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Effects of Processing Temperature and Lignin on Properties of Starch/PVA/Lignin Film Prepared by Melt Compounding

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Abstract. Starch/PVA/lignin blends with gliserol as plasticizer were prepared by melt compounding method using an internal mixer for compounding and compression molding for film forming. The lignin concentration and compounding temperature were varied at two levels. Starch/PVA/lignin film produced was analyzed for mechanical properties (tensile strength, elongation at break, and tear resistance), thermal property with Thermogravimetric analysis (TGA), and morphology with scanning electron microscope (SEM). The results indicate that interaction of processing temperature and lignin concentration has significant effect on mechanical properties. The presence of lignin in starch/PVA blend improves thermal properties. Morphologically, higher lignin concentration causes lignin to agglomerate.

Keywords: lignin, melt compounding, properties, PVA, starch

1. Introduction

The usage of traditional plastics derived from petroleum can cause problems in waste disposal because these materials are not easily biodegradable and resistant to microbial degradation so they accumulate in the environment. Plastic production based on renewable raw material sources is still around 2% of total production in 2013 and is predicted around 4% in 2020 [1]. This fact drives further study about biodegradable plastics, especially from renewable materials [2].

Starch is widely used as renewable material for biodegradable plastics [3]. Starch is cheap, abundantly available, non-toxic, and environmentally friendly [1]. However, the mechanical and thermal properties of starch are poor, so it needs to be blended with other biodegradable polymers for improving these properties [3,4].

Polyvinyl alcohol (PVA) is a biodegradable synthetic polymer with high mechanical properties that are compatible with starch [3-5], due to the existence of hydroxyl groups in both polymers. Incorporating starch into PVA can also increase the biodegradation speed of PVA [3]. Mixing PVA and starch to improve mechanical properties while maintaining the biodegradability has been widely explored [4,6-8].

The main problem in blending starch and PVA is its sensitivity to moisture [3]. One way to overcome this weakness is by adding a reinforcement filler, of which lignin is the best choice [9]. The complex structure of lignin with low hydrophilicity can hinder water penetration [10]. In addition, lignin is cheap, biodegradable, abundantly available with production capacity reaching 50 million



tons/year [11, 12]. Mixing starch, PVA, and lignin is expected to improve the mechanical properties and barrier properties toward water of the film.

The addition of plasticizer in blending starch and PVA by melt compounding is necessary to reduce the melting temperature, stiffness, and increase flexibility and ease of PVA processing [5, 13, 14]. Addition plasticizer in blending starch and PVA has been conducted in a various amount such as 20% glycerol plasticizer [6], 35 - 40% glycerol [7, 8, 15], and 66.7% glycerol [4].

To process starch-based biodegradable plastics with melt compounding using an extruder is more complex and difficult than most synthetic polymers. This process involves starch plasticization and also degradation of starch molecules [16]. Processing with an internal mixer can provide information that can be used to determine the initial conditions of the extrusion process. The internal mixer is able to provide rapid response with a smaller sample volume than processing in an extruder [17].

This study was aimed to study the effect of lignin and compounding temperature on mechanical properties (tensile strength, elongation at break and tear resistance) of starch/PVA/lignin film. Starch/PVA/lignin blends with glycerol as a plasticizer were prepared by melt compounding method using an internal mixer for compounding and compression molding for film making.

2. Material and method

2.1. Materials

PVA JP-18 with a hydrolysis degree of 87-89% and viscosity of 23-27 mPa.s (4% m/v, 20°C) was purchased from VAM & Poval Co., Ltd., Japan. Alkaline lignin with methoxy group of 12%, pH of 8.8 (50 gr / L at 20 °C) and water content of 7.4% was obtained from Tokyo Chemical Industry. Cassava starch with Gunung Agung brand was obtained from a local supplier, PT. Budi Acid Jaya. Glycerol as a plasticizer with purity 99.7% was also obtained from a local supplier, PT. Wilmar Nabati Indonesia.

