



Response Surface Methodology for Formulating PVA/Starch/Lignin Biodegradable Plastic

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Abstract

The use of petroleum-based plastics has raised environmental issues as more plastic waste enters and accumulates in the environment. It has led to the development of biodegradable plastics. Starch is one of the potential materials to make biodegradable plastic, but starch-based plastic has poor mechanical strength. Blending starch with poly(vinyl alcohol) (PVA) and lignin is expected to improve the mechanical properties of the plastic. Biodegradable plastic films from PVA/starch/lignin blends with glycerol as a plasticizer were prepared using an internal mixer for compounding and a hot press molding machine for film making. The percentage of lignin (2-10%), glycerol (25-65%), and mixing temperature (190-230 °C) were varied according to the three levels of the Box-Behnken design. The ANOVA evaluation revealed that glycerol had the most significant effect on the mechanical properties of the film. Then, three models for the estimation of tensile strength, elongation at break, and tear resistance were developed. As expected, the models satisfactorily predict the effect of all input variables on the response variables. The optimum conditions for preparing the film were acquired from the equations, namely 197.6 °C for the temperature, 10% for lignin, and 45.1% for glycerol. The biodegradable plastic prepared using the optimum conditions possessed a tensile strength of 8.46 ± 1.08 MPa, an elongation at break of $139.00 \pm 8.59\%$, and a tear resistance of 69.50 ± 2.50 N/mm. These values are in good agreement with the predicted values.

Keywords:

Melt Compounding;
Optimization;
Tensile Strength;
Tear Resistance.

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1- Introduction

Over the last few decades, the production and use of petroleum-based plastics has caused a lot of problems for the environment. AS a response to environmental concerns, much effort has been dedicated to the development of biodegradable plastics as substitutes for petroleum-based plastics [1]. Starch has been considered as a promising natural polymer as the raw material for producing biodegradable plastic due to its superior availability, renewability, lower toxicity, and biodegradability [2]. Unfortunately, biodegradable plastic with desirable properties cannot be prepared from starch alone due to its poor mechanical strength, hydrophilicity, and high susceptibility to microbial attack. The properties of the plastic can be improved by blending starch with synthetic biodegradable polymers [3, 4]. One of them is polyvinyl alcohol (PVA), which has excellent mechanical properties and the ability to form a uniform mixture with starch [5, 6]. Therefore, the addition of PVA to starch for the preparation of biodegradable plastic can be expected to improve the tensile strength and the elongation at break [6–8].

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A number of modification techniques have been applied to improve the processability and properties of PVA/starch blends. The addition of a plasticizer to the PVA/starch blend can decrease the melting point and increase the flexibility and workability of the polymer blend. The most frequently used plasticizer for PVA/starch composite is glycerol and water [5]. PVA/starch blends with glycerol as the plasticizer for food packaging applications have been investigated in many previous works [1, 4, 9]. Although the addition of glycerol to the PVA/starch blend had been found to increase the elongation at break, it was reported to cause deterioration of the tensile strength of the plastic.

To enhance the mechanical properties, a reinforcement filler, such as lignin can be added to the polymer blend [5]. Lignin is the second most abundant natural polymer in the world after cellulose with an annual production capacity of about 50 million tons/year. As an amorphous and highly complex phenolic polymer, lignin is generally synthesized by plants with sinapyl alcohol (S-type), coniferyl alcohol (G-type), and para-coumaryl alcohol (H-type) being the repeating units. Figure 1 shows a sample of the molecular structure of lignin (type 2) [10]. The presence of the phenolic group in the lignin structure makes this natural polymer becomes a potential candidate for the enhancement of the mechanical properties of biodegradable plastic [11]. Many researchers observed that the incorporation of lignin into PVA could increase the tensile strength of the biodegradable plastic [12–14]. In addition, lignin was also reported improving the tensile strength of starch-based biodegradable plastic [15–18]. However, as far as the literature survey has been performed, there is a very limited number of publications about the effect of lignin addition on the mechanical properties of PVA/starch-based biodegradable plastic [19].

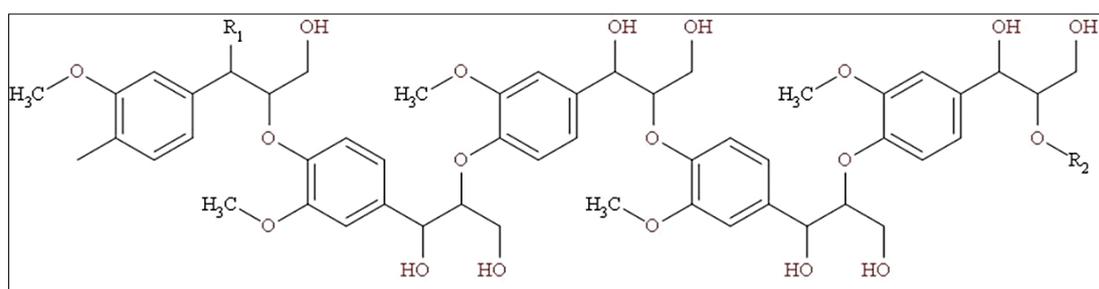


Figure 1. Molecular structure of lignin [10]

The simplicity has made the solution casting method becomes the most applicable method for biodegradable plastic preparation [7, 8, 13, 14]. However, this method is not suitable for industrial-scale production due to its requirement of the removal of a large amount of water (up to 90% of the solution). This dehydration step is an energy-intensive and time-consuming operation. Therefore, this process is considered to be expensive, inefficient, and not environmentally benign. These problems encourage researchers to develop an efficient, cost-effective, and environmentally friendly process through the melt extrusion technique [20].

The objective of this work was to investigate the influence of lignin and glycerol concentration, as well as mixing temperature on the mechanical properties of PVA/starch/lignin plastic for biodegradable plastic preparation via the melt extrusion method. The Box-Behnken experimental design was applied in this study to determine the optimum conditions to produce biodegradable plastic with the best mechanical properties. It is expected that the resulting biodegradable plastic is suitable for food packaging material with the mechanical properties that meet the quality standard set by the Board of Indonesian National Standard through a standard document of SNI 7818:2014. This report is organized as follows. Section 1 briefly describes the background and the objective of this research. The details of the materials and methods used in this research are explained in Section 2. The research results are presented in Section 3 along with their in-depth discussion. Finally, the conclusion of this study is presented in Section 4.

2- Materials and Method

2-1- Materials

Materials used in this work were PVA, alkaline lignin, cassava starch, and glycerol. The PVA (POVALTM JP-18) with a degree of hydrolysis of 87-89% was obtained from Japan Vam & Poval Co., Ltd. Alkaline lignin (product number L0082) was purchased from Tokyo Chemical Industry. The lignin has a methoxy group of 12% and a water content of 7.4%. Cassava starch and glycerol (99.7% purity) were obtained from local suppliers, namely PT. Budi Acid and PT. Wilmar Nabati Indonesia, respectively. Before biodegradable plastic preparation, all materials, except glycerol were dehydrated at 105°C for 4 hours in an electric oven (Binder, Type: 1815300002020).

2-2- Experimental Design

This work employed response surface methodology (RSM) to analyze the effect of parametric quantity inputs (independent variables) on the outcome responses (dependent variables). Different experimental design models can be used in the RSM analysis, which includes the central composite designs (CCD), Doehlert matrix (DM), and the Box-

Behnken design (BBD) as the more complicated three-level designs [21]. The Box-Behnken is selected in this work for three chosen independent variables at three levels.

This work studied the influence of three selected independent variables, namely mixing temperature (T), lignin (L), and glycerol (G), on the tensile strength (TS), elongation at break (EB), and tear resistance (TR) of the biodegradable plastic. The independent variables T , L , and G were ranged from 190 to 230°C, 2 to 10%, and 25 to 65%, respectively. For the sake of statistical analysis, the independent variables are transformed to dimensionless coded variables (X_i) according to Equation 1,

$$X_1 = \frac{T-(T_{high}-T_{low})/2}{(T_{high}-T_{low})/2} \quad X_2 = \frac{L-(L_{high}-L_{low})/2}{(L_{high}-L_{low})/2} \quad X_3 = \frac{G-(G_{high}-G_{low})/2}{(G_{high}-G_{low})/2} \quad (1)$$

where the subscripts high and low indicate high and low levels, respectively. The coded and actual values of the parameters used in this work are listed in Table 1.

