OPTIMIZATION OF EDIBLE FILM-BASED FORMULA OF CORN STARCH, CARRAGEENAN, AND RICE BRAN FOR HARD CANDY PACKAGING

OPTIMASI FORMULA EDIBLE FILM BERBASIS MAIZENA, KARAGENAN DAN BEKATUL PADI SEBAGAI PENGEMAS HARD CANDY

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Abstract

Plastic packaging has dominated the waste, and the number is increasing every year. Candy plastic packaging waste is most often considered trivial because of its small size, so it is usually disposed of carelessly. Due to its non-biodegradable, it causes environmental pollution. Edible film packaging is an alternative to reduce the impact of candy packaging waste pollution. The purpose of this study was to obtain the optimum formula of the edible film between corn starch, carrageenan, and rice bran as a hard candy packaging with the Response Surface Methodology (RSM) Central Surface Composite Design using the Design Expert 10.0.7. The prediction data obtained is then verified and tested by t-test at a 5% reliance interval.The optimum formulation of RSM results is 3.4% of corn starch, 1.1% of carrageenan and 0.38% of rice bran with predicted response of water content of 14.51%, WVTR 61,06 g/m^2/hour, viscosity of 258.8 cP, tensile strength of 107.9 kgf/cm^2, elongation of 19.41%, and modulus of response young 586.28 kgf/cm^2. The verification of the optimum formula had a moisture content of 14.37%, WVTR 63.34 g/m^2/hour, viscosity of 244.9 cP, tensile strength of 96.9 kgf/cm^2, elongation of 20.96%, and young modulus of 462.49 kgf/cm^2.

Key Words : Corn starch; Carrageenan; Rice bran; Formula optimization; Edible film; Hard candy

Abstrak

Kemasan plastik selama ini mendominasi sampah dan setiap tahunnya jumlahnya meningkat. Kemasan permen yang paling sering dianggap sepele karena ukurannya yang kecil sehingga biasanya dibuang dengan sembarangan. Sifatnya yang non-biodegradable menimbulkan pencemaran lingkungan. Kemasan berupa edible film merupakan alternatif untuk mengurangi dampak pencemaran sampah kemasan permen. Tujuan dari penelitian ini adalah untuk mendapatkan formula optimum edible film antara pati maizena, karagenan dan bekatul padi sebagai pengemas hard candy dengan metode Response Surface Methodology (RSM) Central Composite Design menggunakan program Design Expert 10.0.7. Data prediksi yang diperoleh kemudian diverifikasi dan diuji dengan statistik t-test pada selang kepercayaan 5%.. Formulasi optimum hasil RSM yaitu 3,4% pati maizena, 1,1% karagenan dan 0,38% bekatul padi dengan prediksi respon kadar air 14,51%, WVTR 61,06 *g/m²/jam, viskositas 258,8 cP, kuat tarik 107,9 kgf/cm², elongasi 19,41%, dan modulus young 586,28 kgf/cm². Verifikasi yang dilakukan dengan formulasi optimum tersebut menghasilkan edible film yang memiliki kadar air 14,37%, WVTR 63,34 g/m²/jam, viskositas 244,9 cP, kuat tarik 96,97 kgf/cm², elongasi 20,96%, dan modulus young 462,49 kgf/cm².*

Kata kunci : Pati Maizena; Karagenan; Bekatul; Optimasi formula; Edible film; Hard candy

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INTRODUCTION

Plastic packaging has dominated the trash, and every year the number has increased by 8%[1)]. Of all plastic waste, no more than 5% is recycled, and the rest is left to accumulate in the environment. Candy packaging plastic waste is most often considered trivial because of its small size so that it is usually disposed of carelessly and causes environmental pollution. The accumulation of candy packaging plastic waste will cause environmental pollution due to the nature of the plastic that is non-biodegradable or not easily decomposed by microorganisms. So we need biodegradable packaging that is more environmentally friendly.

Hard candy is a type of non-crystalline candy with the characteristics of a hard texture, the appearance that is shiny and clear. Sucrose, water, and glucose syrup are the main ingredients in making hard candy. Hard candy is expected to be non-sticky and does not crystallize when received by consumers. The packaging is one factor that influences the final characteristics of hard candy when accepted by consumers. We need the right packaging specifications, so that hard candy is not easily wet and sticky[2)].

One of the polysaccharides that are widely used as material for making edible films is starch. This is because starch is a renewable natural resource with abundant availability, low cost, naturally biodegradable, and forms transparent, odourless, and non-toxic film[3)]. Like other types of polysaccharides, cornstarch also has hygroscopic properties. Among other types of starch, the hygroscopic nature of corn starch is lower than cassava starch, rice starch, or potato starch.

Carrageenan is a polymer in the form of polysaccharide sulfate extracted from red seaweed (*Rhodophyceae*). Based on its chemical structure and characteristics, carrageenan is classified into three types: lambda, iota, and kappa carrageenan. Kappa carrageenan is one type of carrageenan that is most often used in edible film research because it forms a hard and strong gel so that the strength of the gel-forming agent can increase the ability to form a good film[4)].

The use of fillers is also an alternative to improve the characteristics of edible films from polysaccharide-based composites in terms of mechanical properties. The addition of filler will increase the mechanical characteristics of modulus young and tensile strength. Some fillers used include cassava pulp, lignin, wheat bran, and rice bran. In this study, rice bran was used as a filler because the fiber content was high enough to improve the mechanical characteristics of edible film. Both soluble and insoluble fiber can be used in edible film formulations. In this research, the production of corn starch edible film and carrageenan was made by adding filler using rice bran. This research aims to optimize the formulation of corn starch-carrageenan-rice bran as the base material for the edible film. Edible film produced from corn starch composite-carrageenan-rice bran will be applied as hard candy packaging.

MATERIALS AND METHODS

Materials and Tools

This research uses ingredients which include commercial brand cornstarch "Maizenaku", grade I carrageenan produced by PT. Indoflora Cipta Mandiri Malang, commercial brand rice bran flour "Bekatul Sehat Barokah Jaya" sifted with 100 mesh size sieve, food-grade glycerin, aquades, "KIS" and "FOX'S" hard candy brands.

The tools used in this research are beaker glass, thermometer, hotplate stirrer (Thermo Scientific Cimarec), magnet stirrer, aluminum foil, analytical scales (Kern ABS 220-4N), spatula, measuring cup, measuring pipette, stainless steel print media size 35 cm x 21 cm, oven, desiccator, hygrometer, universal testing machine (Instron 3369, USA), dehumidifier (KRIS PD20E-20, RRC), and scanning electron microscope (SEM) (FEI type Inspect S50, Japan).

Rice Bran Preparation

Rice bran used is commercial rice bran brand "Barekat Healthy Barokah Jaya" which has been roasted at 90ºC for 1 hour to reduce the risk of lipolytic damage to rice bran by inhibiting the activity of the lipase enzyme. Furthermore, the bran is roasted for 5 minutes with low heat accompanied by stirring. The rice bran is then reduced and sieved using a 100 mesh sieve.

