



Biodegradable Plastics from PVA/Starch/Lignin Blend: Mechanical Properties, Water Absorption, and Biodegradability

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Abstract

Biodegradable plastics from Polyvinyl Alcohol (PVA), starch, and lignin with glycerol as a plasticizer were prepared by melt compounding method using an internal mixer for compounding and a hot press molding machine for the plastics film forming. The tensile strength, elongation at break, functional group, water absorption, and biodegradability were analyzed. The plastic made of merely PVA and glycerol had the highest tensile strength (13.6 MPa) and elongation at break (347%). Substituting 40% of PVA with starch and adding 10% of lignin to the PVA/starch blend reduced the tensile strength and elongation at break to 8.5 MPa and 139%, respectively. Adding lignin reduced water absorption while adding starch and lignin accelerated the biodegradation of the plastics. FTIR spectra indicated new hydrogen bonds formed between PVA, starch, and lignin.

Keywords: biodegradability; elongation at break; tensile strength; water absorption

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1. Introduction

Petroleum-based plastics are mainly synthetic polymers dominated by polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polyvinyl chloride (PVC) [1]. They are utilized in every aspect of daily modern life [2]. Global plastics production soared from 234 million tons/year in 2000 to 460 million tons/year in 2019, with annual plastic waste reaching 353 million tons/year. Less than 10% of plastic waste was recycled, about 19% was incinerated, almost 50% ended up in sanitary landfills, and 22% needed better management [1]. Most plastic waste eventually accumulates in soil and water because of its long lifetime. Petroleum-based plastics are resistant to biological degradation. For example, it takes 450 years for PP to decompose naturally [3]. Therefore, it is essential to minimize the use of petroleum-based plastics.

One effort to reduce petroleum-based plastics is by substituting it with biodegradable plastics. Polyvinyl alcohol (PVA) is one of the potential biodegradable synthetic polymers for plastics and packaging applications. However, PVA is expensive and has low biodegradability with a low water barrier property [4]. Therefore, PVA is often blended with starch to reduce the cost while increasing the biodegradability [5, 6].

PVA/starch blends have poor processability, and the resulting plastics are brittle with high hydrophilicity [7]. Many researchers have tried to improve the property and processability by adding a plasticizer, but it reduces the

strength of the plastics [4, 5]. Therefore, fillers are usually used to improve the properties [5, 8]. Lignin is one of the reinforcement fillers that has recently received widespread attention [9]. Lignin is a complex polymer with low hydrophilicity to prevent water penetration [8]. Lignin is also a biodegradable biopolymer abundantly available as a byproduct of the paper and ethanol industries, with a production capacity of more than 50 million tons/year [10, 11]. Blending PVA with starch, lignin, and glycerol as a plasticizer is expected to improve the mechanical and water barrier properties while maintaining the biodegradability of the plastics.

This study aimed to investigate the effect of processing temperature and the composition of the PVA/starch/lignin/glycerol blend on the mechanical properties and the biodegradability of the plastics. The plastics were prepared by the melt compounding method.

2. Materials and methods

2.1 Materials

The materials used in this work were PVA JP-18, alkaline lignin, cassava starch, and glycerol. PVA with 87-89% degree of hydrolysis was obtained from VAM & Poval Co., Ltd., Japan. Alkaline lignin was purchased from Tokyo Chemical Industry. The lignin has a methoxy group of 12%, moisture content of 7.4%, and pH of 8.8 (in a solution with a concentration of 50 g/L at 20°C). Cassava starch and glycerol (99.7% purity) were purchased from local suppliers, i.e., PT. Budi Acid Jaya and PT. Wilmar Nabati Indonesia, respectively.

2.2 Preparation of the Plastics

All materials, except glycerol, were dried in an oven (Binder, Type 1815300002020) at 105°C for 4 hours. Next, PVA, starch, lignin, and glycerol with various compositions (Table 1) were mixed in a beaker glass and stirred with a glass rod until homogeneous. Next, the blends were placed in a closed container and left in the oven at 50°C for 24 hours. Next, the blend was compounded in an internal mixer (Haake Rheomix 3000P) equipped with a counter-rotating Banbury rotor with a speed of 100 rpm. The compounding was completed in 5 minutes at various processing temperatures (see Table 1). Then the compounded blends were formed into films using a hot press molding machine (Toyoseiki Mini Test Press-10) operated at 180°C and 100 MPa.