Table 1. The Box-Behnken design of experiment applied in this study

Independent variable	Symbol	Unit	Level		
			Low (-1)	Mid (0)	High (+1)
Mixing temperature	T	°C	190	210	230
Lignin	L	% *)	2	6	10
Glycerol	G	% *)	25	45	65

* g/100 gr of PVA/starch

The response and the dimensionless input parameters involved in this study can be correlated according to the second-order polynomial equation as presented in Equation 2 [22]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j \neq i}^k \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

where Y represents the predicted response, β_0 is a constant, β_i is the coefficient of the linear effects, β_{ii} is the coefficient of the square effects, β_{ij} is the coefficient of interactions between two independent input variables, and ε is a random error. Fifteen experiments were formulated using MINITAB Version 19. The experimental design with dimensionless and actual variables is presented in Table 2.

Table 2. Box-Behnken experimental design

Run	Coded independent variable			Actual independent variable		
	X_1	X_2	X_3	T (°C)	L (%)	G (%)
1	0	0	0	210	6	45
2	0	+1	-1	210	10	25
3	0	-1	-1	210	2	25
4	+1	0	+1	230	6	65
5	0	0	0	210	6	45
6	+1	+1	0	230	10	45
7	-1	-1	0	190	2	45
8	+1	0	-1	230	6	25
9	-1	0	-1	190	6	25
10	+1	-1	0	230	2	45
11	0	0	0	210	6	45
12	-1	0	+1	190	6	65
13	0	-1	+1	210	2	65
14	-1	+1	0	190	10	45
15	0	+1	+1	210	10	65

2-3- Preparation of Biodegradable Plastic Films

The PVA and starch were blended with a composition of 60% and 40%, respectively. This mixture was then used in the entire experiment. Lignin was added to the PVA/starch blend with various compositions (see Table 2) and mixed to obtain a uniform blend. A predetermined amount of glycerol (see Table 2) was then added and further mixed to the

attainment of a homogeneous mixture. The mixture was then let to stand in the oven at 50°C for 24 hours to ensure the incorporation of glycerol. The mixture was compounded using Haake Rheomix 3000P Internal Mixer with a counter-rotating Banbury rotor with a rotation speed of 100 rpm. The compounding process was conducted at various temperatures (see Table 2) for 5 minutes. The compounded mixture was then extruded to form a film by using a hot press molding machine (Toyoseiki Mini Test Press-10) at 180-200°C and 100 MPa for 20 minutes. A schematic diagram of the biodegradable plastic film processing is depicted in Figure 2.

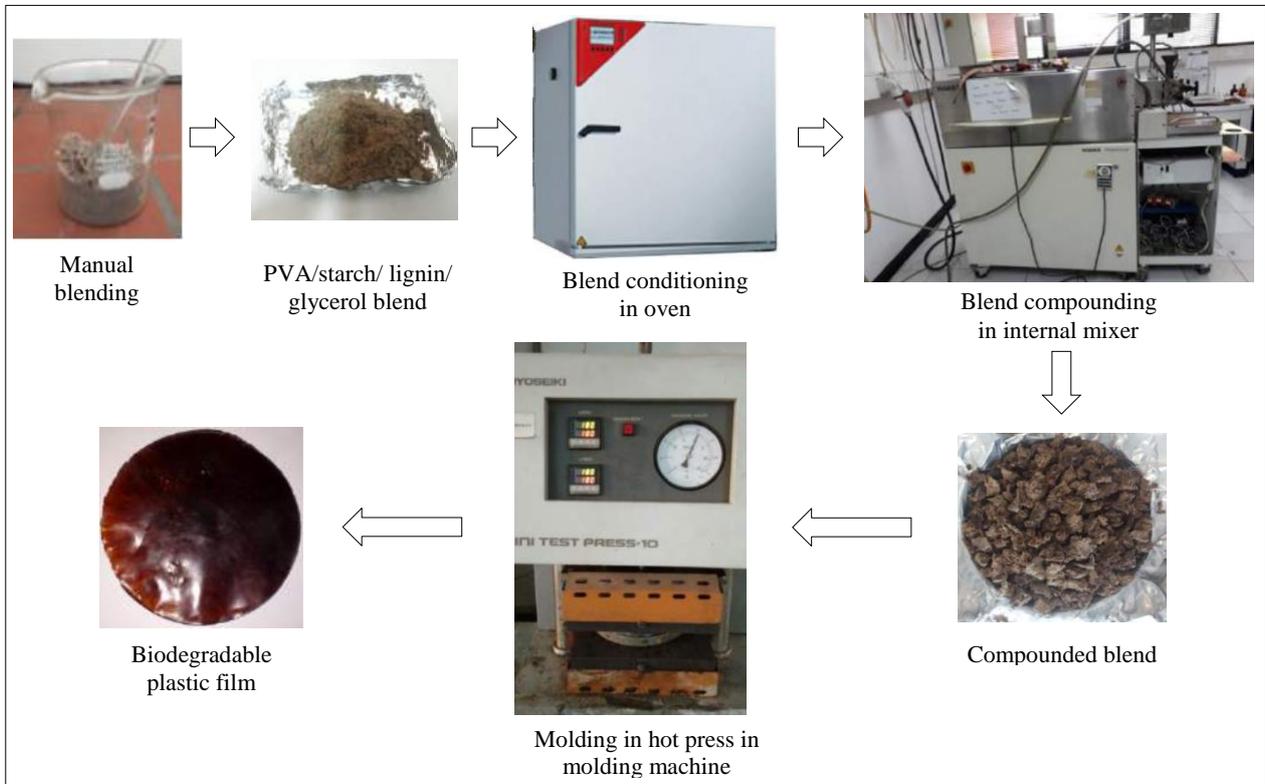


Figure 2. Schematic diagram of biodegradable plastic film making

2-4- Characterization of Films

The films were tested for *TS*, *EB*, and *TR*. The measurement of *TS* and *EB* were conducted following the ASTM D882, while *TR* measurement was conducted following the ASTM D1004. All the measurements were conducted using Universal Testing Machine (Shimadzu AGS-10kNG) as shown in Figure 3.



Figure 3. Universal testing machine (Shimadzu AGS-10kNG)

3- Results and discussion

3-1- Process Analysis

3-1-1- Effect of Mixing Temperature on Film Properties

The effect of mixing temperature (T) on the TS , EB , and TR of the film is presented in Figures 4-a, 4-b, and 4-c, respectively. It is observed in Figures 4-a and 4-b that as the temperature rises from 190°C to 210°C, the TS of the film increases from 6.44 MPa to 7.14 MPa, while the EB increases from 22.9% to 134.3%, but at 230°C both the TS and the EB decrease to 6.30 MPa and 103.3%, respectively. A similar trend is also observed in Figure 4-c in which the TR of the film at 190°C, 210°C, and 230°C are 54.74 N/mm, 62.25 N/mm, and 56.49 N/mm, respectively. The increase of the TS and the EB of PVA/starch film at higher temperature was reported by Zanela et al. [4] who used five types of PVA with different degrees of hydrolysis. They extruded the PVA/starch blend at two different temperatures (170 and 200°C). They stated that the tensile strength was influenced by the extruding temperature and the type of the PVA. For four types of PVA they used (Selvol 523, 540, 107, and 325) they found that the TS of the film extruded at 170°C varied from 1.46 MPa to 2.2 MPa, while that at 200°C was found to be 2.46 – 4.56 MPa. The EB followed the same trend as the TS , in which it increased from 66 – 166% (for film extruded at 170°C) to 95 – 391% (for film extruded at 200°C).