Table 1.
The range of independent variable values

Independent variable	*Process factors*	Level				
		- 1,41	- 1	0	+ 1	+ 1,41
Corn Starch (%)	X_1	0.82	1,5	2.5	3.5	4.18
Carrageenan (%)	X_2	0.45	0.67	1	1.33	1.55
Rice bran(%)	X_3	0.03	0.12	0.25	0.38	0.47

Design

Design the formulation using Design Expert 10.0.7 software. The optimization of the edible film formula uses three variables, namely X1 (cornstarch,%), X2 (carrageenan,%), and X3 (rice cooker,%) (Table 1). All treatments consisted of 20 experimental units. The RSM experimental design was used to optimize the formulation of corn starch, carrageenan, and rice bran to get the best edible film formulation based on water content, WVTR, the viscosity of edible film formula, tensile strength, elongation, and young modulus.

Formulation

The formulation stage is making products based on formulas obtained from the Design Expert 10.0.7 design software formulation. The film making process uses the gel casting method, which starts with dissolving and heating cornstarch in 150 ml of distilled water to a temperature of 70ºC and carrageenan and bran 150 ml of distilled water to a temperature of 60ºC[5]. After each solution reaches this temperature, the temperature is maintained for 30 minutes. Then mix the two solutions and glycerin (2% v / v) for 20 minutes is stirred using a magnetic stirrer to make it homogeneous. Then the solution is poured into a film mold and dried with RH conditions 40% ± 5 (temperature conditions 30 ± 5ºC) for 24 hours. After drying, the edible film to be used is separated from the mold and then wrapped in aluminum foil and stored in a closed container filled with silica gel before analysis.

Measurement of response

The results of the measurement of the response of each formula from the results of the Design Expert 10.0.7 program design are then inputted to be analyzed for data with multiple regression to fit the second-order polynomial regression model that contains the coefficient of linear, quadratic, and two-factor interaction (2FI) interaction effects. The model with the highest level and has a significant value in Analysis of Variance (ANOVA) and not significant in Lack of Fit is the chosen model.

Optimization

The results of the analysis of each response are then used to optimize to produce the most optimum formula. The program will optimize based on the maximum value of viscosity, tensile strength, per cent of elongation and Modulus young, as well as the minimum value in the analysis of water content and Water Vapor Transmission Rate (WVTR). This optimization phase provides recommendations for new formulas according to the optimal program, which is a formula with a maximum desirability value.

Verification

The verification phase is carried out after the optimum formula is obtained, making the best formula obtained from the optimization results of Design Expert 10.0.7. The verification phase aims to see the suitability of the predicted response value generated by the program with the actual value obtained. Verification is done with two replications, and the results will be compared with the response value predicted by Design Expert 10.0.7[6].

Table 2.

Experimental design and response

	Factors			Responses					
Std	CS (%)	CR[2] (%)	RB[3] (%)	MC[4] (%)	WVTR[5] ($g/m^2/h$)	Vis[6] (cP)	TS[7] (kgf/cm^2)	Elo[8] (%)	M Y[9] (kgf/cm^2)
1	-1	-1	-1	19.17	66.22	92.3	40.18	13.83	261.36
2	+1	-1	-1	15.63	64.26	102.9	44.85	22.31	201.09
3	-1	+1	-1	17.86	63.42	290.0	70.46	24.77	285.99
4	+1	+1	-1	14.29	65.03	391.1	93.42	17.90	469.05
5	-1	-1	+1	17.53	65.11	102.2	58.75	21.63	272.28
6	+1	-1	+1	15.23	61.33	150.7	70.95	23.86	298.48
7	-1	+1	+1	16.73	66.01	227.0	74.60	22.63	331.83
8	+1	+1	+1	14.23	62.69	343.9	109.0	14.22	726.40
9	-1.41	0	0	18.65	66.54	142.7	31.50	18.65	169.10
10	+1.41	0	0	14.56	64,14	286.5	91.50	21.73	422.92
11	0	-1.41	0	16.38	66.68	67.4	49.59	21.78	199.68
12	0	+1.41	0	15.68	63.48	392.9	95.43	23.15	427.89
13	0	0	-1.41	16.35	62.16	171.3	73.76	22.64	330.83
14	0	0	+1.41	15.63	61.29	162.4	109.8	24.55	487.57
15	0	0	0	15.21	59.83	169.0	76.02	23.99	346.82
16	0	0	0	15.54	61.98	177.3	105.4	21.44	472.61
17	0	0	0	15.04	61.44	168.8	75.64	20.58	370.21
18	0	0	0	15.17	60.48	178.2	91.98	23.79	429.79
19	0	0	0	15.31	61.16	177.9	101.2	23.24	401.67
20	0	0	0	14.81	61.58	166.7	77.87	22.61	348.93

Description : [1]CS : corn starch, [2]CR : carrageenan, [3]RB: rice bran, [4]MC : moisture content, [5]WVTR: Water Vapour Transmission Rate, [6]Vis: viscosity, [7]TS: tensile strength, [8]Elo: elongation, [9]MY: modulus young.

Edible Film Application as a Package of Hard Candy

Edible film application as a package of hard candy is made by two methods, namely sealing and double-twisting. Edible film samples were cut with a size of 7 x 5 cm. Two edible film strips are placed on top of each other 1 cm and edge 0.5 cm. Sealing was carried out using a Model-SP-200H impulse heat sealer (Prohex, Germany) with a time of 3 seconds. Hard candy is packaged with the sealing method using the brand "KIS" with an oval shape with a size of 2 cm x 1.2 cm x 0.5 cm. Whereas the double-twisting or threaded model packaging is done by cutting edible film samples with 8 x 6 cm. candy is wrapped in edible film. Both edible film edges are rotated so that there are no holes.

The block-shaped commercial hard candy brand "FOX'SS" with a size of 2.5 cm x 1.5cm x 1.0 cm is placed right in the middle of the edible film then rolled up so that the hard candy is wrapped in the edible film. Both edges of the edible film are rotated so that there are no holes.

RESULTS AND DISCUSSION

Research result

The results of measurements of water content response, viscosity, water vapor transmission rate, tensile strength, elongation, and modulus of elasticity can be seen in Table 2.

Table 3.
Analysis of Variance for the Experimental Results Using Design Expert 10.0.7

Responses	Model	Equation	*Significance (p-value)*	*Lack of fit (p-value)*	R^2
Viscosity	Quadratic	$Y_1 = +172.74 + 38.01X_1 + 98.93X_2 - 4.94X_3 + 19.87X_1X_2 + 6.72 X_1X_3 - 20.99 X_2X_3 + 16.15 X_1^2 + 21.65 X_2^2 - 0.73 X_3^2$	<0.0001	0.0900	0.9961
Water Content	Quadratic	$Y_2 = +15.18 - 1.38X_1 - 0.41X_2 - 0.33X_3 - 0.028X_1X_2 + 0.29X_1X_3 + 0.11X_2X_3 + 0.52 X_1^2 + 0.31X_2^2 + 0.30X_3^2$	<0.0001	0.1590	0.9707

