Xiao, C., Lu, Y., Gao, S., and Zhang, L. 2001. Characterization of konjac glucomannan-gelatin blend films. Journal of Applied Polymer Science, **79**:1596-1602.