The increase of the TS , EB , and TR of the film from 190 to 210°C might be related to a more homogeneous blend as mixed at higher temperatures. With increasing temperature from 190 to 210°C, the lignin and other components become softer, and the composite is more homogeneous [23] permitting a better interaction among the components [4]. As a result, the film shows higher TS , EB , and TR as the temperature rises from 190 to 210°C. However, the TS , EB , and TR of the films become smaller at mixing temperature of 230°C. It could be related to the thermal degradation of the components. When lignin is heated, some molecular rearrangement associated with softening of lignin starts to take place at 127-193°C [23, 24]. At higher temperatures, starting at 230°C, lignin undergoes decomposition to smaller molecules with the main products of Guaiacol and Syringol [25]. Another molecule susceptible to degradation is PVA. The thermal decomposition of PVA starts at 200°C [26] with the most significant decomposition occurring at 240-340°C [27, 28]. Meanwhile, starch decomposes at 300-400°C [29]. At 230°C it is most likely that lignin and PVA start to decompose, while starch is still stable. Therefore, a lower value of TS , EB , and TR at 230°C could be related to the thermal decomposition of lignin and PVA.

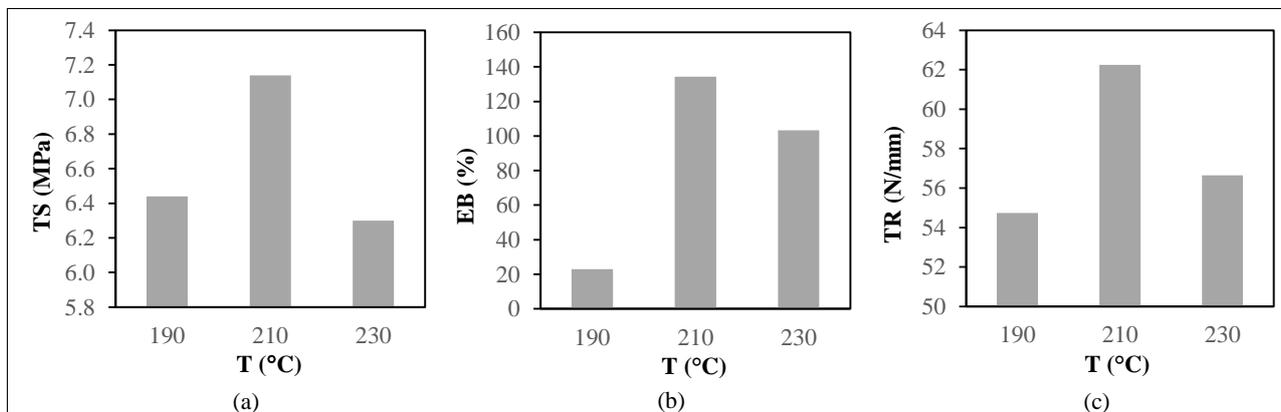


Figure 4. Effect of mixing temperature on: (a) tensile strength, (b) elongation at break, and (c) tear resistance of the film with 45% of glycerol

3-1-2- Effect of Lignin on Film Properties

Figure 5 depicts the effect of lignin (L) on the TS (Figure 5-a), EB (Figure 5-b), and TR (Figure 5-c) of the film. It can be observed in Figure 5-a that increasing lignin from 2% to 6% and 10% results in the increase of the TS by 13.5% and 16.8%, respectively. Similar results were reported by other researchers who used the solution casting method [13–17, 25] and melt extrusion method [18] in preparing the film. Adding 1% to 20% of lignin to starch was able to increase the tensile strength of the starch-based film by 2.9 to 86.3% [15–18]. Meanwhile, the tensile strength of PVA-based film could be increased by 16.7 to 62.5% when lignin as much as 1 to 20% was added to the PVA [12–14]. The enforcement effect of lignin could be related to the strong interaction between lignin and other components in the film. Having hydroxyl groups, lignin can interact with both starch [30] and PVA [31] molecules through hydrogen bonds forming a rigid continuous three-dimensional network [17]. Hence, the film has a higher TS with the increase of lignin. Figure 6 schematically depicts the possible interaction between PVA, starch, and lignin through hydrogen bond in which starch is represented by amylose [30, 31].

The effect of lignin (L) on the EB is shown in Figure 5-b, in which the EB of the film with 6% and 10% of lignin increases by 282% and 597% compared to that of the film with 2% of lignin. Several groups of researchers reported a

similar trend that incorporating 1 to 20% of lignin could increase the *EB* by 2.9 to 900% [12–15, 18]. However, the negative effect of lignin on the *EB* of the film was also reported by other researchers, that adding 1 to 20% of lignin led to the decrease of the *EB* by 1.3 to 38.7% [14, 16, 17]. The different effects of lignin on the *EB* of the film might be due to the different composition and molecular weight of lignin, as well as the preparation methods of the plastics [32]. It was reported that lignin with high molecular weight led to brittle plastics, while low molecular weight lignin resulted in plasticizing effect [15]. Therefore, it is possible that the lignin used in this work has low molecular weight so that it has a plasticizing effect on the plastics.

Figure 5-c presents the effect of lignin on the *TR* of the film. The value of *TR* increased by 18.8 and 29.3% when the lignin addition was increased from 2% to 6 and 10%, respectively. Previous research found a similar result in which the tear resistance of polyurethane-based biodegradable film increased by 75.7% when the addition of lignin was increased from 24.18 to 43.15% [33]. It was explained that the positive effect of lignin on the *TR* was related to the role of lignin as the crosslinking agent where the hydroxyl group of the lignin reacted with the isocyanate group of the polyurethane [34]. However, it is presumable that there is no such reaction between PVA, starch, and lignin in the biodegradable plastic preparation in this work. The positive effect of lignin on the *TR* could be related to the strong interaction through hydrogen bonds among the components of the plastics, thus forming a rigid continuous three-dimensional network [17].

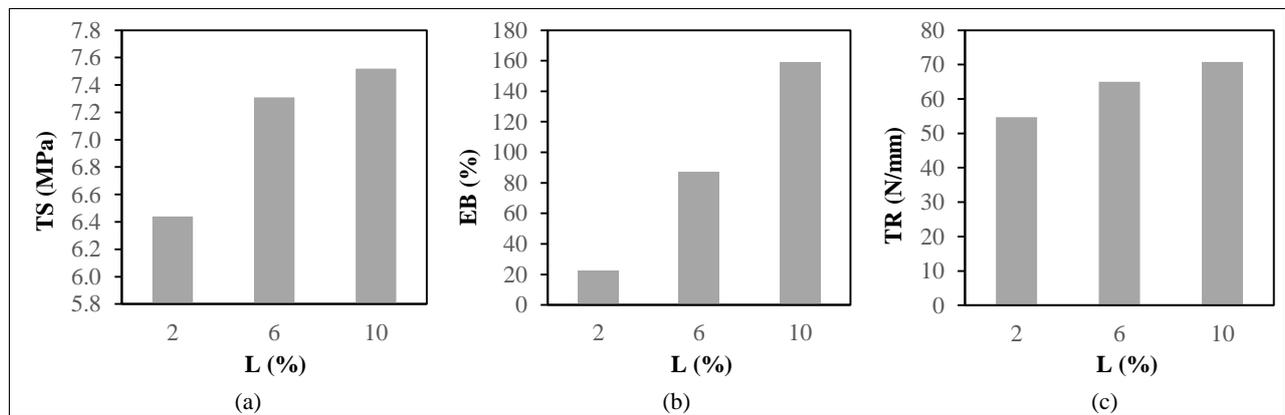


Figure 5. Effect of lignin on: (a) tensile strength, (b) elongation at break, and (c) tear resistance of the film with 45% of glycerol