2.3 Characterization

The plastics were tested for tensile strength (TS), elongation at break (EB), functional group, water absorption, and biodegradability. The samples were kept in a room with $55 \pm 2\%$ relative humidity (RH) for 40 hours before testing. The mechanical properties were tested according to ASTM D882 using a universal testing machine (Shimadzu AGS 10kNG Universal). The initial distance between grips was 65 mm, and the crosshead speed was 50 mm/min. The measurements were done in triplicate. The functional group analysis was conducted using the Fourier Transform Infrared (FTIR). The samples were scanned at a wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ and measured in the attenuated total reflectance (ATR). The water absorption was measured by a weight reduction method. Three specimens were stored at 50% RH for seven days and then dried in the oven at 105°C for 24 hours. These samples were weighed before (w_i) and after (w_f) being dried in the oven. The water absorption (WA) was calculated using Eq. (1) [8].

$$WA (\%) = \frac{w_f - w_i}{w_i} \times 100 \quad (1)$$

The biodegradability of the plastics was determined by testing the resistance of the plastics to fungi according to ASTM G21. Three samples (FC, FV, and FW), along with a sample of non-biodegradable plastic, were used in this test. The specimens were placed on an agar medium surface and inoculated with *Trichoderma sp.* Samples were incubated at 28–30°C for seven days. The growth of the fungi was observed and assessed. In addition, the surface characteristic of the plastics (before and after incubation) was scanned using a scanning electron microscope (Jeol, JSM-6510LA).

3. Results and Discussions

3.1 Mechanical Properties

The TS and EB of the plastics are presented in Table 2. The plastics prepared without starch and lignin (FC sample) has the highest TS and EB, i.e., 13.6 MPa and 347%, respectively. The FV sample was made with the same amount of glycerol by substituting 40% of PVA with starch and adding 10% of lignin to the PVA/starch blend. The TS and the EB of the resulting plastics were reduced to 8.5 MPa and 139%, respectively, meaning that adding starch lowers both the TS and EB. Similar results were reported by other researchers [12, 13]. Adding starch decreases hydrogen bonding density, thus lowering TS [12]. The FW sample has the highest amount of glycerol (60%). It has the lowest TS

and EB. Similar results were reported by other researchers. Excess glycerol in the mixture can weaken the intermolecular interaction of polymers, thereby reducing the TS [14, 15]. In addition, the processing temperature (230°C) and the shear speed of the rotor during processing could cause degradation of the polymer, which leads to a decrease in the mechanical properties [16, 17].

The addition of lignin increases the TS and EB. For example, increasing lignin content from 6% (FW sample) to 10% (FV sample) can increase the TS from 3.7 to 8.5 MPa, and EB from 108 to 139%. Baumberger et al. [18] reported that incorporating lignin into starch-based film increased both TS and EB. Hydroxyl groups in lignin make it interact with starch and PVA molecules through hydrogen bonds. It results in a rigid continuous three-dimensional network, resulting in films with higher TS [17, 18].

3.2 FTIR Spectra

The FTIR spectra of FC, FV, and FW samples are shown in Figure 1 and the identified functional groups are listed in Table 3. The band peaks of the OH group for FC, FV, and FW samples are observed at a wavenumber of 3352, 3330, and 3329 cm^{-1} , respectively. The peaks of the OH functional group for the FV and FW sample shift to lower wavenumbers than that of the FC sample. It could be related to new hydrogen bonds formed between PVA, starch, and lignin. It confirms that lignin and starch have compatibility in the PVA matrix [8, 19]. The other peaks have a similar pattern, except that a weak peak at 1592 cm^{-1} is observed in the spectrum of the FV sample. This peak is attributed to the aromatic C=C present in the molecular structure of lignin.