WVTR	Quadratic	$Y_3 = + 61.08 - 0.84X_1 - 0.38X_2 - 0.38X_3 + 0.50X_1X_2 - 0.84X_1X_3 + 0.54X_2X_3 + 1.51X_1^2 + 1.42X_2^2 + 0.24X_3^2$	0.0004	0.3331	0.9109
Tensile Strenght	Quadratic	$Y_4 = +88.15 +12.83X_1 + 15.37X_2 + 9.15X_3 + 5.06X_1X_2+ 2.37X_1X_3 - 3.12X_2X_3 -10.26X_1^2 - 6.37X_2^2 + 0.44X_3^2$	0.0016	0.8330	0.8778
Elongation	2FI	$Y_5 = +21.46 + 0.046X_1 + 0.014X_2 + 0.50X_3 - 3.25X_1X_2 - 0.97X_1X_3 - 1.90X_2X_3$	0.0092	0.1053	0.8207
Modulus Young	Quadratic	$Y_6 = +394.37 + 71.06X_1 + 85.22X_2 + 49.43X_3 + 76.46X_1X_2 + 37.25X_1X_3+ 24.36X_2X_3 - 30.89X_1^2 - 24.60X_2^2 + 9.13X_3^2$	<0.0001	0.7582	0.9390

Description : X_1: cornstarch, X_2: carrageenan, X_3: rice bran.

The model analysis is needed to find out which model is suitable for predicting response in RSM. The evaluated model covers linear, two-factor interaction (2FI), and quadratic. The determination of the model is based on the description of the sum of the squares of the sequence of the model (sequential model sum of a square), the model deviation test (lack of fit test), and the statistical model summary (model summary statistic). The suitability of the model is measured by the p-value, where if the p-value is less than 0.05, then the variable contributes significantly to the model[7)]. Lack of fit test shows the accuracy of the model if the value is not statistically significant at a certain level α. The α level used in this study was 0.05. Model summary statistics show a summary of the model statistically.

Based on Table 2, it can be seen that the range of response values in the water content ranged from 14.23 to 19.17%, viscosity 67.4 - 392.9 cP, the rate of water vapor transmission ranged from 59.83 - 66.68 g/m^2/hour, tensile strength between 31.5 - 109.8 kgf/cm^2, elongation of 13.83 - 24.77% and the value of elastic modulus response ranged from 169.1 - 726.4 kgf / cm^2. Variance analysis results (ANOVA) (Table 3), showed that the model was chosen for the response of water content, viscosity, WVTR, tensile strength, and modulus of young was quadratic. The quadratic model has the lowest p-value and with a value of less than 0.05. This indicates that the quadratic model has a significant effect on the response of water content, viscosity, WVTR, tensile strength and Young modulus. The choice of model can also be seen from the maximum values of adjusted R^2 and predicted R^2. The quadratic model has the highest adjusted R^2 and predicted R^2 values compared to the linear and 2FI models. The elongation response of the selected model is 2FI. In this response, the 2FI model has the lowest p-value and a value of less than 0.05. This indicates that the 2FI model significantly influences the elongation response. The adjusted R^2 and predicted R^2 values also show the highest values, which are 0.8207.

In addition, the model suggested by the program is significant, with a p-value less than 0.05 (<0.0001) for all responses. ANOVA results also showed that the percentage of corn starch, carrageenan, and rice bran significantly affected all responses with an insignificant lack of fit values greater than 0.05. The insignificant lack of fit value indicates the suitability of the response data with the suggested model and is a condition that a model can be used for optimization.

Formulation optimization is done using the Design expert program that aims to get the best input variables that produce optimal responses in edible film formulations. The criteria set up are as follows: cornstarch, carrageenan flour, and rice bran in range, response to moisture content and minimum WVTR value, viscosity, tensile strength, percent elongation, and maximum young modulus. The optimistic response is obtained through statistical analysis and based on desirability values.

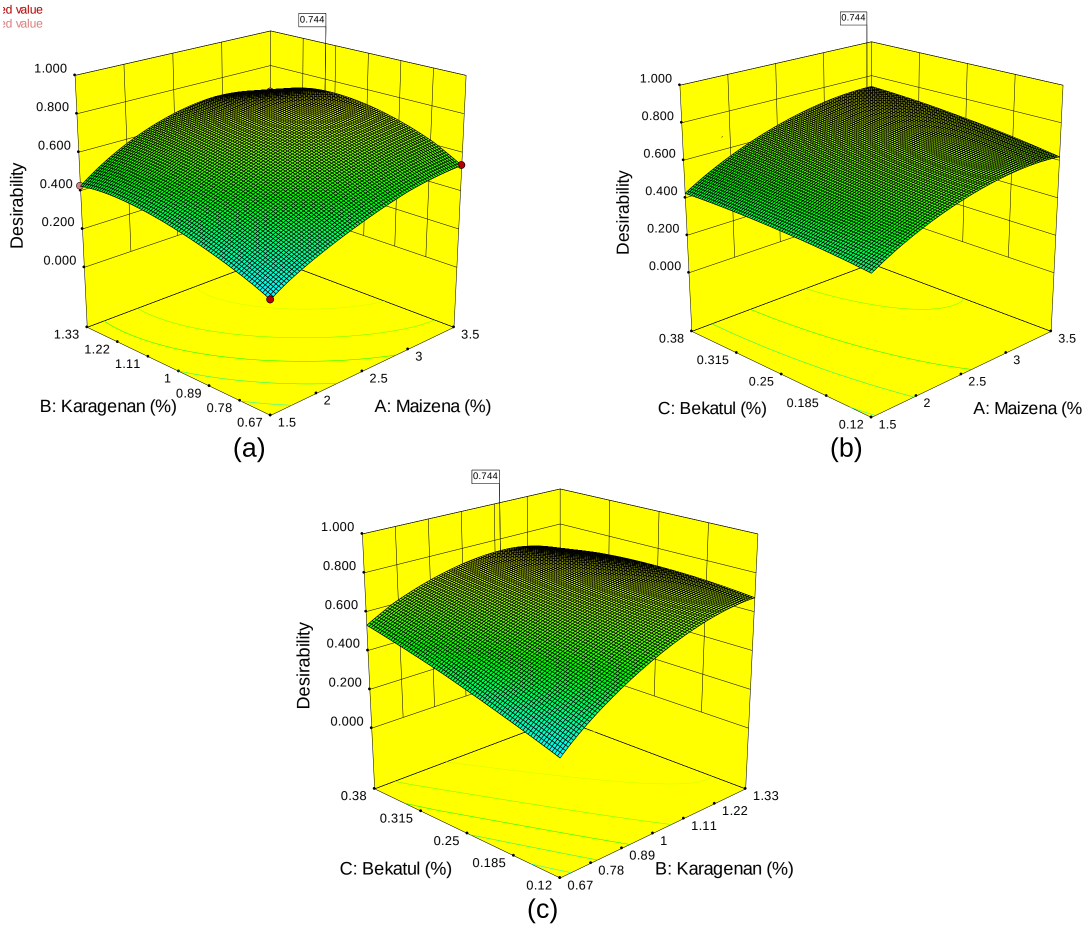

Figure 1.
Surface Response Curve (3D) for response desirability

The optimum point solution shown by the Design Expert 10.0.7 program is 3.4% corn starch, 1.1% carrageenan, and 0.38% rice bran with a desirability value of 0.744. The formulation produced a prediction of response of 14.51% moisture content, WVTR 61.07 g/m^2/hour, the viscosity of 258.8 cP, the tensile strength of 107.96 kgf/cm^2, elongation of 19.41%, and young modulus of 586.28 kgf/cm^2. Verification carried out with the recommended formulation of RSM produces an optimal response: the water content of 14.37%, WVTR 63.34 g/m^2/hour, viscosity 244.9 cP, tensile strength 96.97 kgf/cm^2, elongation 20.96%, and young modulus 462.49 kgf/cm^2. T-test results of the response of water content, viscosity, tensile strength, and elongation have a p-value of more than 0.05. In comparison, the WVTR and modulus young responses have p-values smaller than 0.05.