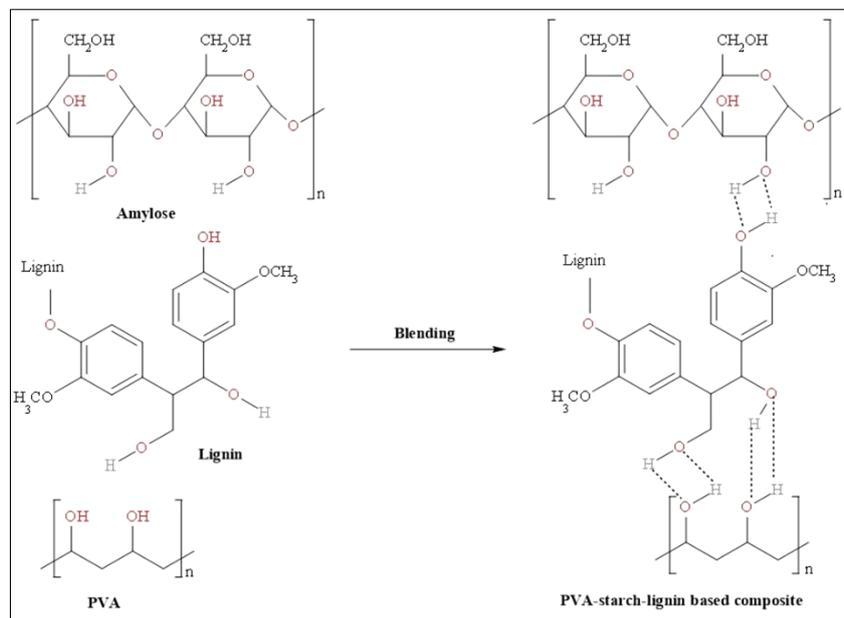


Figure 6. Possible interaction between PVA, lignin, and starch

3-1-3- Effect of Glycerol on Film Properties

Figure 7 shows the effect of glycerol on the mechanical properties of the film. It is shown in Figures 7(a, and b) that the *TS* decreases while the *EB* becomes higher as glycerol increases. Other groups of researchers found similar results [12, 35, 36]. Sue et al. [12] varied the amount of glycerol from 3.3 to 20.8% in making PVA/lignin film. They found that as the percentage of glycerol increased from 3.3 to 20.8%, the *TS* of the film decreased from 35 to 26 MPa while the *EB*

increased from 300 to 440%. Other groups of researchers manufactured a biodegradable film from durian and jackfruit seed flour with various ratios [35]. For a biodegradable plastic film made of mixed flour with a jackfruit to durian seed flour ratio of 1:1, the *TS* of the film decreased from 4.39 to 3.35 MPa, while the *EB* increased from 29.3 to 37.2% when the glycerol used in the film making increased from 30% to 40%. Tarique et al. [36] reported that increasing glycerol from 0 to 45% in making a biodegradable film from arrowroot starch caused a decrease of *TS* from 16.48 to 1.95 MPa and an increase of *EB* from 2.49 to 27.33%.

The influence of glycerol on the *TS* and *EB* of the film can be explained in terms of molecular interaction between the components. Cassava starch is composed of amylose and amylopectin. Both starch components molecules, and polyvinyl alcohol, have hydroxyl groups which allow the interaction between molecules through hydrogen bonds. With a smaller molecule, glycerol fills the space between starch and PVA, thereby reducing the intermolecular attraction between starch and PVA molecules, and hence, decreasing the *TS* of the film. The effect of glycerol on the *EB* is related to the presence of glycerol in between PVA and starch molecules which makes the film more flexible. As a consequence, the *EB* increases with the addition of glycerol [35, 36].

Figure 7-c shows the effect of glycerol on the *TR* in which it increases from 45.0 to 62.2 N/mm as glycerol increases from 25% to 45%. Similar results were reported by other researchers [37, 38]. Jusoh et al. [38] made blown film from polypropylene with crude palm oil as a plasticizer. They found that both the transverse-direction (TD) and machine-direction (MD) *TR* of the film increased with the increase of the plasticizer. Kim et al. [37] also made blown film from poly(butylene adipate-co-terephthalate) with poly(lactic acid) and adipic acid ester as the plasticizer. They also found that both TD and MD-*TR* were positively influenced by the addition of the plasticizer. The positive effect of plasticizer on the *TR* could be related to the small size of the plasticizer molecule compared to those of the polymer. The plasticizer molecules fill the spaces between the polymer molecules which enhance the interfacial adhesion between polymer molecule layers resulting in the reduction of defects such as void. Any stress resulting in tearing action can be absorbed and distributed to the neighboring polymer chains. Hence, the plasticizer increases the *TR* [37]. However, Figure 7-c shows that at higher concentration of glycerol (65%) the *TR* decreases. Although the film could be more homogeneous, it is so flexible and the distance between polymer molecules layers is apart that the interaction becomes weaker. As a result, the *TR* of the film with 65% glycerol is lower than that with 45% glycerol.

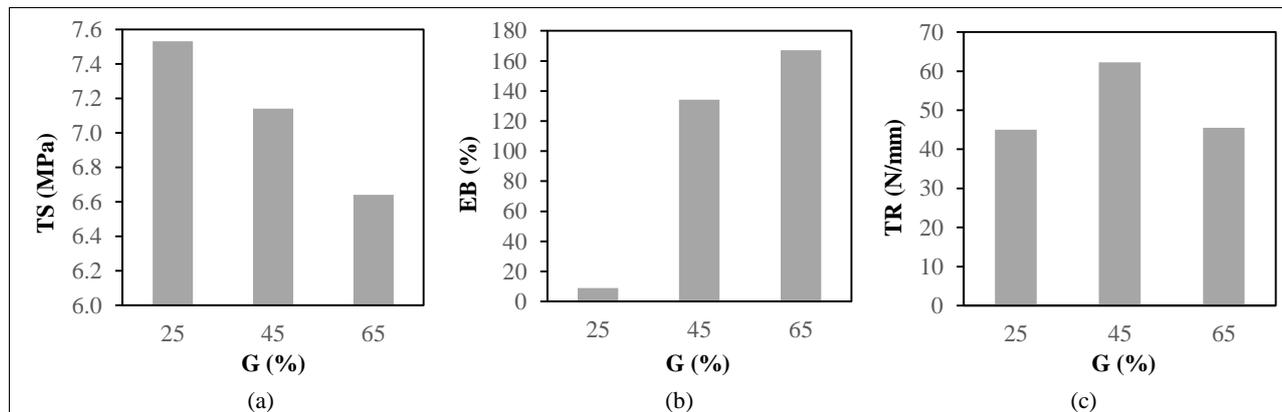


Figure 7. Effect of glycerol on: (a) tensile strength, (b) elongation at break, and (c) tear resistance of the film with 6% of lignin

3-2- Statistical Analysis

The experimental results along with the predicted values for the mechanical properties are presented in Table 3. The data were statistically analyzed to fit the model (Equation 2) for the *TS*, *EB*, and *TR* using response surface methodology.

Table 3. Observed and predicted mechanical characteristics of biodegradable plastic

Run	Experimental Response			Predicted Response		
	<i>TS</i> (MPa)	<i>EB</i> (%)	<i>TR</i> (N/mm)	<i>TS</i> (MPa)	<i>EB</i> (%)	<i>TR</i> (N/mm)
1	7.31	87.31	65.00	7.03	116.44	62.65
2	9.35	9.90	57.05	8.81	29.29	57.10
3	10.07	18.24	63.00	9.58	9.93	59.80
4	3.73	107.90	38.07	3.41	117.73	34.19
5	7.14	134.30	62.25	7.03	116.44	62.65
6	5.57	57.65	54.84	5.40	39.51	55.51
7	6.44	22.88	54.74	6.61	41.02	54.06

8	6.82	12.70	56.86	7.53	11.45	56.13
9	7.53	9.04	45.00	7.86	-0.79	48.88
10	6.30	103.30	56.65	6.09	112.86	60.58
11	6.65	127.70	60.70	7.03	116.44	62.65
12	6.64	167.20	45.51	5.93	168.45	46.24
13	5.02	168.70	41.00	5.56	149.31	40.95
14	7.52	159.40	70.76	7.74	149.84	66.83
15	6.28	157.10	48.16	6.78	165.41	51.37

