Improving Degradation Ability of Composite Starch/Chitosan by Additional Pineapple Leaf Microfibers for Food Packaging Applications

I Mutmainna¹, D Tahirk*, P L Gareso¹, S Ilyas¹, A Saludung²

¹Department of Physics, Hasanuddin University, Makassar 90245 Indonesia
²Department of Civil and Environmental Engineering, Hiroshima University
1-4-1 Kagamiyama, Hiroshima, Japan

*Email: dtahir@fmipa.unhas.ac.id

Abstract. Structural, mechanical properties, and bonding characteristic of plastic bio-composites (starch/chitosan) with an additional Pineapple leaf microfibers (PLM) for 3%, 6% and 9% were carried out by using X-Ray diffraction (XRD), tensile strength test, and Fourier transform infra-red (FTIR) spectroscopy, respectively. The value of tensile strength shows highest for plastic bi-composite with 9% PLM and also XRD spectra shows the amorphous phase with new structure was formed for all bio-composite + PLM. FTIR spectra shows the strong bonding formation as the effect of PLM indicated by increase the intensity of C-H and C=C bond with increasing the amount of PLM. From the biodegradation test shows the PLM strongly influenced to the degradation ability of bio-composite and the highest is for 9% PLM (>80%). In addition, the lowest browning index is about 37.5% for bio-composite with additional 9% PLM which was determined by using fresh cherry (Muntingia calabura. L). It’s indicated that the plastic bio-composite with an additional PLM shows high potentials for new food packaging applications.

1. Introduction

Environmental problems are increase in every years and become a great concern, due to the increasing number of problems in every year. Environmental effect is the primary reason for the research and development of functional products based on natural resources [1]. Bioplastics are plastics developed from natural resources such as biomass materials from agricultural which were environmentally friendly [2].

Previous studies reported bioplastics based natural resources to form composite such as; PVA / chitosan [3], PVA / fiber pineapple [4-5], and gelatin / chitosan [6]. The focus of their research was about mechanical properties, biodegradation, the level of transparency, effect of temperature and other properties [7-8]. Based on these studies, the alternative base materials for bioplastics are starch, which is low prices, and easily decompose [9]. The disadvantages of bioplastics based on the starch are low mechanical properties, which can be overcome by the additional of chitosan and microfiber from the nature resources as reported in Ref. [10-11]. In Ref. [12] was reported, the bioplastic with addition (1% and 2%) chitosan, shows good mechanical properties [12].

In this study we have used starch and chitosan to form composites and additional Pineapple leaf microfiber (PLM) to increase the mechanical properties, strong bonding formation, and stable structural properties. These properties strongly influenced to the degradation ability, which was determined by using Texture Analyzer MCT - 2150, FTIR spectroscopy, and XRD spectroscopy, respectively. In addition we
determined also browning index and biodegradable test for measure the level of moisture and the biodegradation ability by microorganism, respectively.

2. Experimental Program

2.1 Materials
Glycerin (C₃H₈O₃) (molecular weight 92.09, boiling point 290°C) (Merck), acetic acid (CH₃COOH) with concentration of 6% (Merck), chitosan (molecular weight 200 Kda, particle size 200-300 mesh, viscosity 55.31 MPa.s, deacetylation rate 94.88%), corn starch (Merck), and aquades (Merck). The acetic acid was diluted from 6% to 1%.

2.2 Preparation of pineapple leaf microfiber
Pineapple leaf microfibers (PLM) are obtained from pineapple leaves by cutting in size of 15-20 cm and heated for 2 hours at 100°C until the color was changed and the leaves were cooled down to room temperature. The PLM were obtained by slicing the cooked pineapple leaves using a cutter. The microfibers were soaked with sodium hydroxide (NaOH) solution 1 Molar for 60 minutes and cleaned using distilled water, and then heated again at a temperature 70°C for 90 minute, the PLM ready for further use.