Discussion Modeling and Analysis of Viscosity Response of Edible Films Films

Program analysis of the viscosity response shows that the quadratic model is the recommended model with a p-value <0.0001, indicating that the quadratic model is significant at the 95% level. Lack of fit quadratic model with a p-value of 0.0900 indicates that the model is not significant to the pure error. The large and insignificant lack of fit p-value implies the model used is good enough so that it is as expected[8], so that the mathematical model can be used to explain the effect of independent variables in the experiment and predict the optimum conditions to obtain the expected response value[9].

Table 4.
Results of experimental verification of the optimum formula

Formula			CS[1] (%)		CR[2] (%)		RB[3] (%)
			3,4		1,1		0,38
	MC[1] (%)	**WVTR[2] ($g/m^2/h$)**	**Vis[3] (cP)**	**TS[4] (kgf/cm^2)**	**Elo[5] (%)**	**M Y[6] (kgf/cm^2)**	***Desirability***
Prediction	14.51[a]	61.06[a]	258.8[a]	107.96[a]	19.41[a]	586.28[a]	0.744
Verification	14.37[a]	63.34[b]	244.9[a]	96.97[a]	20.96[a]	462.49[b]	
p-value	0.103	0.013	0.066	0.052	0.067	0.003	

Description : [1]CS : corn starch, [2]CR : carrageenan, [3]RB: rice bran, [4]MC : Moisture Content, [5]WVTR : Water Vapour Transmission Rate, [6]Vis : viscosity, [7]TS : Tensile Strength, [8]Elo : elongation, [9]MY : modulus young.

Modeling and Analysis of Moisture Response

Program analysis of the water content response shows that the quadratic model is the suggested model. Based on the sum of square sequential model testing, the quadratic model has the lowest p-value and is less than 0.05, 0.0003. This indicates that the quadratic model has a significant effect on the response of water content. The choice of model is also seen from the maximum values of adjusted R^2 and predicted R^2. The quadratic model has the highest adjusted R^2 and predicted R^2 values.

Regression model obtained is $Y_2 = +15.18 - 1.38X_1 - 0.41X_2 - 0.33X_3 - 0.028X_1X_2 + 0.29X_1X_3 + 0.11X_2X_3 + 0.52 X_1^2 + 0.31X_2^2 + 0.30X_3^2$.

The above equation is used to determine the value of the water content obtained if the starch variable corn starch, carrageenan, and rice bran required are different or vice versa. Based on these mathematical equations, it can be seen that the response of the water content will be smaller with increasing corn starch, carrageenan, and rice bran, which is marked by a negative value that is negative. The interaction between corn starch and carrageenan variables will cause the water content to get smaller, marked by a negative constant value.

The interaction between the variables of corn starch and carrageenan will make the water content of edible film smaller. According to Bourtoom, the availability of free OH groups from starch is reduced as a result of interactions with the anionic sulfate groups from carrageenan.

The interaction between variables of corn starch and rice bran and interaction between variables of carrageenan and rice bran starch will increase water content which is indicated by a constant positive value. The addition of rice bran may cause changes in the amorphous phase and starch crystals, which can further weaken the intermolecular force between polymer chains. In addition, rice bran is a starchy material which tends to absorb moisture and thus might affect the water content of the edible film. Rice bran has a starch content ranging from 22-30%. According to Abdul-Khalil *et al*.[10)], the similarity of chemical structures in both polysaccharide structures encourages the formation of hydrogen bonds between starch and bran components. Many free hydroxyl groups are polar, and the multiplied matrix structure provides an opportunity for the binding of water through hydrogen bonds.

WVTR Response Modeling and Analysis

Program analysis of the WVTR response shows that the quadratic model is the recommended model with a p-value of 0.0004, indicating that the quadratic model is significant at the 95% level. Lack of fit quadratic model with a p-value of 0.3331 indicates that the model is not significant to the pure error. The large and insignificant lack of fit p-value implies the model used is good enough so that it is as expected, so that the mathematical model can be used to explain the effect of independent variables in the experiment and predict the optimum conditions to obtain the expected response value[27)]. Regression model obtained is $Y_3 = + 61.08 - 0.84X_1 - 0.38X_2 - 0.38X_3 + 0.50X_1X_2 - 0.84X_1X_3 + 0.54X_2X_3 + 1.51X_1^2 + 1.42X_2^2 + 0.24X_3^2$.

The above equation can be used to determine the value of WVTR obtained if the starch variables of corn starch, carrageenan, and rice bran are needed differently or vice versa. Based on these mathematical equations, it can be seen that the response of WVTR will be smaller with the increase of corn starch, carrageenan, and rice bran, which is marked by a negative value. The interaction between corn starch-carrageenan and carrageenan-rice bran starch variables will cause greater WVTR, marked by a positive value constant, while the interaction of carrageenan-rice bran variable will cause a smaller WVTR, which is indicated by a constant negative value.

The increased value of WVTR due to interactions between corn starch and carrageenan can be related to the number of free hydroxyl groups on cornstarch and carrageenan. This can cause more interaction with hydrophilic water molecules. Similar results have been reported on edible cassava starch films and carrageenan by Poeloengasih et al.[11)], where the polysaccharide films usually show high WVTR values due to their hydrophilic character. According to Handito[12]), more carrageenan with hydrophilic characteristics in the film matrix increases the film area that can be used to transfer water vapor. Therefore, the rate of water vapor transmission will be higher.

Corn starch-rice bran starch interactions resulted in the reduction of WVTR edible film. This is related to the interaction between proteins from bran and starch, which makes the matrix between polymers from starch and bran stronger and decreases the free volume. As a result, the mobility of water in the matrix is limited, and the diffusion of water vapor is inhibited[13)]. The fiber and fat content in rice bran also contributes to the decreasing value of WVTR. Fiber and fat from rice bran increase the hydrophobicity of the matrix, which effectively prevents the movement of water vapor.

Modeling and Analysis of Tensile Response

Program analysis of the tensile strength response shows that the quadratic model is the recommended model with a p-value of 0.0016, which indicates that the quadratic model is significant at the 95% level. Lack of fit quadratic model with a p-value of 0.8330 indicates that the model is not significant to the pure error. The large and insignificant lack of fit p-value implies the model used is good enough so that it is as expected, so that the mathematical model can be used to explain the effect of independent variables in the experiment and predict the optimum conditions to obtain the expected response value[27)].