3-2-1- Tensile Strength

The *TS* values of the films obtained in this work are ranged from 3.73 to 10.07 MPa. The *TS* value of 3.73 MPa is obtained in run 4 with *T* of 230°C, *L* of 6%, and *G* of 65%, while the film with the highest value of *TS* is obtained in run 3 with *T*, *L*, and *G* of 210°C, 10%, and 25%, respectively. The *TS* of the biodegradable plastic obtained in this work are comparable to that of PVA/starch-based biodegradable plastic film as reported by Kong et al. (1.6 – 12 MPa) [39], Kochkina and Lukin (7.82 – 13.52 MPa) [40], Domene-Lopez et al. (4.5 – 10.5 MPa) [41], and Zou et al. (2.22 – 12.96 MPa) [9]. It is even comparable to LDPE film with *TS* of 7.7 MPa [42] and HDPE/PE granules/additive d2w film with *TS* of 7.35 MPa [43]. Several other researchers reported lower value of *TS*, such as Zanela et al. (0.72 – 4.66 MPa) [4], Kaur et al. (0.0275 – 2.475 MPa) [7], and Patil et al. (2.5 – 4 MPa) [8]. Meanwhile, higher values of *TS* were reported by Mittal et al. (9.20 – 18.54 MPa) [44], Tanwar et al. (10.68 – 32.77 MPa) [45], Ray et al. (11.034 – 16.86 MPa) [46], and Zhou et al. (23 – 27 MPa) [47]. The difference in the *TS* obtained by various researchers could be related to different types of starch, plasticizer, and reinforcement, as well as the formulation of the film. The results of the analysis of variance for the *TS* are presented in Table 4. The contribution percentage of the input variables on the response variables is defined as the ratio of each adjusted sum of squares (linear, square, and 2-way interaction) to the total adjusted sum of squares. The analysis can depict the major contributors to the response. In addition, the F-value can also be utilized to find the significant contributors for the corresponding response. The contribution of any input variable is considered significant if its F-value is greater than 4 [48].

Table 4. Analysis of variance (ANOVA) for the tensile strength surface model

Source	DF	Adj. SS	Adj. MS	F-value	p-value	Contrib. percentage
Model	9	30.7364	3.4152	6.36	0.028	
Linear	3	22.4824	7.4941	13.95	0.007	
<i>T</i>	1	4.0712	4.0712	7.58	0.040	13.41
<i>L</i>	1	0.1008	0.1008	0.19	0.683	0.33
<i>G</i>	1	18.3103	18.3103	34.08	0.002	60.29
Square	3	5.2450	1.7483	3.25	0.118	
<i>T</i> ²	1	3.9661	3.9661	7.38	0.042	13.06
<i>L</i> ²	1	0.7841	0.7841	1.46	0.281	2.58
<i>G</i> ²	1	0.1285	0.1285	0.24	0.645	0.42
2-way interaction	3	3.0090	1.0030	1.87	0.253	
<i>TL</i>	1	0.8199	0.8199	1.53	0.272	2.70
<i>TG</i>	1	1.2100	1.2100	2.25	0.194	3.98
<i>LG</i>	1	0.9791	0.9791	1.82	0.235	3.22
Error	5	2.6865	0.5373			
Lack-of-fit	3	2.4483	0.8161	6.85	0.130	
Pure error	2	0.2382	0.1191			
Total	14	33.4229				
R ²		0.9196				
Adj. R ²		0.7749				

Multiple regression analysis with a confidence interval of 95% was used to find the correlation between each response and the independent variables. The mathematical model for the *TS* is presented in Equation 3.

$$TS \text{ (MPa)} = -113.0 + 1.148 T + 0.59 L + 0.134 G - 0.002591 T^2 + 0.0288 L^2 + 0.000466 G^2 - 0.00566 TL - 0.001375 TG + 0.00618 LG \quad (3)$$

The positive and negative signs in Equation 3 indicate the positive and negative effects of the independent variables on the TS . The ANOVA results listed in Table 4 show that the model for the TS has an R^2 value of 91.96% which means that the model can describe 91.96% variations in response to the independent variables. Furthermore, the p-value of the model is 0.028 (< 0.05) which indicates the significance of the developed model and the parameters [49]. Equation 3 is used to calculate the mechanical properties of the film, and the results are presented in Table 3. The relation between the actual and predicted values of TS is shown in Figure 8. The straight line represents the perfect predictive ability of the models. It is shown in Figure 8 that the experimental data which are represented by blue solid circles are close to the line, meaning that the model can predict the TS well.

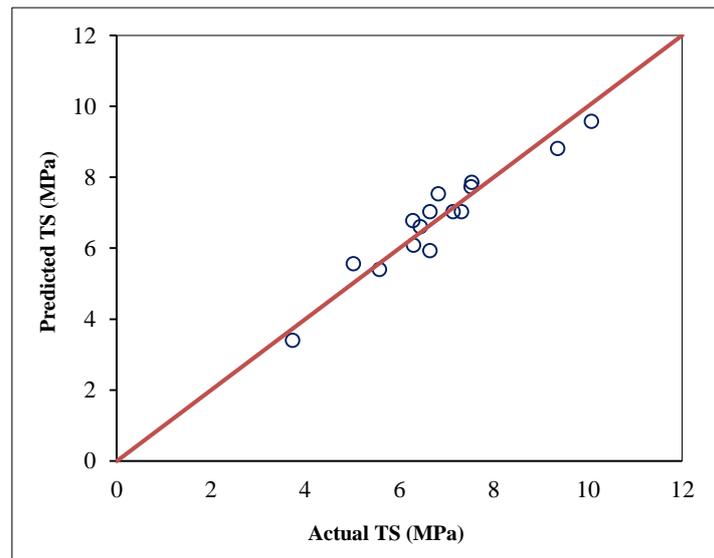


Figure 8. Actual versus predicted plot of tensile strength

The correlation and interaction between the input variables and the TS are depicted in three-dimensional response surface plots as shown in Figures 9 and 10. The results presented in Table 4 show that glycerol (G) has the most significant effect on the TS with a contribution percentage of 60.29%, while G^2 only contributes as much as 0.42%. The dependency of TS on G can be evaluated based on the percentage of contribution of G and G^2 . As the contribution percentage of G (linear effect) is much higher than that of G^2 (quadratic effect), it can be concluded that the effect of G on the TS is approximately linear. It is observed in Figure 9 that the TS decreases almost linearly with the increase of glycerol. It is in good agreement with the experimental data shown in Figure 7-a. Sue et al. [12] also reported that the TR of the PVA-based film decreased almost linearly from 35 to 26 MPa as the amount of glycerol increased from 3.3 to 20.8%.

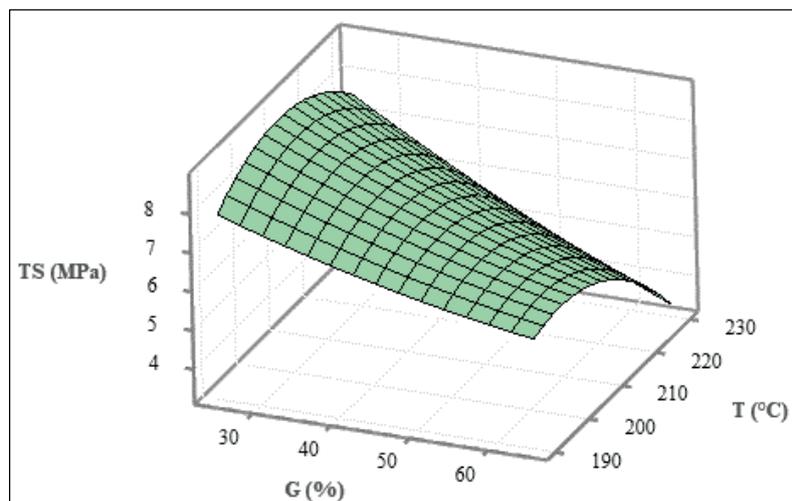


Figure 9. Effect of glycerol and the mixing temperature on the tensile strength of the film with 6% of lignin