2.2. Preparation of composites

Starch, PVA, and lignin were dried at 105°C for 4 hours in an oven (Binder, Type: 1815300002020) before the mixing process was carried out. Dry mixing was conducted by mixing starch, PVA, and lignin in certain compositions (see Table 1) in a glass beaker and stirring with a glass stirring rod until homogeneous. A certain amount of glycerol (see Table 1) was added and the mixture was stirred again until homogeneous. The blends were then conditioned in the oven at 50°C for 24 hours to incorporate glycerol as plasticizer.

The blends were compounded in Haake Rheomix 3000P Internal Mixer with a counter-rotating Banbury rotor. The rotor speed was set at 100 rpm for 5 minutes at various temperatures according to Table 1. The sample films were prepared by using a compression molding machine (Collin P 300 P/M) at 200°C for 15 minutes (5 minutes at 25 bar and 10 minutes at 30 bar).

Table 1. Experimental design

Run	Temperature (°C)	Lignin (%)
F2	190	2
F3	190	10
F4	230	2
F13	230	10

*Composition: PVA/Starch = 60/40, glycerol 45% (based on the weight of PVA and starch).

2.3. Characterization

Specimens for testing were cut from sample films. The tensile strength and elongation at break tests were performed according to ASTM D882 using Universal Testing Machine (Shimadzu AGS 10 kNG Universal) with an initial distance between grips of 50 mm and a crosshead speed of 500 mm/min. Prior to testing, samples were conditioned at 23°C and a relative humidity of $55 \pm 2\%$ for 40 hours. Five specimens were tested for every formulation. The tear resistance determination was performed according to ASTM D1004 using Universal Testing Machine (Shimadzu AGS-10kNG) at very low rates of loading of 51 mm/min until the specimen tears. Prior to testing, samples were conditioned at a relative humidity of $55 \pm 2\%$ for 40 hours. Five specimens were tested for every formulation. Analysis of the effect of each variable on tensile strength, elongation at break and tear resistance was done using Minitab software.

The thermal degradation behavior was determined using the Thermogravimetric analyzer Mettler Toledo type TGA / SDTA 851 with a nitrogen flow rate of 50 mL/minute. Samples of 4-5 mg are heated from room temperature to 500°C with a heating speed of 10°C/minute.

The surface morphology of the samples was determined using a scanning electron microscope (SEM) Jeol, JSM-6510LA at 15 kV. Samples were coated with platinum, then measurements were made at 1000x magnification.

3. Result and Discussion

Table 2 shows the tensile strength, elongation at break, and tear resistance of the starch/PVA/lignin film samples. Figures 1 and 2 show that as the compounding temperature rises from 190°C to 230°C, all the mechanical properties, i.e. tensile strength, elongation at break, and tear resistance decrease. On the other hand, the addition of lignin from 2% to 10% results in lower tensile strength and elongation at break, while increases the tear resistance.

Table 2. Mechanical Properties of starch/PVA/Lignin film

Run/sample	Tensile strength (MPa)	Elongation at break (%)	Tear resistance (N)
F2	3.941	223.6	18.18
F3	3.050	136.6	16.00
F4	3.716	191.4	7.640
F13	3.089	142.7	13.66

3.1. Tensile Strength and Elongation at Break

Figure 1(a) shows that the tensile strength is significantly affected by lignin concentration but only slightly influenced by compounding temperature. The decrease of the tensile strength of the film with a higher concentration of lignin could be caused by the agglomeration of the lignin. It is also shown in Figure 2(a) that there is an interaction between compounding temperature and lignin concentration. At both 190°C and 230°C, the increase of lignin concentration from 2% to 10% causes a lower value of tensile strength.

Figure 1(b) shows that the elongation at break is significantly affected by lignin concentration but only slightly influenced by compounding temperature as well. The elongation at break decreases at higher concentration of lignin. This is because lignin provides stiffness in the starch/PVA blend [10]. Figure 2(b) shows an interaction between compounding temperature and lignin concentration. At compounding temperature 190°C and 230°C, the elongation at break of the film with 10% lignin is much lower than that with 2% lignin. At a compounding temperature of 190°C, the increase of lignin concentration from 2% to 10% decreases the elongation at break from 223.6% to 136.6%, while those at 230°C, the elongation at break decreases from 191.4% to 142.7%.