2.3 Bio-composite Sample Preparations
For characterization by XRD, FTIR spectroscopy, and biodegradation test, the prepared ratio bio-composite between starch and chitosan is 50% / 50% with additional PLM 3%, 6%, and 9%.. We prepare also for ratio of the bio-composites are 0/100, 45/55, 50/50, 55/45, 65/35 for comparison and for characterization of tensile strength. We have added the first solution by mixing the starch with glycerin and distilled water for 30 minutes stirring at 95°C and called starch solution, similar for the second solution but use chitosan mixed with 1% acetic acid, chitosan solution. Both solutions were mixed by using magnetic stirrer for 10 minutes to form composite. The PLM with different amount (3%, 6%, and 9%) was added into the composite solution. Finally, composite + PLM solution was formed and then heated at 120°C for 10 hours. For clearly illustration of synthesis process in this study is shown in Figure 1.

![Synthesis processes of the composite with additional pineapple leaf microfiber (PLM).](image-url)
2.4 Characterization
The X-Ray diffraction (XRD) was used for analyzing the structural properties, (Shimadzu 7000 X-ray diffraction) with CuKα radiation (λ = 1.5405 Å) for 2θ from 15 ° to 60 °, operates at 30 kV and 10 mA. The time for composite bioplastics to be decomposed was observed by stockpiling the sample under the ground for 3 days, 7 days, 14 days, and 30 days. All samples were weighted for initial weight of the samples and then weighted again after stockpiling the samples to determine the final weight. The bonding characteristics of the sample are determined by the FTIR spectroscopy and mechanical properties were investigated through tensile strength test. The degree of discoloration is determined by using testing the browning index of the fresh cherry (*Muntingia calabura* L). We have divided the fresh cherry into 4 groups with three groups are packaging with composite with different composition of starch / chitosan with 9% of PLM and one group used as a control. The weight and the index of browning of cherry are calculated after the 7th days packaged, this method similar reported in Ref. [3]. The color index was determined by following the quantity: 1 for no brownish, 2 for less than 1/4 brownish, 3 for less than 1/4 - 1/2 brownish, and 4 for more than 1/2 brownish. Browning index is calculated using the following formula:

\[
\text{Browning Index} = \frac{\sum (\text{browning scale} \times N_i)}{N} \quad (1)
\]

where \(N_i\) and \(N\) are the number of fruits at the level of maturity and the total number of fruits in the treatment, respectively [3].

3. Results and discussion

3.1 X-Ray Diffraction (XRD)
Figure 2 shows the XRD spectra of starch, chitosan, and bio-composite for starch/chitosan ratio is 50/50 with PLM 3%, 6%, and 9%.

Starch contain two components, first is amylose which has a linear chain structure and the second is amylopectin which has a branch chain structure [8]. The branch structure is the main contribution to form amorphous structures [13-16]. Chitosan also has a linear polymer chain structure, which is usually contributed to forms a crystalline phase by the connection each chains to form regularly polymer [16-17]. In Figure 2, diffractogram (A) shows the structure of starch material which is usually characteristics peaks of amorphous structure at 15° to 25°. Difractogram (B) shows chitosan material which shows more broad peaks at 25° to 35° and small sharp peak indicating the crystalline phase at 48° to 55°. The diffractogram C, D, and E are the XRD spectra for bio-composite (starch/chitosan: 50/50) with the addition of 3%, 6%, and 9% of PLM, respectively, which is similar with diffractogram (B) indicated strong effect of chitosan in the bio-composites.
Figure 2. X-ray Diffraction (XRD) spectra of starch (A), chitosan (B), bio-composite (Starch/Chitosan 50/50) with additional pineapple leaf microfiber (PLM) 3% (C), 6% (D), and 9% (E) in this study.

The main peak at 30° for bio-composite (starch/chitosan + PLM) is contributed from the starch and peak at around 20° from chitosan, diffraction peak at 34° is contributed from combination of chitosan and PLM and the broad peak at around 48° contributed only from PLM. From these diffraction peaks for composite (starch/chitosan + PLM) indicated the new structure was formed as the contribution from the each base materials.

3.2 Tensile Strength

Figure 3 shows the tensile strength for plastic bio-composites with additional PLM; 3%, 6% and 9%.

Figure 3 shows the additional of pineapple leaf microfiber was improved the tensile strength with highest values is 51,659 MPa for ratio composite starch/chitosan is 65/35 with PLM 9%. This result confirms that the pineapple leaf microfiber (PLM) play important role in increasing the tensile strength of composite bioplastics.
3.3 FTIR analysis
FTIR characterization was carried out to determine the bonding characteristics of the composites bioplastic with additional PLM 3%, 6%, and 9% for weight ratio of composite starch/chitosan is 50/50.