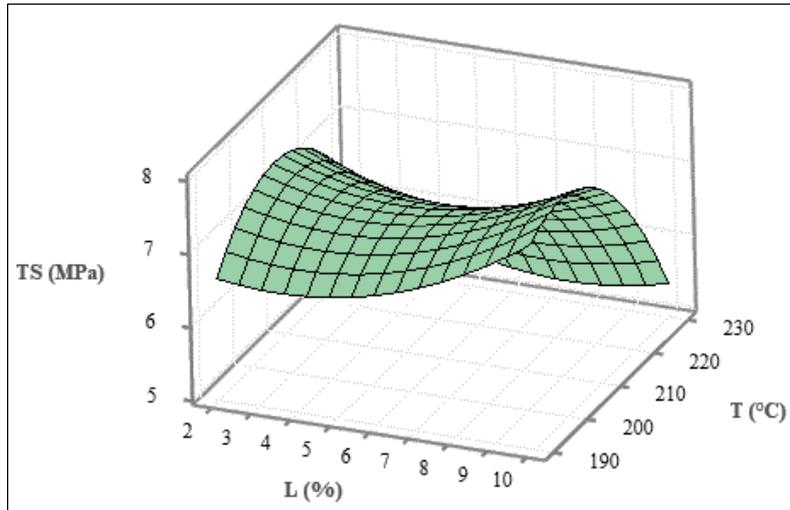


Figure 10. Effect of lignin and the mixing temperature on the tensile strength of the film with 45% of glycerol

The second and third most significant effects are the mixing temperature (T) and the T^2 with the contribution percentage of 13.41%, and 13.06%, respectively. This finding suggests an almost equal contribution of both linear and quadratic effects of the mixing temperature on the TS . Both Figures 9 and 10 also clearly demonstrate a non-linear effect of the mixing temperature on the TS . Initially, the TS increases as the temperature increases from 190 to 210°C. However, the TS value decreases as the temperature further increases beyond 210°C. It is also confirmed by the experimental data presented in Figure 4-a. The significance of G , T , and T^2 are confirmed by their p-values which are less than 0.05 (0.002, 0.040, and 0.042, respectively). The increase of TS of PVA-based film as the extruding temperature increased from 170 to 200°C was reported by Zanela et al. [4]. However, the information about the effect of temperature higher than 200°C on the mechanical properties of biodegradable plastic film is not found in the literature.

Although the effect of lignin on the TS is not significant, it can be analyzed by using the ANOVA results presented in Table 4. Both L and L^2 have contribution percentages of 0.33 and 2.58%, respectively. Hence, the model predicts that the effect of lignin on the TS is not linear. The TS slightly increases with the increase of lignin from 0 to 10%, as depicted in Figure 10, which is in agreement with the actual data shown in Figure 5-a. Other researchers also found that the effect of lignin on the TS was positive and non-linear [12, 13, 17].

3-2-1- Elongation at Break

Table 3 shows that the EB of the biodegradable plastic films varies from 9.04% (run 9) to 168.7% (run 13), which is in the same range as reported by other researchers who manufactured PVA/starch-based biodegradable plastic films [14, 17, 18]. The EB values of the films obtained in this work are also comparable to LDPE, HDLPE, mixed LDPE-HDPE [42], and HDPE-based degradable films [43]. While researchers reported lower values of the EB [15, 16], many others found higher values of the EB [12, 13]. The different values of EB might be due to the different source and molecular weight of the lignin, as well as the difference in the formulation of the biodegradable plastic.

Table 5 presents the analysis of variance for the EB as the response variable. The model developed for the EB is written in Equation 4. The mechanical properties of the film calculated using Equation 4 are presented in Table 3. The relation between the actual and predicted values of the elongation at break is shown in Figure 11.

$$EB (\%) = -3637 + 28.3 T + 128.4 L + 16.22 G - 0.0561 T^2 - 0.511 L^2 - 0.0494 G^2 - 0.569 TL - 0.0394 TG - 0.010 LG \quad (5)$$

Table 5. Analysis of variance (ANOVA) for the elongation at break surface model

Source	DF	Adj. SS	Adj. MS	F-value	p-value	Contrib. percentage
Model	9	51783.5	5753.7	8.93	0.013	
Linear	3	39322.5	13107.5	20.34	0.003	
T	1	740.5	740.5	1.15	0.333	1.42
L	1	628.9	628.9	0.98	0.369	1.21
G	1	37953.2	37953.2	58.91	0.001	72.76
Square	3	3170.6	1056.9	1.64	0.293	

T^2	1	1861.4	1861.4	2.89	0.150	3.57
L^2	1	246.8	246.8	0.38	0.563	0.47
G^2	1	1443.9	1443.9	2.24	0.195	2.77
2-way interaction	3	9290.3	3096.8	4.81	0.062	
TL	1	8296.5	8296.5	12.88	0.016	15.90
TG	1	991.1	991.1	1.54	0.270	1.90
LG	1	2.7	2.7	0.00	0.951	0.01
Error	5	3221.4	644.3			
Lack-of-fit	3	1927.1	642.4	0.99	0.537	
Pure error	2	1294.3	647.2			
Total	14	55004.9				
R^2		0.9414				
Adj. R^2		0.8360				

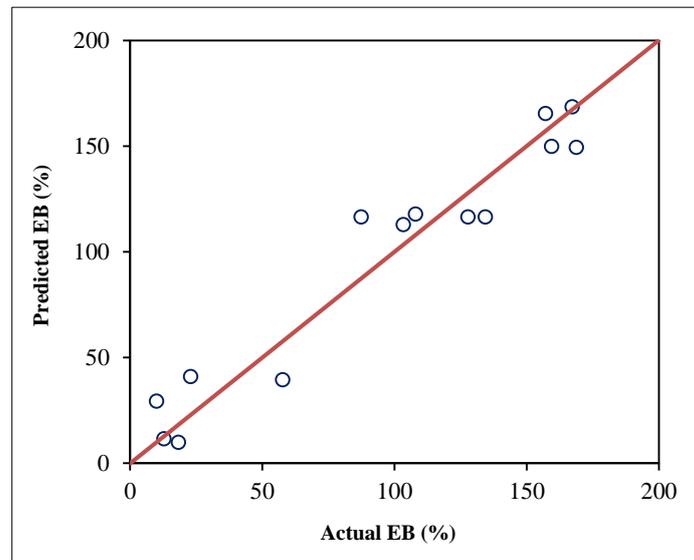


Figure 11. Actual versus predicted values of the elongation at break

Three-dimensional response plots (Figures 12 and 13) clearly present the correlation between the input variables and the *EB*. As tabulated in Table 5, glycerol (*G*) provides the most significant effect on the *EB* with a contribution percentage of 72.76% and a p-value of 0.001, while the G^2 contributes only 2.77% to the variation of the *EB*. Therefore, the model estimates that the glycerol effect on the *EB* follows an almost linear function. Accordingly, Figure 12 also presents that the *EB* increases almost linearly with glycerol. The experimental data depicted in Figure 7-b confirm the effect of glycerol on the *EB* in which the *EB* almost linearly increases with the increase of *G*. Several researchers reported similar results, i.e., a positive effect of *G* on the *EB* [12, 35, 36]. Sue et al. [12] found that the effect of glycerol on the *EB* was linear for the percentage of glycerol ranged from 10 to 21%, while Tarique et al. [36] who used 15 to 45% of glycerol reported that the effect of glycerol on the *EB* was not linear. The different effects (linear or non-linear) of *G* on the *EB* could be due to different formulations of the biodegradable plastic.

The second most significant effect on the *EB* is the interaction between the mixing temperature and lignin (*TL*) with a contribution percentage of 15.90% and a p-value of 0.016. When the effect of 2-way interaction is significant and the value of the coefficient of interactions is negative, the response surface is twisted as shown in Figure 13. At 190°C, the *EB* increases with the increase of lignin, which is exactly shown in Figure 5-b. Meanwhile, at 230°C the *EB* decreases as the lignin increases. The experimental data presented in Table 3 demonstrate the same trend in which at 230°C and 45% of glycerol, the *EB* decreases from 103.30% to 57.65% as lignin increases from 2 (run 10) to 10% (run 6). The negative effect of *L* on the *EB* at 230°C could be related to the decomposition of lignin at 230°C [25, 50].