The regression model obtained is $Y_4 = +88.15 + 12.83X_1 + 15.37X_2 + 9.15X_3 + 5.06X_1X_2 + 2.37X_1X_3 - 3.12X2X_3 - 10.26X_1^2 - 6.37X_2^2 + 0.44X_3^2$.

The above equation can be used to determine the tensile strength value obtained if the corn starch variable, carrageenan, and rice bran needed are different or vice versa. Based on these mathematical equations, it can be seen that the response of tensile strength will be greater with the increase of cornstarch, carrageenan, and rice bran characterized by a constant positive value. Interaction between corn starch variable-carrageenan and corn starch-bran will cause greater tensile strength marked by a positive value constant, whereas the interaction between the carrageenan-rice bran variable will cause smaller tensile strength marked by a negative value constant.

The interaction between corn starch-carrageenan in increasing the tensile strength of edible films occurs due to the formation of hydrogen bonds between molecules between starch and carrageenan, resulting in a more compact structure on the edible film. Wittaya[14)] states that the three-dimensional network structure formed by carrageenan provides strong intermolecular interactions formed between starch and carrageenan, thus minimizing the free volume and intermolecular distance in the film structure. As a result of increasing hydrogen bonds in the intermolecular bonds, the film's tensile strength will be higher with a compact network.

Interaction between corn starch-rice bran starch in increasing the tensile strength of edible film occurs due to chemical and structural compatibility between corn starch and rice bran, enabling strong adhesion between the starch polymer matrix and the fiber of rice bran. In addition, the chemical structure similarity between corn starch and rice bran can induce strong intermolecular interactions through hydrogen bonds. This is consistent with research conducted by Chen et al.[15)] and Nordin et al.[16),] where adhesion of the fiber to the film matrix increases tensile strength.

The increased tensile strength can also be associated with strong interactions between cornstarch and proteins from rice bran that form a dense and strong matrix. Bourtoom & Chinnan[17)] stated that the increase in tensile strength resulted from increased protein addition to edible starch-based rice films. The inter-polymer matrix of starch and bran is stronger, accompanied by a decrease in free volume. In contrast, the interaction between rice carrageenan and rice bran in reducing edible film tensile strength occurs related to agglomeration and poor rice bran distribution in the carrageenan matrix. Decreasing tensile strength shows that rice bran does not form an effective network with a film matrix.

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WVTR Response Modeling and Analysis

Program analysis of the WVTR response shows that the quadratic model is the recommended model with a p-value of 0.0004, which indicates that the quadratic model is significant at the 95% level. Lack of fit quadratic model with a p-value of 0.3331 indicates that the model is not significant to the pure error. The large and insignificant lack of fit p-value implies the model used is good enough so that it is as expected, so that the mathematical model can be used to explain the effect of independent variables in the experiment and predict the optimum conditions to obtain the expected response value[21].

Regression model obtained is $Y_3 = +61.08 - 0.84X_1 – 0.38X_2 - 0.38X_3 + 0.50X_1X_2 - 0.84X_1X_3 + 0.54X_2X_3 + 1.51X_1^2 + 1.42X_2^2 + 0.24X_3^2$

The above equation can be used to determine the value of WVTR obtained if the starch variables of corn starch, carrageenan, and rice bran are needed differently or vice versa. Based on these mathematical equations, it can be seen that the response of WVTR will be smaller with the increase of corn starch, carrageenan, and rice bran, which is marked by a negative value. The interaction between corn starch-carrageenan and carrageenan-rice bran starch variables will cause greater WVTR, which is marked by a positive value constant, while the interaction of carrageenan-rice bran variable will cause a smaller WVTR, which is indicated by a constant negative value.

The increased value of WVTR due to interactions between corn starch and carrageenan can be related to the number of free hydroxyl groups on cornstarch and carrageenan. This can cause more interaction with hydrophilic water molecules. Similar results have been reported on edible cassava starch films and carrageenan by Poeloengasih et al.[24], where the polysaccharide films usually show high WVTR values due to their hydrophilic character. According to Handito[12], more carrageenan with hydrophilic characteristics in the film matrix increases the film area that can be used to transfer water vapor. Therefore, the rate of water vapor transmission will be higher.

Corn starch-rice bran starch interactions resulted in the reduction of WVTR edible film. This is related to the interaction between proteins from bran and starch, which makes the matrix between polymers from starch and bran stronger and decreases the free volume. As a result, the mobility of water in the matrix is limited, and the process of diffusion of water vapor is inhibited[13]. The fiber and fat content in rice bran also contributes to the decreasing value of WVTR. Fiber and fat from rice bran increase the hydrophobicity of the matrix, which effectively prevents the movement of water vapor.

Modeling and Analysis of Tensile Response

Program analysis of the tensile strength response shows that the quadratic model is the recommended model with a p-value of 0.0016, which indicates that the quadratic model is significant at the 95% level. Lack of fit quadratic model with a p-value of 0.8330 indicates that the model is not significant to the pure error. The large and insignificant lack of fit p-value implies the model used is good enough so that it is as expected[25], so that the mathematical model can be used to explain the effect of independent variables in the experiment and predict the optimum conditions to obtain the expected response value[21].

Regression model obtained is
$Y_4 = +88.15 +12.83X_1 + 15.37X_2 + 9.15X_3 + 5.06X_1X_2+ 2.37X_1X_3 - 3.12X_2X_3 - 10.26X_1^2 - 6.37X_2^2 + 0.44X_3^2$.

The above equation can be used to determine the tensile strength value obtained if the corn starch variable, carrageenan, and rice bran needed are different or vice versa. Based on these mathematical equations, it can be seen that the response of tensile strength will be greater with the increase of corn starch, carrageenan, and rice bran characterized by a constant positive value. Interaction between corn starch variable-carrageenan and corn starch-bran will cause greater tensile strength marked by a positive value constant, whereas the interaction between the carrageenan-rice bran variable will cause smaller tensile strength marked by a negative value constant.

The interaction between corn starch-carrageenan in increasing the tensile strength of edible films occurs due to the formation of hydrogen bonds between molecules between starch and carrageenan, resulting in a more compact structure on the edible film. Wittaya[14] states that the three-dimensional network structure formed by carrageenan provides strong intermolecular interactions formed between starch and carrageenan, thus minimizing the free volume and intermolecular distance in the film structure. As a result of increasing hydrogen bonds in the intermolecular bonds, the film's tensile strength will be higher with a compact network.

The reaction between corn starch-rice bran in increasing the tensile strength of edible film occurs due to chemical and structural compatibility between corn starch and rice bran, enabling strong adhesion between the starch polymer matrix and the fiber of rice bran. In addition, the chemical structure similarity between corn starch and rice bran can induce strong intermolecular interactions through hydrogen bonds. This is consistent with research conducted by Chen et al.[15] and Nordin et al.[16], where adhesion of the fiber to the film matrix increases tensile strength.

The increased tensile strength can also be associated with strong interactions between corn starch and proteins from rice bran that form a dense and strong matrix. Bourtoom & Chinnan[17] stated that the increase in tensile strength resulted from increased protein addition to edible starch-based rice films. The inter-polymer matrix of starch and bran is stronger, accompanied by a decrease in free volume. In contrast, the interaction between rice carrageenan and rice bran in reducing edible film tensile strength occurs related to agglomeration and poor rice bran distribution in the carrageenan matrix. Decreasing tensile strength shows that rice bran does not form an effective network with a film matrix.