3.2. Tear resistance

Figure 1(c) shows that the tear resistance is influenced by compounding temperature and lignin concentration. Figure 2(c) also shows an interaction between the compounding temperature and the lignin concentration. At compounding temperature of 190°C, the increase of lignin concentration from 2% to 10% causes 15.4% decrease in tear resistance, i.e. from 18.18 N to 16 N. This is probably due to the lignin agglomeration, reinforced by Figure 3b. At compounding temperature of 230°C, the addition of lignin from 2% to 10% causes a 78.8% increase in tear resistance, i.e. from 7.64 N to 13.66 N. The increase of tear resistance is due to the reinforcement of the film by lignin [19].

3.3. Thermogravimetric analysis

Thermal stability and decomposition temperature of starch/PVA/lignin films were determined by thermogravimetric analysis (TGA). The TG curves of all samples in Figure 3 show the same pattern. The initial degradation occurs at temperatures 60°C to 120°C which is the evaporation of water. The subsequent degradation step at a temperature of about 200°C is the polymer decomposition, followed by the decomposition of lignin at higher temperatures, 250°C to 350°C. At the end of the test, at 500°C, the mass of the remains of the starch/PVA films with 10% lignin (b and d) are higher than those with 2% lignin (a and c). This is because the addition of lignin will increase the thermal stability of the material [10, 18, 20]