3.3 Water Absorption

Figure 2 presents the water absorption for FC, FV, and FW samples after storage at 23°C and 50% RH for seven days. Different water absorption values of the samples could be related to the composition. The FV sample has the lowest water absorption. It could be attributed to the lignin content, where the FV sample has the highest lignin content. Lignin is a natural polymer containing aliphatic and aromatic groups. It is amorphous and hydrophobic [20], so it could inhibit water molecules from penetrating the plastics. It also indicates good compatibility between lignin and the PVA/starch matrix. It makes a strong intermolecular interaction between lignin and the PVA/starch matrix, thereby reducing free absorption points for water molecules [21]. The FW sample has the highest water absorption, which can be related to glycerol content. The FW sample has the highest content of glycerol (60%). Glycerol is a small hydrophilic molecule that easily interacts with starch and PVA molecules. It fills the spaces between starch and PVA, making the distance between PVA/starch molecules longer [17]. As a result, water molecules can penetrate the plastics easier.

Table 1: The compositions and processing temperatures for plastics preparation

Sample	FC	FV	FW
PVA/starch ratio	100/0	60/40	60/40
Lignin (%)*	0	10	6
Glycerol (%)*	45.1	45.1	60
Temperature (°C)	197.6	197.6	230

* g/100 g of PVA and starch

Table 2: The mechanical properties of the plastics

Sample	TS (MPa)	EB (%)
FC	13.6	347
FV	8.5	139
FW	3.7	108

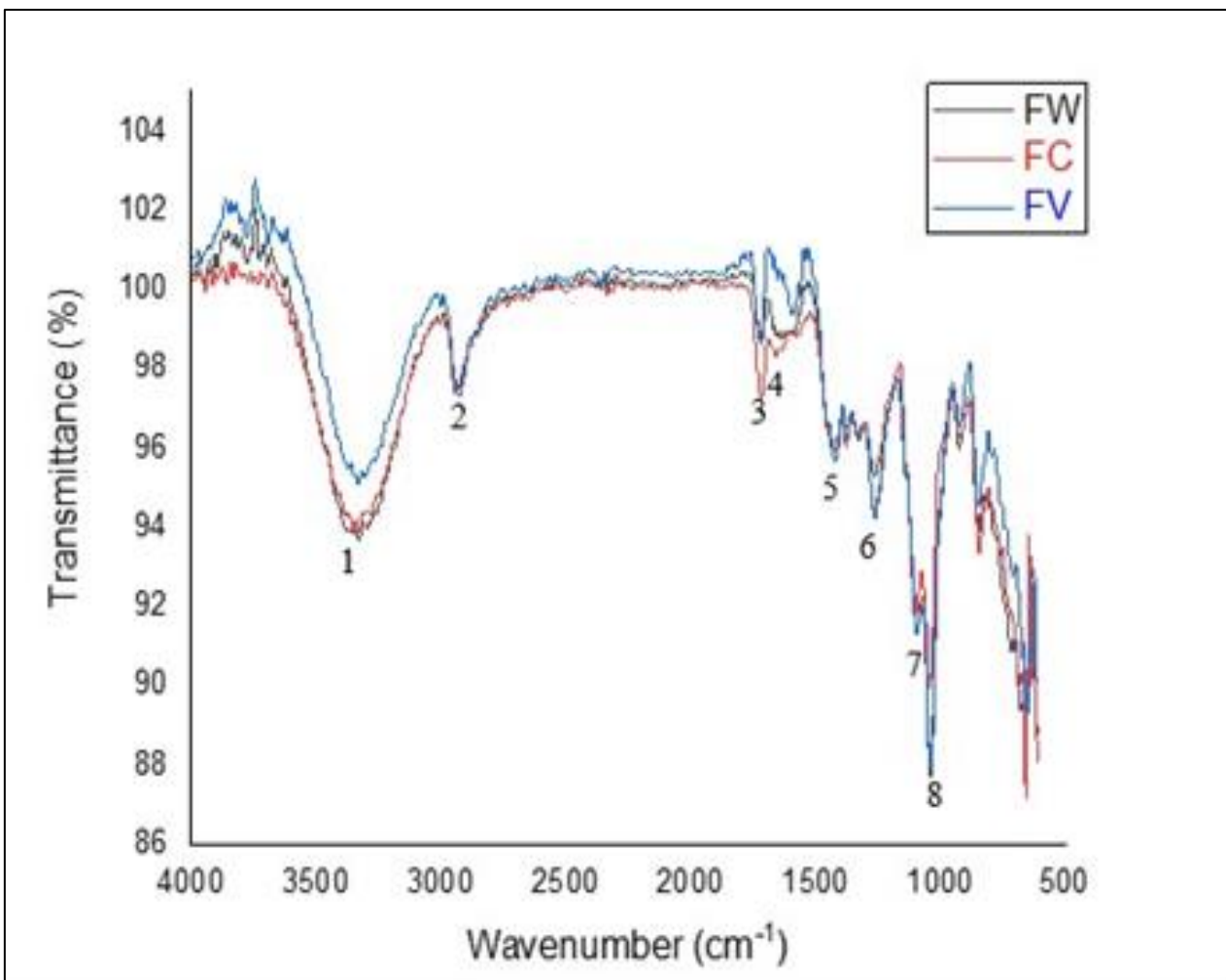


Figure 1: FTIR spectra of FC, FV, and FW samples

Table 3: Identification of FTIR spectra for FC, FW, and FV samples

Number	Wavenumber (cm ⁻¹)			Functional group
	FC	FV	FW	
1	3352	3330	3329	-OH
2	2926	2925	2926	-CH ₂
3	1717	1719	1718	C=O
4	-	1592	-	C=C
5	1422	1421	1421	O-H bend
6	1266	1262	1263	C-O
7	1096	1095	1095	C-O
8	1040	1041	1040	C-O