Tensile strength indicates the maximum tensile stress that a film can maintain. Tensile strength is a physical property related to the strength of the edible film to withstand physical damage when packaging food. Edible films with the highest strength values are expected to withstand maximum physical damage so that damage to the product will be minimal. Edible films with high tensile strength will be able to protect packaged products from mechanical interference. Increasing the concentration of starch and carrageenan will affect dissolved solids in the edible film. Corn starch and carrageenan will dissolve in each polymer chain and fill all the spaces, thereby reducing the movement of polymer molecules and will increase the glass transition temperature. The more the glass transition temperature increases, the stronger the polymer formed and the stronger the tensile strength formed.

Elongation Response Modeling and Analysis

Program analysis of the elongation response shows that the 2FI model is a recommended model with a p-value of 0.0092, which indicates that the model is significant at the 95% level. The 2FI Lack of Fit model with a p-value of 0.1053 indicates that the model is not significant to the pure error. The large and insignificant lack of fit p-value implies the model used is good enough so that it is as expected, so that the mathematical model can be used to explain the effect of independent variables in the experiment and predict the optimum conditions to obtain the expected response value[9].

Model Regresi yang didapatkan yaitu $Y_5 = +21.46 + 0.046X_1 + 0.014X_2 + 0.50X_3 - 3.25X_1X_2 - 0.97X_1X_3 - 1.90X_2X_3$.

The above equation can be used to determine the elongation value obtained if the starch variables of corn starch, carrageenan, and rice bran are needed differently or vice versa. Based on these mathematical equations, it can be seen that the elongation response will be even greater with the increase of corn starch, carrageenan, and rice bran, which is marked by a positive value constant. In contrast, the interaction between variables will cause a smaller elongation, indicated by a constant value, which is negative.

Interaction between corn starch-carrageenan reduces the elongation of edible film. The three-dimensional network structure and the formation of hydrogen bonds between molecules between carrageenan and starch retain the mobility of the polysaccharide chain and then decrease the elongation value. Similar interactions with the results of research conducted by Abdul-Khali[18] the formation of hydrogen bonds and the three-dimensional structure between starch and carrageenan make the movement of starch macromolecular chains limited, causing film flexibility to be reduced.

Interaction between corn starch-rice bran starch in reducing the elongation of the edible film occurs due to the stiffness of the fiber in rice bran, which acts as a filler that holds back the flexibility of the starch molecular chain. Similar polysaccharide structures form homogeneous dispersions with strong adhesion between carrageenan and rice bran fillers. The similarity in chemical structure between carrageenan and rice bran causes a strong interaction between the carrageenan matrix phase and rice bran as a filler with hydrogen interactions so that the film's flexibility is limited and causes elongation to fall.

Elongation shows the change in maximum edible film length when obtaining the tensile force until the edible film breaks.

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Elongation values indicate the ability of the film to elongate. This property depends on the type of film-forming material, which will influence the cohesion properties of the edible film structure. Elongation is the percentage increase in the length of the film when pulled until torn or broken. Handito[37] states that the value of elongation is inversely proportional to the value of tensile strength. The higher the concentration of carrageenan used in making edible films, the carrageenan molecules will form a film matrix that is stronger so that the film is more inelastic or brittle, and consequently, the percentage of elongation decreases.

Modeling and Analysis of Modulus Young's Response

Program analysis of the modulus young response shows that the quadratic model is the recommended model with a p-value <0,0001, indicating that the quadratic model is significant at the 95% level. Lack of fit quadratic model with a p-value of 0.7582 indicates that the model is not significant to the pure error. The large and insignificant lack of fit p-value implies that the model used is good enough so that it is as expected so that the mathematical model can be used to explain the effect of the independent variables in the experiment and predict the optimum conditions to obtain the expected response value [9].

Model Regresi yang didapatkan yaitu $Y_6 = +394.37 + 71.06X_1 + 85.22X_2 + 49.43X_3 + 76.46X_1X_2 + 37.25X_1X_3 + 24.36X_2X_3 - 30.89X_1^2 - 24.60X_2^2 + 9.13X_3^2$

The above equation can be used to determine the modulus young value obtained if the starch variable corn starch, carrageenan, and rice bran required are different or vice versa. Based on these mathematical equations, it can be seen that the response of modulus young will be even greater with the increase of cornstarch, carrageenan, and rice bran, which is marked by a positive value constant. Interaction between variables will cause the young modulus to be greater, which is marked by a constant positive value.

The interaction between corn starch and carrageenan in improving the modulus of the young edible film occurs due to the formation of hydrogen bonds between molecules between starch and carrageenan, which results in a more compact structure on the edible film. Wittaya[13] states that the three-dimensional network structure formed by carrageenan provides strong intermolecular interactions formed between starch and carrageenan, minimizing the free volume and intermolecular distance in the film structure. This results in increasing hydrogen bonds in intermolecular bonds so that the modulus young value of the edible film will be higher with a compact network.

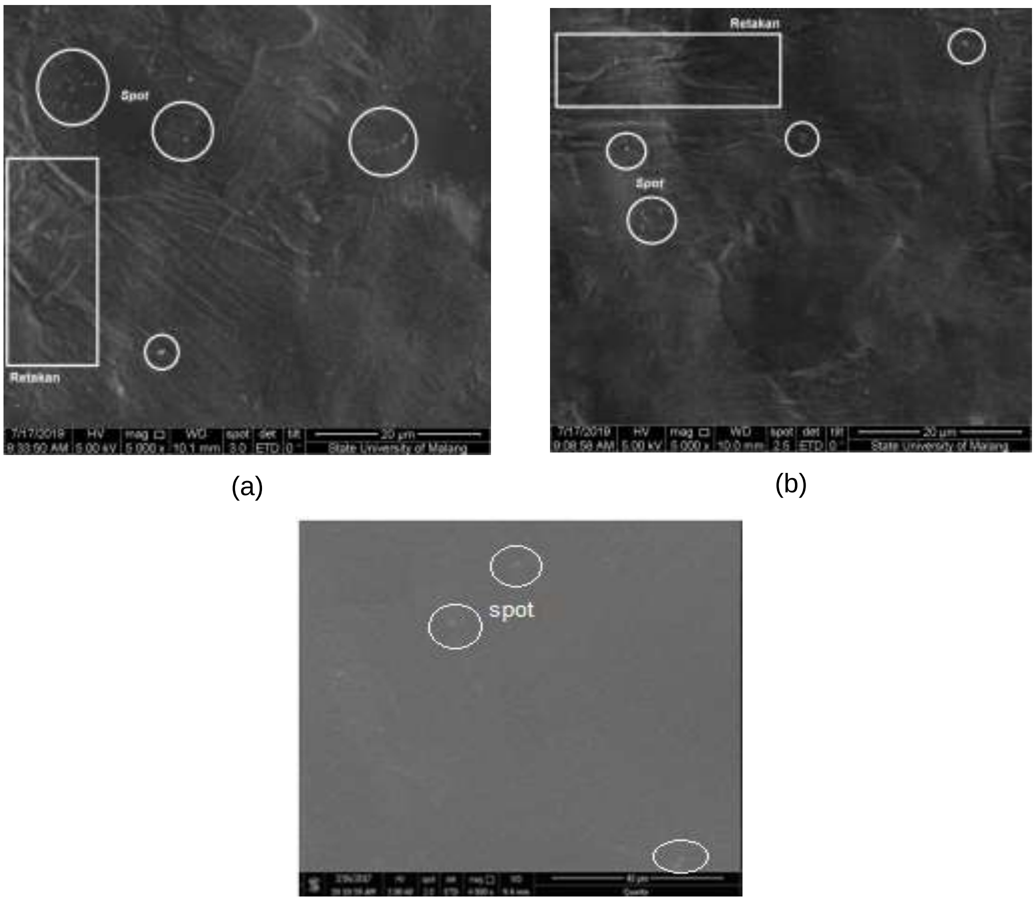
Interaction between corn starch-rice bran in improving the modulus of the young edible film occurs due to strong interactions due to chemical and structural compatibility between corn starch and rice bran. This occurs because of the strong adhesion between the starch polymer matrix and the fiber of rice bran so that the film formed will have the strength and high sturdiness. This is in accordance with research conducted by Yang, J, Ching, Y.C. and Chuah, C.H.,[19], where strong interactions between lignin to starch-based film matrices increase the modulus of young. In contrast, the interaction between rice carrageenan and rice bran in reducing the edible film tensile strength was related to the agglomeration and poor distribution of rice bran in the carrageenan matrix. Decreasing tensile strength shows that rice bran does not form an effective network with a film matrix.