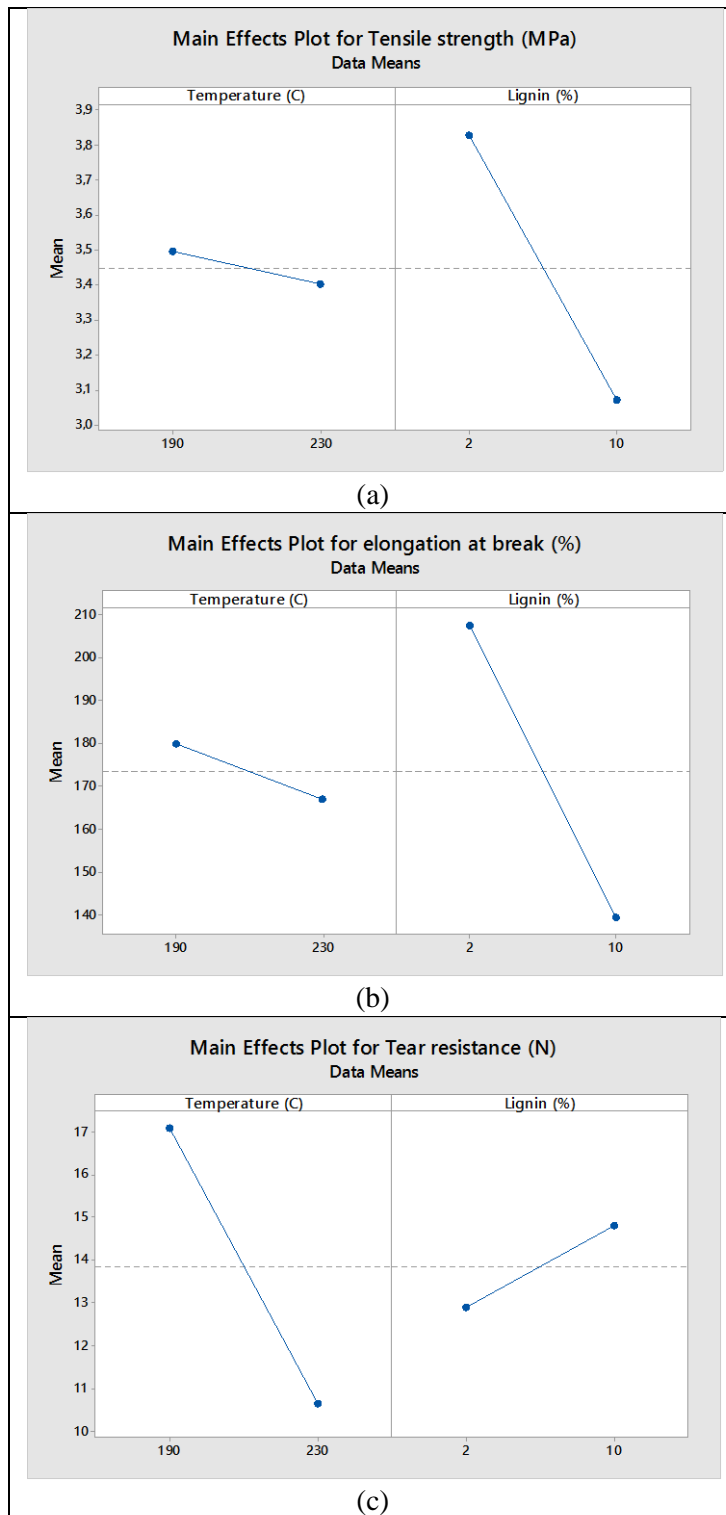


Figure 1. The main plot of starch/PVA/Lignin film for tensile strength (a); elongation at break (b); tear resistance (c)