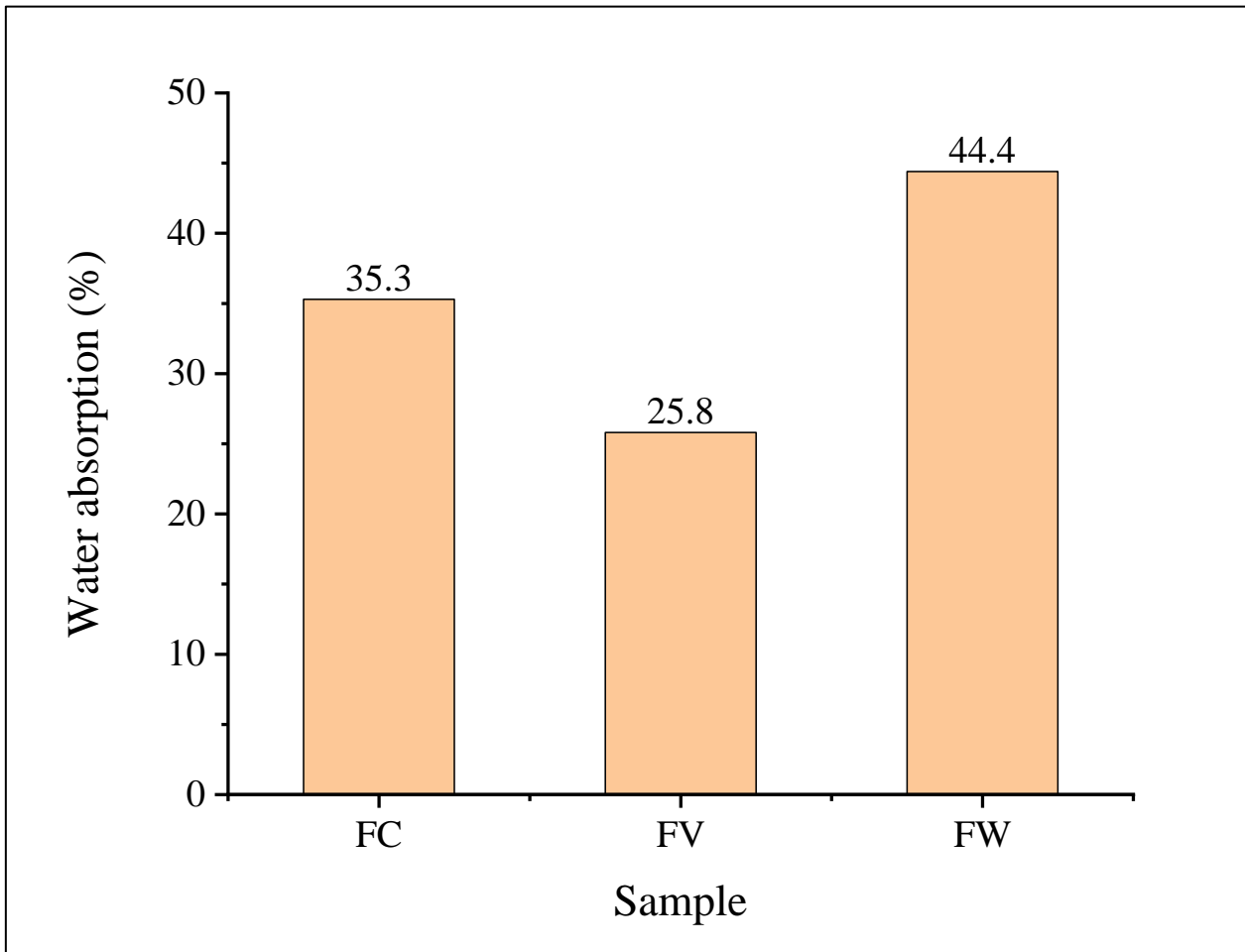


Figure 2: Water absorption of plastics samples

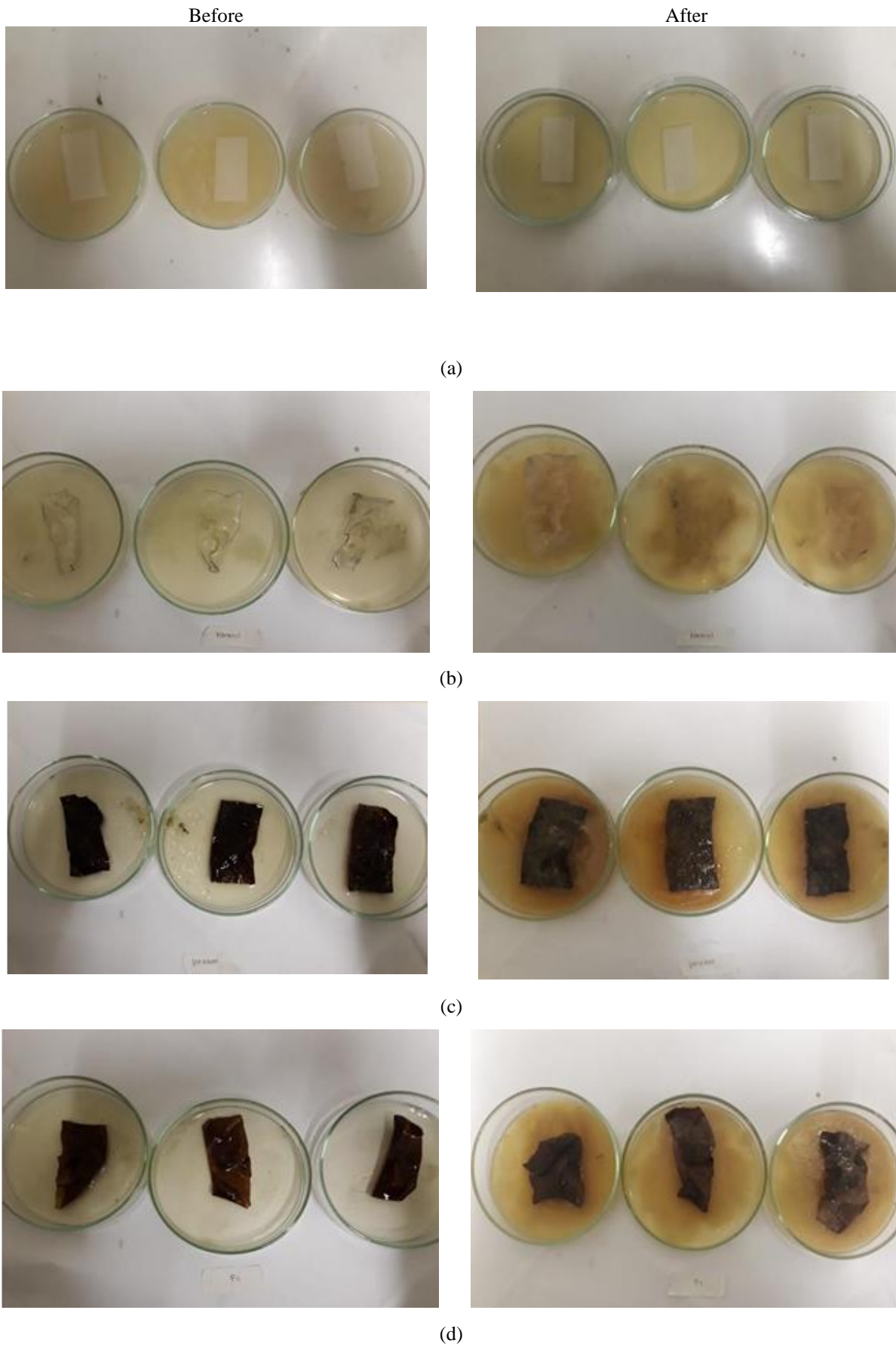


Figure 3. Biodegradation behavior of plastics before and after incubation for 7 days: (a) the non-biodegradable plastic sample, (b) the FC sample, (c) the FV sample, and (d) the FW sample.