Optimization Formulation

The optimization formulation is done by using the Desaign expert program that aims to get the best input variables that produce optimal responses in edible film formulations. The criteria set up are as follows: cornstarch, carrageenan flour and rice bran in range, response to moisture content and minimum WVTR value as well as viscosity, tensile strength, percent elongation and maximum young modulus. The optimistic response is obtained through statistical analysis and based on desirability values. The optimization results will provide a response prediction which is then verified by comparing the results of the software prediction by testing empirically on the optimum formulation three times repetition using the Minitab t-test software. If the p-value of the verification results with a prediction of more than 0.05, then the predicted value and the results of the study were not significantly different, indicating the accuracy of the model.

The optimum point solution shown by the Desaign Expert 10.0.7 program is 3.4% corn starch, 1.1% carrageenan, and 0.38% rice bran with a desirability value of 0.744. The formulation produced a prediction of response of 14.51% moisture content, WVTR 61.07 g/m^2/hour, the viscosity of 258.8 cP, the tensile strength of 107.96 kgf/cm^2, elongation of 19.41%, and young modulus of 586.28 kgf/cm^2.

Based on Figure 1, at the optimization stage in the RSM program, the optimal formula is determined from the maximum desirability value. The desirability value close to 1 shows a good optimization function, where the program can meet the objectives based on the desired criteria on the final product. Verification carried out with the recommended formulation of RSM produces an optimal response: the water content of 14.37%, WVTR 63.34 g/m^2/hour, viscosity 244.9 cP, tensile strength 96.97 kgf/cm^2, elongation 20.96%, and young modulus 462.49 kgf/cm^2. Based on the t-test, the response of water content, viscosity, tensile strength and elongation showed that the verification and prediction of optimization did not have a significant difference with a p-value of more than 0.05. In comparison, the WVTR and modulus young responses indicate that the verification and optimization predictions have significant differences with p-values smaller than 0.05.



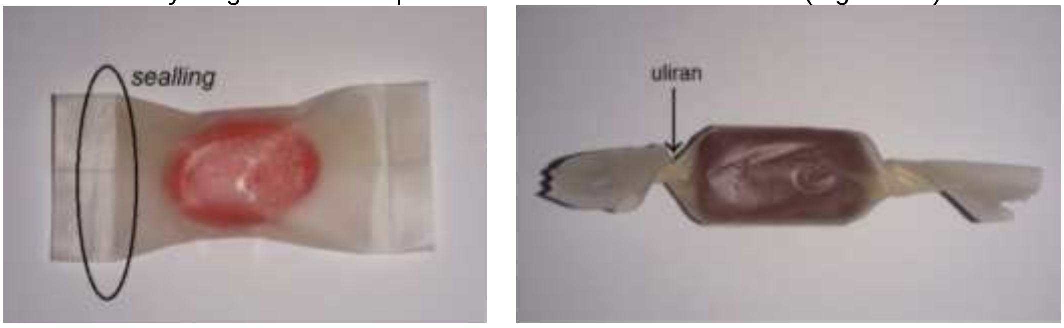
(a) (b)

(c)

Figure 2.
The Scanning Electron Microscopic images of edible film (a) formula 1, (b) optimum formula and (c) maize-wheat starch edible film reference

Morphological analysis

Morphological analysis using Scanning Electron Microscopy (SEM) aims to visualize and identify the surface structure of the edible film and evaluate its homogeneity. The edible film analyzed is the sample edible film formula 1 and the optimum formula with a sample size of 5 mm x 5 mm and analyzed at a magnification of 5000 times. SEM is a microscope that uses the principle of electron beams fired at a sample. The surface of the edible film formula 1 (Figure 2.a) and the optimum formula (Figure 2.b) shows that the surface has cracks and spots that indicate the presence of rice bran fillers. Figure 2.b it can be seen that small cracks and spots are seen on the surface of the edible film. While Figure 2.a, there are more cracks and spots suspected to cause edible films to have a greater WVTR value and tensile strength, smaller percent elongation and modulus of young than the optimum edible film formula (Figure 2.b).



(a) (b)

Figure 3.
Edible film application as packaging for hard candy by (a) seal and (b) threaded

The Scanning Electron Microscopic analysis results show that the surface of the film obtained has different homogeneity. For example, the SEM result of an edible film based of corn starch-wheat starch conducted by Zuo *et al*.[20] (2017) in Figure 2.c, which has a surface without cracks and few spots, showing that the edible film has good homogeneity. Inhomogeneity shown by the edible film formula 1 (Figure 2.a) occurs because the edible film formula based on polysaccharides and proteins is unstable when associative interactions. Polysaccharides are adsorbed onto the protein surface because the amount of polymer is not large enough to completely cover the protein.

The spots in Figures 2 (a) and (b), which are suspected rice bran fillers, show insufficient uniform dispersion of bran particles into the cornstarch matrix and carrageenan. The spots on the surface of the edible film are also due to the protein content of the bran. Alshammari, B.A., et al.[21] stated that the uniform dispersion shown by the SEM morphological analysis results for the film given the filler shows good adhesion between the filler and the matrix. The presence of the filler provides an important role in improving mechanical properties and decreasing the value of WVTR if the fillers in the matrix are uniformly distributed and dispersed.

Edible film application for Hard Candy Packers

The packaging in this study uses edible film to package hard candy. The application of packaging with the resulting edible film is carried out by a sealer using a double sealer and using a screw (twist wrapping). Figure 3 is the result of candy packaging using edible film.