The effect of the mixing temperature on the *EB* is not significant. However, as seen in Figures 12 and 13, the effect of *T* on the *EB* is not linear, because the contribution percentage of T^2 (3.57%) is higher than that of *T* (1.42%). It increases as the temperature increases from 190 to 210°C, but it then decreases as the temperature further increases from 210 to 230°C. The experimental data depicted in Figure 4-b also exhibits the same phenomenon.

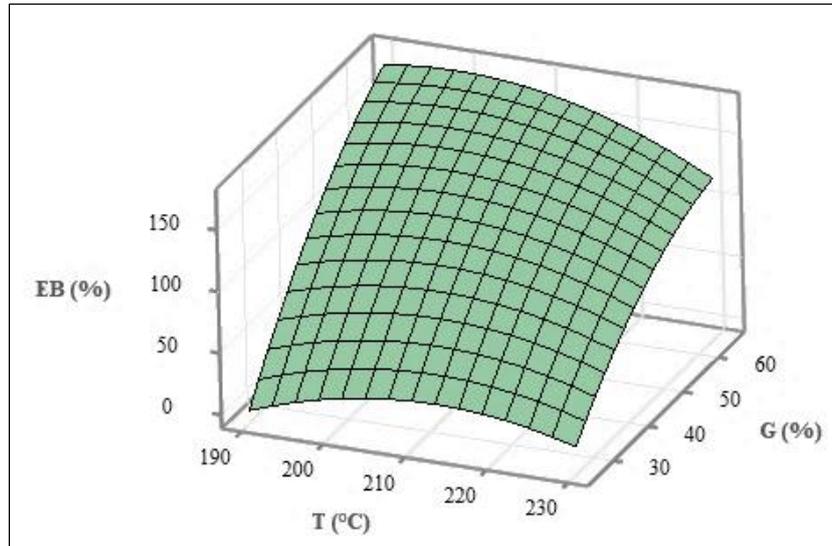


Figure 12. Effect of the mixing temperature and glycerol on the elongation at break of the film with 6% of lignin

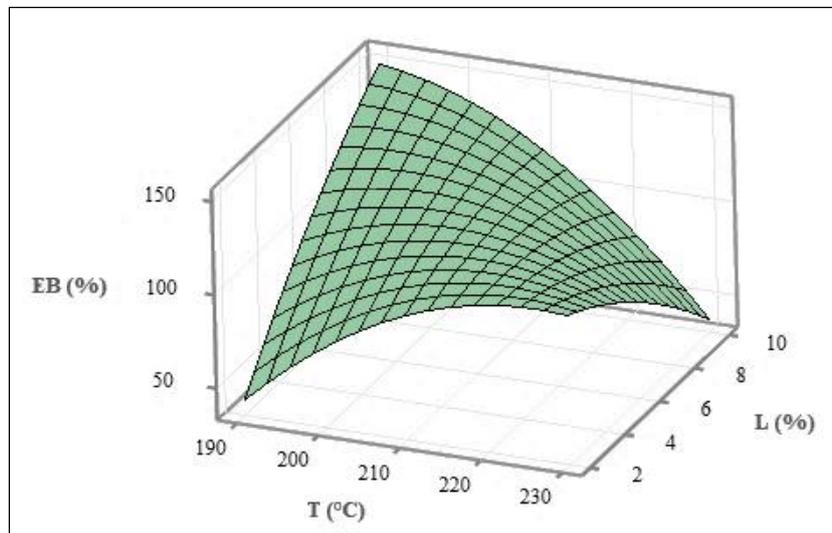


Figure 13. Effect of the mixing temperature and lignin on the elongation at break of the film with 45% of glycerol

3-2-3- Tear Resistance

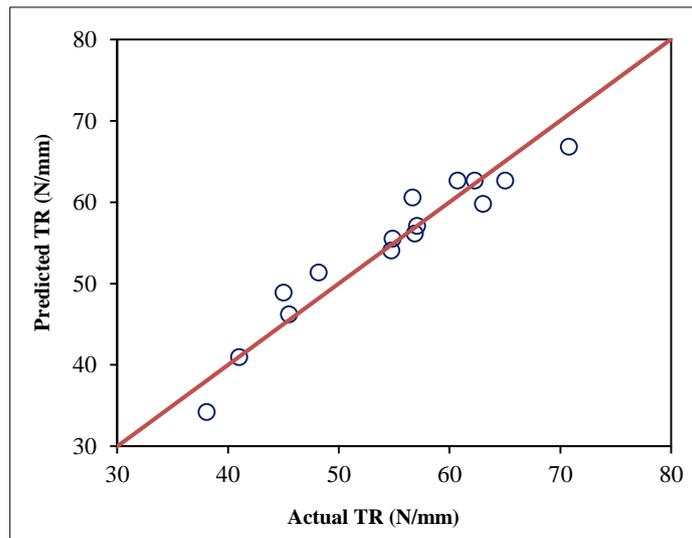
The *TR* of the film obtained in this work are ranged from 38.07 N/mm (run 4) to 70.76 N/mm (run 14). This result cannot be compared to the *TR* of other PVA/starch-based biodegradable plastic film, as such data are not found in the literature. However, the *TR* of the film obtained in this work is comparable to that of polyurethane-based bioplastics (25.66 – 45.09 N/mm) [33], LDPE, and mixed LDPE-HDPE films (45 – 57 N/mm) [42]. It is even higher than the *TR* of poly(butylene adipate-co-terephthalate) blown film plasticized by poly(lactic acid) and adipic acid ester both in machine direction (4.63 – 8.67 N/mm) and transverse direction (13.19 – 16.16 N/mm) [37]. The analysis of variance for the effect of the mixing temperature, lignin, and glycerol on the *TR* is presented in Table 6. The model correlating the input variables to the *TR* is written in Equation 5.

$$TR \text{ (N/mm)} = -658 + 5.73 T + 9.39 L + 4.59 G - 0.01169 T^2 + 0.079 L^2 - 0.02904 G^2 - 0.0557 TL - 0.01206 TG + 0.0410 LG \quad (5)$$

Equation 5 is used to calculate the mechanical properties of the film, and the results are presented in Table 3. The relation between the actual and predicted values of the *TR* are shown in Figure 14.

Table 6. Analysis of variance (ANOVA) for the tear resistance surface model

Source	DF	Adj. SS	Adj. MS	F-value	p-value	Contrib. percentage
Model	9	1132.36	125.818	6.77	0.024	
Linear	3	343.37	114.457	6.16	0.039	
T	1	11.49	11.493	0.62	0.467	1.00
L	1	29.71	29.707	1.60	0.262	2.60
G	1	302.17	302.173	16.25	0.010	26.42
Square	3	573.40	191.133	10.28	0.014	
T ²	1	80.71	80.714	4.34	0.092	7.06
L ²	1	5.96	5.962	0.32	0.596	0.52
G ²	1	498.15	498.147	26.80	0.004	43.55
2-way interaction	3	215.59	71.863	3.87	0.090	
TL	1	79.52	79.520	4.28	0.093	6.95
TG	1	93.07	93.069	5.01	0.075	8.14
LG	1	43.00	43.000	2.31	0.189	3.76
Error	5	92.95	18.591			
Lack-of-fit	3	83.48	27.826	5.87	0.149	
Pure error	2	9.48	4.739			
Total	14	1225.31				
R ²		0.9241				
Adj. R ²		0.7876				

**Figure 14. Actual versus predicted values of tear resistance**

The correlation between the input variables and the *TR* is presented in three-dimensional response plots (Figures 15 and 16). Table 6 shows that G^2 and G have the most significant effect on the *TR* with the contribution percentage of 43.55% (p-value = 0.004) and 26.42% (p-value = 0.010), respectively. Therefore, the model predicts that the effect of G on the *TR* is non-linear as depicted in Figure 15, in which the *TR* increases and then decreases as G increases from 25% to 65%. It is the same as the experimental data shown in Figure 7-c. Jusoh et al. [38] reported that the MD-*TR* of polypropylene blown film plasticized by crude palm oil increased from 279 g (neat polypropylene film) to 400 g (polypropylene + 5% plasticizer), while the TD-*TR* increased from 469 g (neat polypropylene film) to 673 g (polypropylene + 5% plasticizer). Kim et al. [37] found that incorporation of 10% of poly(lactic acid) as the plasticizer in manufacturing of poly(butylene adipate-co-terephthalate) blown film could increase the MD-*TR* from 4.63 to 8.67 N/mm, and the TD-*TR* from 13.19 to 16.16 N/mm.