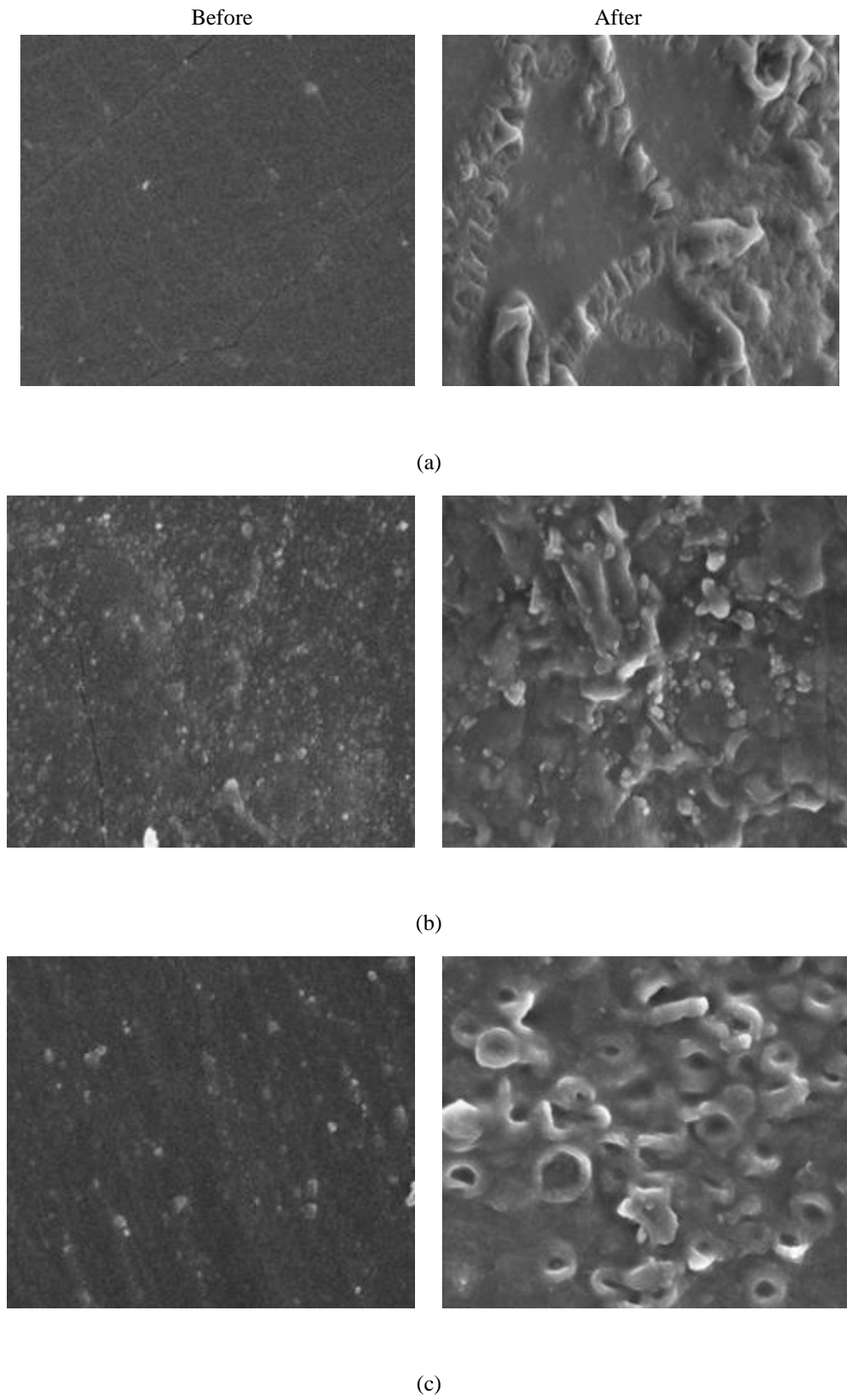


Figure 4: SEM images (magnification of 3000×) of plastics before and after incubation for 7 days: (a) FC sample, (b) FV sample, and (c) FW sample

3.4 Biodegradability

Figures 3(a)-(d) show the samples before and after seven days of incubation. This observation was carried out to determine the level of plastic degradation because of fungi. It is seen in Figure 3(a) that there is no difference observed on the surface of the non-biodegradable plastic sample before and after incubation. It means that fungi did not grow on the surface of non-biodegradable plastics. Figures 3(b)-(d) show the difference in the appearance of the surface of the samples before and after the incubation. It is because fungi grow and cover the surface of the plastic samples. The fungi grow the most on the surface of the FW sample, which indicates the highest biodegradation rate among others. Furthermore, the FW sample has the highest glycerol (60%) and mixing temperature (230°C). The more the amount of glycerol, the more amount of moisture can be absorbed by the plastics. Therefore, it made plastics more easily overgrown with fungi and degraded rapidly [22]. Furthermore, PVA and lignin may decompose at 230°C [17].

3.5 Surface morphology

The SEM images of the FC, FV, and FW samples before and after incubation with *Trichoderma sp.