Figure 3 (a) is an edible film application as a hard candy packer using the seal, and Figure 3 (b) is an edible film application as a hard candy packer by screw. The results of the application by means of thread show that the edible film is not very strong after being rolled or rotated and prone to open threads. Whereas the results of the application by sealing can be perfectly attached. The success of packaging applications in foodstuffs is influenced by the basic ingredients of the product and the manufacturing process, treating the product after the production process and how to package it. The lack of good application on the hard candy packaging by screw because the percentage of edible elongation film optimization results is still relatively low at 20.96%. The greater the elongation percent value indicates that the packaging has flexibility so that when it is carried out, the rolling is not easily damaged. The results of the thread are not easily separated. Food products, such as hard candy require flexible packaging. Referring to Japan Industrial Standard (JIS) Z 1707 - 1975 in Ariska and Suyatno (2015), films are categorized as good packaging materials with a minimum elongation of 50%[22].

CONCLUSION

The combination of corn starch carrageenan and rice bran influences the water content, water vapor transmission rate (WVTR), solution viscosity, tensile strength, elongation and modulus of young edible film produced. The optimum formulation of RSM results is 3.4% corn starch, 1.1% carrageenan and 0.38% rice bran with the prediction of water content response of 14.51%, WVTR 61.06 g/m^2/hour, the viscosity of 258.8 cP, the tensile strength of 107.9 kgf/cm^2, elongation of 19.41%, and young modulus of 586.28 kgf/cm^2.

Verification carried out with the optimum formulation produces an edible film which has a moisture content of 14.37%, WVTR 63.34 g/m^2/hour, the viscosity of 244.9 cP, a tensile strength of 96.97 kgf/cm^2, elongation of 20.96%, and young modulus 462.49 kgf/cm^2.

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REFERENCES

1. Singh, P., Sharma, V.P., *Integrated Palctic Waste Manajement: Environmental and Improved Health Approaches,* Procedia Environmental Science, 2016, Vol. 35, p692 -700.
2. Karunanithy, C. & Venitia, S., *Packaging of Cereals, Snacks, and Confectionery*, Reference Module in Food Science, Elsevier, 2016.
3. Nouraddini, M., Esmaiili, M., Mohtarami, F, *Development and characterization of edible films based on eggplant flour and corn starch*, International Journal of Biological Macromolecules, 2018, vol.120, p1639-1645.
4. Farhan, A.R., & Hani, N.M., *Characterization of edible packaging films based on semi-refined kappa-carrageenan plasticized with glycerol and sorbitol*, Food Hydrocolloids, 2017, vol.64, p48-58.
5. Heri dan Jeni, *Optimasi Formula Edible Film Berbasis Amilopektain Pati Singkong dan Karagenan*, Majalah Pengkajian Industri, No. 1, 2016, p31.
6. Ramadhani, R.A., Riyadi, D.H.S., Triwibowo, B., Kusumaningtyas, R.D., *Pemanfaatan Desain Expert untuk Optimasi Komposisi Campuran Minyak Nabati Sebagai Bahan Baku Sintesis Biodiesel,* Jurnal Teknik Kimia dan Lingkungan, 2017, Vol. 1 (1), p11-16
7. Myers, R. H., Montgomery, D. C., & Anderson-Cook, C. M., *Response surface methodology: process and product optimization using designed experiments*: John Wiley & Sons, 2016.
8. Zuo, G., Song, X., Chen, F., & Shen, Z., *Physical and structural characterization of edible bilayer films made with zein and corn-wheat starch*, Journal of the Saudi Society of Agricultural Sciences, 2017.
9. Rhazi, N., Hannache, H., Oumam, M., Sesbou, A., Charrier, B., Pizzi, A., & Charrier-El Bouhtoury, F., *Green extraction process of tannins obtained from Moroccan Acacia mollissima barks by microwave: Modeling and optimization of the process using the response surface methodology RSM*, Arabian Journal of Chemistry, 2015.
10. Abdul-Khalil, H.P.S., Tye, Y.Y., Saurabh, C.K., Leh, C.P., Lai, T.K., Chong, E.W.N. and Syakir, M.I., *Biodegradable polymer films from seaweed polysaccharides: A review on cellulose as a reinforcement material*, Express Polymer Letters, 2017, vol.11 (4), p244-265.
11. Poeloengasih, C. D., Pranoto, Y., Anggraheni, F. D., & Marseno, D. W., *Potential of sago starch/carrageenan mixture as gelatin alternative for hard capsule material*, International Conference on Chemistry, Chemical Process and Engineering (IC3PE) AIP Conf. Proc. 1823, 2017.
12. Handito, D., *Pengaruh konsentrasi karagenan terhadap sifat fisik dan mekanik edible film*, Agroteksos, 2011, vol.21(2-3), p151-157.
13. Akbari, Z., Ghomashchi, T. & Moghadam, S., *Improvement in food packaging industry with biobased nanocomposites*, Interna-tional Journal of Food Engineering, 2007, vol.3(4), p1-24.
14. Wittaya, Thawien, *Rice starch-based biodegradable films. Properties enhancement*. In Eissa AA (Ed.) Structure and Function of Food Engineering. Ch. 5. Intech. 2012, pp.103-134.
15. Chen, J., Long, Z., Wang, J., Wu, M., Wang, F., Wang, B. and Lv, W., *Preparation and properties of microcrystalline cellulose/hydroxypropyl starch composite films*, Cellulose, 2017, vol.24(10), p4449-4459.
16. Nordin, Norhazirah & Othman, Siti & Kadir, Roseliza & Rashid, S., *Mechanical and thermal properties of starch films reinforced with microcellulose fibres*, Food Research, 2018, vol.2, p555-563.
17. Bourtoom, T. & Chinnan, M.S., *Preparation and properties of rice starch-chitosan blend biodegradable*

film, Lebensmittel–Wissenschaft und-Technologie, 2008, vol.41, p633–1641.

18. Abdul-Khalil, H.P.S., Tye, Y.Y., Saurabh, C.K., Leh, C.P., Lai, T.K., Chong, E.W.N. and Syakir, M.I., *Biodegradable polymer films from seaweed polysaccharides: A review on cellulose as a reinforcement material*, Express Polymer Letters, 2017, vol.11 (4), p244-265.
19. Yang, J., Ching, Y.C., and Chuah. C.H., *Application of Lignocellulose Fibers and Lignin in Bioplastic: Review,* Polimers, 2019, Vol.11 (751), p1-26
20. Zuo, G., Song, X., Chen, F., & Shen, Z., *Physical and structural characterization of edible bilayer films made with zein and corn-wheat starch*, Journal of the Saudi Society of Agricultural Sciences, 2017.
21. Alshammary, B.A., Saba, N., Alotaibi, M.D., Alotaibi, M.F., Jawaid, M., Alothman, O.M., *Evaluation of Mechanical, Physical, and Morphological Properties of Epoxy Composities Reinforce with Difference Date Palm Fillers,* Materials, MDPI, 2019, 12 (2145) p1-17.
22. Ariska, R. E., and Suyatno, *Effect of Carrageenan Concentration on Physical and Mechanical Properties of Edible Films from Starch Banana and Carrageenan with Plasticizer Glycerol*, Proceedings. National Chemistry Seminar, Department of Chemistry, FMIPA, Surabaya State University, 2015.

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