The FTIR spectrum from the previous study shows that the bonding formation is contribution from the constituent raw material [18]. Figure 4 shows the FTIR spectra with broad absorption peak at 3392 cm\(^{-1}\) indicated that the presence of hydroxyl groups in the bio-composites. The C-H bonding at wave number 2917 cm\(^{-1}\), and C=\(\text{C}\) bonding at 1645 cm\(^{-1}\) which is show the effect of PLM, and similar for C-H bonding at 1417 cm\(^{-1}\). C-O bonding was formed at 1051 cm\(^{-1}\), and another. C-H bonding were formed at 916 cm\(^{-1}\),
811 cm\(^{-1}\), and 761 cm\(^{-1}\), respectively. The absorption intensity of C=C and C-H bonding was increases with increasing the amount of PLM in composites indicated the strong bonding formation was formed. The C=C, and C-H, bonding may strong relation in increasing the mechanical strength and the degradation of bioplastic as reported in reference [19] for polymeric materials.

3.4 Biodegradation Test
The results of biodegradation test of bio-composite with additional PLM 3%, 6%, and 9% for 3, 7, 14 and 28 days as can be seen in Figure 5. The degradation ability as a function of time from 3 days to 28 days is clearly effective for high amount of PLM. Composite with 9% PLM show the higher percentage of degradation >80% for 28 days may due to the increasing of C=C and C-H bonding formation in plastics bio-composites. These results confirm that the addition of PLM is significantly affected to the decomposition process. Bioplastics degraded in the environment for the very short period of time probably due to the present of C = C and C-H bond as the effect of PLM which was also contributed to the mechanical properties and the browning index.

![Figure 5. Biodegradation test for composite bioplastic (Starch /Chitosan: 50/50) with additional PLM (3%, 6%, and 9%)](image)

3.5 Measurement Browning Index
We have used ratio of composite is 50/50% + 9% PLM and also for ratio 50/50, 55/45 and 65/35 for comparison in determining the browning index in this study. The decreasing weight and the discoloration of the cherry (*Muntingia calabura*) fruit were observed after 7 days of packaging. For comparison, we used the data control from fruit without packaging.
Table 1. Browning index of composite bioplastic for composition 50/50, we have included compositions 55/45 and 65/35 with 9% PLM for comparison.

| Bio-composite + PLM 9% | Weight Loss (%) | Browning Index (%) |
|------------------------|-----------------|--------------------|
| Control                | 0.540 ± 0.01    | 100                |
| Starch/Cs (55/45)      | 0.472 ± 0.01    | 75                 |
| Starch/Cs (50/50)      | 0.472 ± 0.01    | 75                 |
| Starch/Cs (65/35)      | 0.417 ± 0.01    | 37.5               |

The browning test is used to ensure plastics bio-composite in this study have a good influence for food preservation. In Table 1 shows that the decreasing weight loss of fruit is smaller than that of the fruit control. Browning index shows that bioplastics for ratio 50/50 + 9% PLM is same for the ratio composition is 55/45 and the lowest browning index is for 65/35 due to the highest amount of starch. As reported in Ref. [3] for low moisture permeability on plastics indicated by the low browning index is very good for food packaging applications. In Ref. [20] also reported that the pore formation is decrease which was consistent with decreasing the humidity levels and also decreasing the browning index [3]. The environmental from the outside are also influenced to the humidity levels when the bioplastic applied for food packaging. Low moisture and low humidity levels correlated with low browning index in this study may due to the effect of amount of PLM in the bio-composite due to the strong bonding formation of C = C, and C-H bond.

4. Conclusion

Composite starch/chitosan with the additional Pineapple leaf microfiber has been studied by using FTIR, tensile strength, and XRD for analyzing bonding characteristics, mechanical properties, and structural properties, respectively. The diffraction peak from XRD for composite (starch/chitosan + PLM) shows the new structure was formed as the contribution from the each base materials. FTIR analysis shows the strong bonding formation was formed in bioplastics. Formation are C = C and C-H which was increases with increasing the amount of PLM in composites. Based on the biodegradation test, composites with 9% PLM shows the higher percentage of degradation >80% for 28 days. These results confirm new composite with additional of PLM significantly affect to the decomposition process, contributed to increase the mechanical properties and decrease browning index as an alternative healthy food packaging to maintain freshness.

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