* for seven days are presented in Figures 4(a)-(c). The FC sample is the most homogeneous among others because it consists of only PVA and glycerol. On the other hand, the FV and FW samples containing starch and lignin show small lumps. It could be due to inhomogeneity during the mixing of the components of the plastics. Figures 4(a)-(c) show that the surface of all samples before incubation is rougher than before. After incubation, several holes were observed in all samples due to fungal growth [23]. Sample FW with the highest glycerol content has the most holes. As explained earlier, the FW sample has the highest water absorption making the sample retains more water than the other samples. Hence, more fungi grow on the surface of the FW sample, and the sample is faster to biodegrade.

4. Conclusions

Biodegradable plastics were made by blending PVA/starch/lignin with glycerol as a plasticizer. The blend was melted and compounded using an internal mixer and then pressed using a hot press molding machine for making films. The tensile strength, elongation at break, functional group, water absorption, and biodegradable property were analyzed. The results show that the sample prepared from merely PVA and glycerol has the highest tensile strength and elongation at break values. Adding starch and lignin decreases both tensile strength and elongation at break. The addition of lignin can reduce the water absorption of plastics. The plastic with the highest glycerol is faster to biodegrade. From functional groups analysis, it can also be seen that new hydrogen bonds formed in PVA or between PVA, starch, lignin, and glycerol.

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