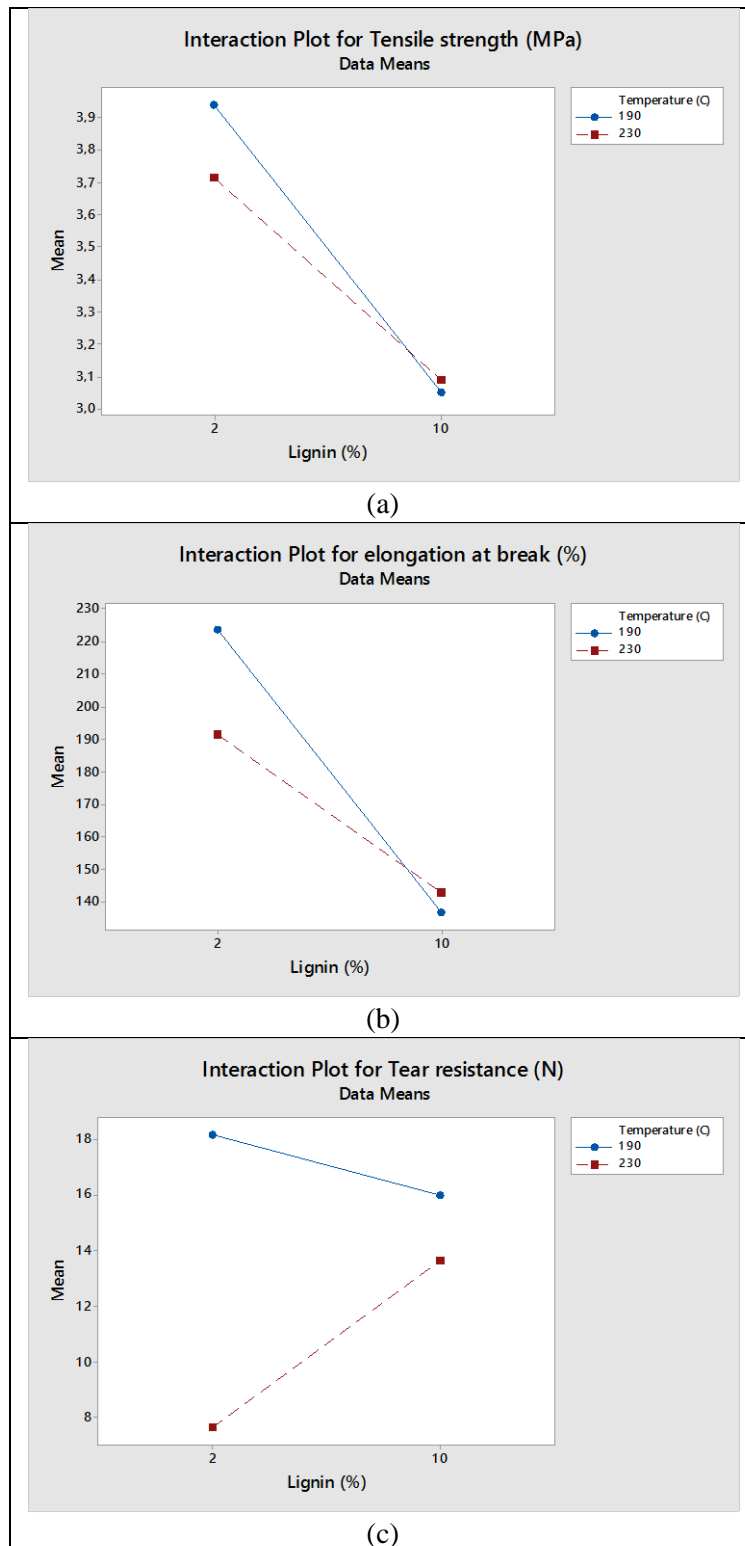


Figure 2. Interaction plot of starch/PVA/Lignin film for tensile strength (a); elongation at break (b); tear resistance (c)

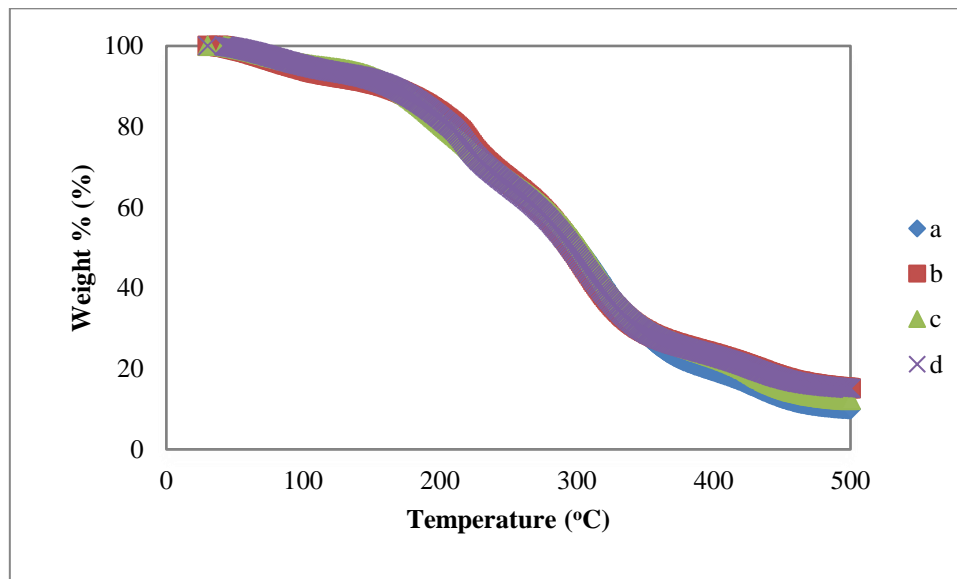


Figure 3. Thermogravimetric curves of starch/PVA/lignin film ; (a) Lignin 2%, Temperature 190 °C; (b) Lignin 10%, Temperature 190 °C; (c) Lignin 2%, Temperature 230 °C; (d) Lignin 10%, Temperature 230 °C

3.4. Morphology

Figure 4 shows the SEM image of the films. Figures 4 (a) and (b) show the surface of the films compounded at 190°C with lignin concentrations of 2% and 10%, respectively. It is observable in the figure that film with a lower concentration of lignin is more homogeneous. High lignin concentration in starch/PVA mixtures causes the lignin to agglomerate.

4. Conclusion

Starch/PVA/Lignin films have been successfully made by melt compounding technique using Haake Rheomix's internal mixer. The films were molded from the compounded materials using compression molding equipment. The resulted films were measured for the mechanical properties, thermal properties, and morphology. The results of this study indicate that the interaction of the compounding temperature and lignin concentration has a significant effect on mechanical properties. The increase of lignin concentration from 2% to 10% causes a decrease in tensile strength and elongation at break. On the other hand, the increase of lignin from 2% and 10% causes a slight decrease in the tear resistance for the film compounded at 190°C, but it causes an increase for that at 230°C. Higher lignin concentration causes the lignin to agglomerate and not evenly distributed through the film.