Although being less significant, the effect of the mixing temperature (T) on the *TR* can be analyzed by using the ANOVA results presented in Table 6. The contribution percentage of T is 1.00%, while that of T^2 is 7.06%. Therefore, it can be concluded that the effect of T on the *TR* is non-linear, as is seen in Figures 15 and 16. A similar effect is

observed in the experimental data (Figure 4-c). Meanwhile, it is shown in Figure 16 that the effect L on the TR is almost linear. It is because the contribution of L is much higher than that of L^2 , i.e., 2.6% and 0.52%, respectively. Experimental data depicted in Figure 5-c shows that the TR increases almost linearly with the increase of L . Zhang et al. [33] found that the TR of polyurethane-based biodegradable film increased from 25.66 to 45.09 N/mm when lignin was increased from 24.18 to 43.15%. The increase in TR with lignin could be due to the hydrogen bond among the PVA, starch, lignin, and glycerol molecules, and thus forming a strong three-dimensional network [17].

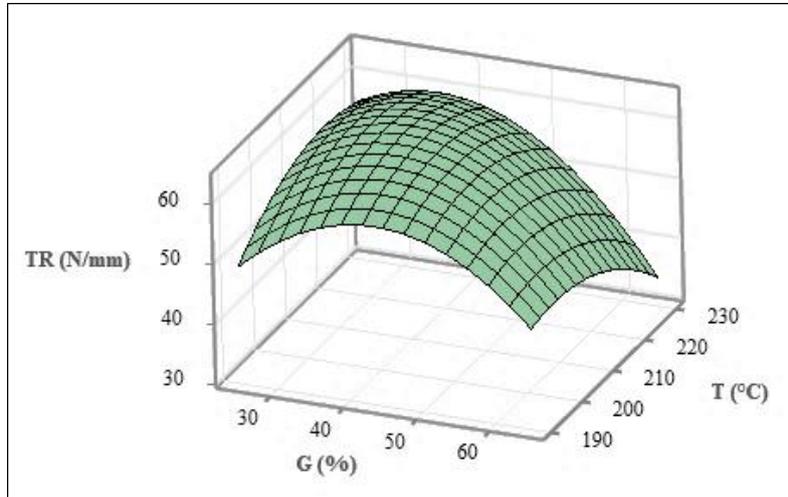


Figure 15. Effect of the mixing temperature and glycerol on the tear resistance of the film with 6% of lignin

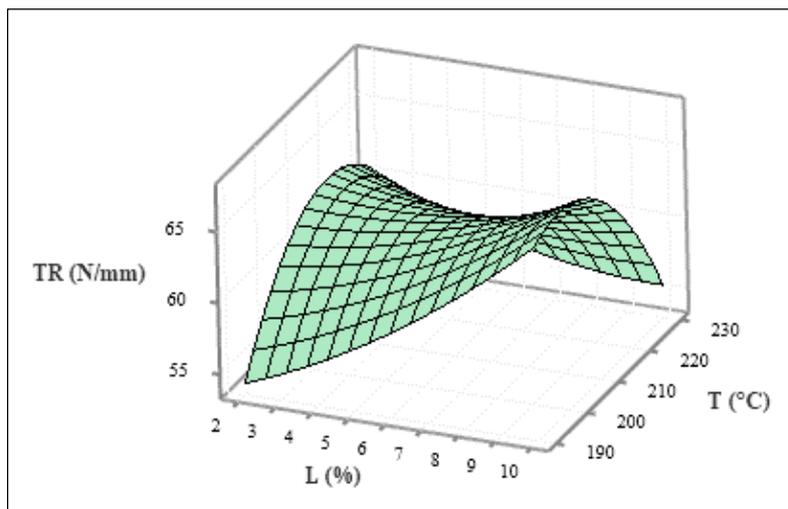


Figure 16. Effect of the mixing temperature and lignin on the tear resistance of the film with 45% of glycerol

3-3- Optimization of Film Formulation

The optimum conditions for the preparation of biodegradable plastic film were estimated by the response optimizer by which the influence of both single and interacted parameters can be obtained [51]. This step resulted that the optimum conditions being 197.6°C for temperature, 10% for lignin, and 45.1% for glycerol. Applying these conditions to the model would result in 7.93 MPa for the TS , 143% for the EB , and 68.50 N/mm for the TR .

Model validation was also conducted by performing a verification experiment at the optimum condition. The mechanical values of the verification sample were 8.46 ± 1.08 MPa, $139.00 \pm 8.59\%$, and 69.50 ± 2.50 N/mm for the TS , the EB , and the TR , respectively. The TS and the TR values are slightly higher than the predicted values, while the value of EB is lower than the predicted value. Nevertheless, they are still within 95% confidence interval, i.e., 7.120 - 9.798 MPa, 128.34 - 149.66%, and 63.29 - 75.71 N/mm for the TS , the EB , and the TR , respectively. Therefore, the models are capable to predict reasonable responses.

Table 7 shows the TS , the EB , and the TR of biodegradable plastic bags according to SNI 7818:2014 along with the biodegradable plastic made with the optimum condition in this work. Among the three properties, only the TR value exceeds the standard. Hence, further research is required to enhance the TS and the EB , while maintaining the TR .

Table 7. Mechanical properties of biodegradable plastic bag according to SNI 7818:2014

Property	Unit	SNI 7818:2014	This work
Tensile strength	MPa	> 13.7	8.46 ± 1.08
Elongation at break	%	400 – 1120	139 ± 8.59
Tear resistance	N/mm	> 50 (TD)	69.50 ± 2.50

4- Conclusion

Biodegradable plastic films from PVA/starch/lignin blends incorporating glycerol as a plasticizer were successfully manufactured through melt compounding and hot press molding machines. Three models were developed for the tensile strength, the elongation at break, and the tear resistance. The results show that glycerol, lignin, and mixing temperature affect the mechanical properties. The glycerol percentage was found to be the most significant factor. The optimum conditions to produce the biodegradable plastic film with good mechanical properties are 197.6 °C for temperature, 10% of lignin, and 45.1% of glycerol. The mechanical properties of the biodegradable plastic obtained at the optimum condition predicted using the proposed model are 7.93 MPa, 143%, and 68.50 N/mm for tensile strength, elongation at break, and tear resistance, respectively. Model validation was performed by model verification with experimental data at the optimum condition. The tensile strength of the verification sample was 8.46 ± 1.08 MPa, the elongation at break was 139.00 ± 8.59%, and the tear resistance was 69.50 ± 2.50 N/mm. These mechanical properties are within a 95% confidence interval. Furthermore, the models can predict the effects of individual and two-way interactions of the input variables on the response variables. Therefore, the models offer reasonable results to predict the response.

5- Declarations

5-1- Author Contributions

Conceptualization, R.R. and R.W.; data collection R.W.; data validation A.C.K. and H.H.; data processing R.R. and R.W.; data analysis and interpretation R.R., R.W., A.C.K., and H.H.; writing—original draft preparation, R.W. and R.R.; writing—review and editing, R.R. and A.C.K.; project funding and administration, R.W. All authors have read and approved to the final manuscript.

5-2- Data Availability Statement

The data presented in this study are available in article.

5-3- Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

5-5- Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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