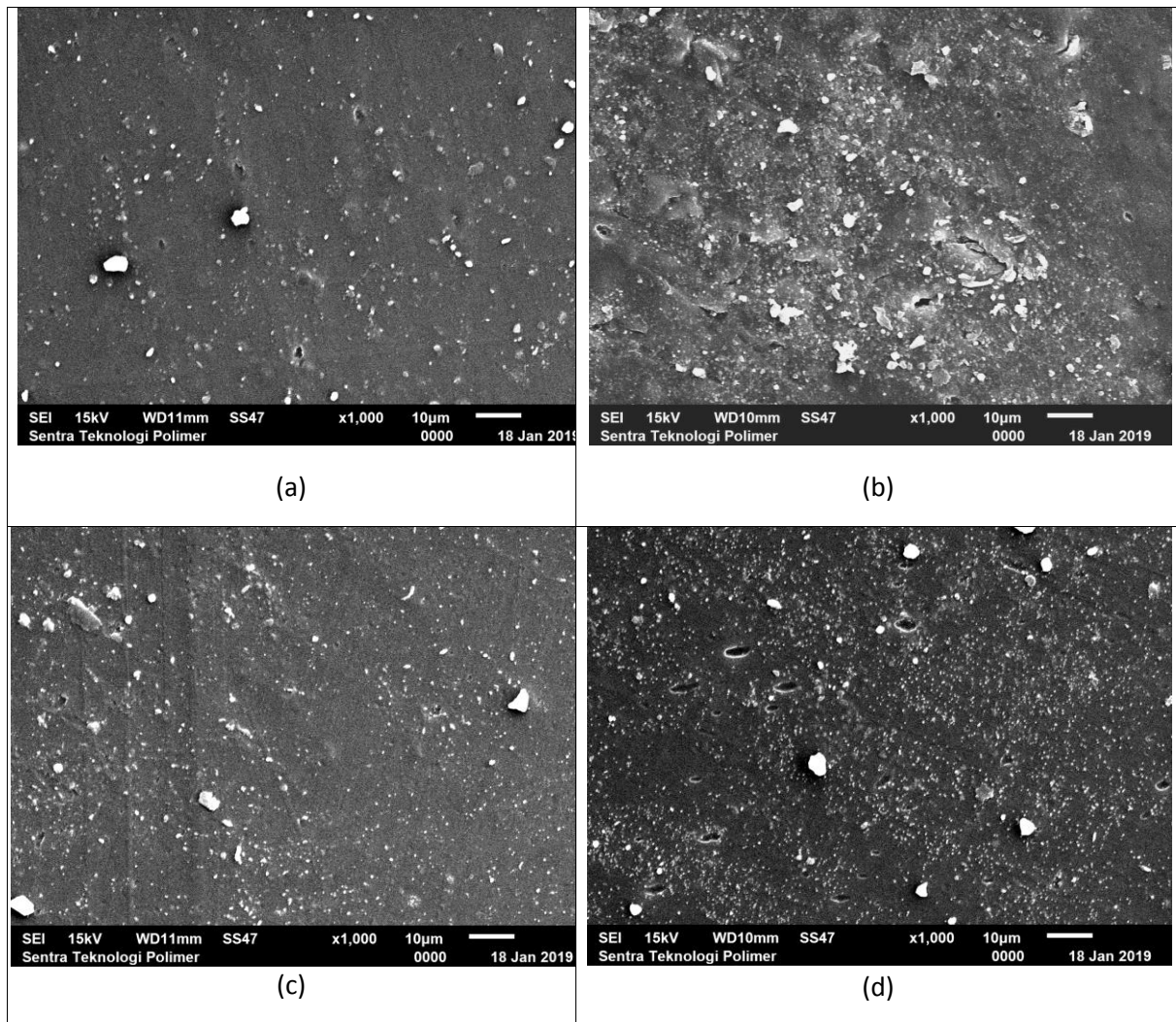


Figure 4. SEM of starch/PVA/lignin film; (a) Lignin 2%, Temperature 190 °C; (b) Lignin 10%, Temperature 190 °C; (c) Lignin 2%, Temperature 230 °C; (d) Lignin 10%, Temperature 230 °C

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