Comparative Production of Bioplastics from the Waste Newspaper with Rice Starch and Polyvinyl Alcohol Rice Starch

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Abstract

Recently, environmental problem caused by petroleum–based plastics has been increasing. For this reason, researchers have been focusing on the utilization of the wastes as bioplastics products. In this study, the bioplastics was produced from waste newspaper by casting method. Some properties of the produced bioplastics such as water absorption capacity and biodegradability were analyzed. And then, the physico-mechanical properties, the functional group, the thermal stability and the morphological structure of prepared bioplastics were identified by Fourier Transform Infrared (FT.IR) Spectroscopy. Thermo Gravimetric Differential Thermal Analysis (TG-DTA) and Scanning Electron Microscopy (SEM).

Keywords: Bioplastics, Absorption capacity, Biodegradability, Scanning Electron Microscopy

Introduction

Plastics are more useful than metals, papers, and other materials because of their properties such as lightness, cheapness and durability. Therefore, they are used in almost every industrial field. The whole world, even the oceans, is full of plastic wastes. It is said that, the plastics industry causes economic and environmental problems.

It was known that plastics are not biodegradable and it can remain in the environment for hundreds of years. These environmental concerns have led to the development of the green materials, such as bioplastics, in recent years. In many countries, bioplastics are mostly used as cutlery, diapers, packing material etc, in many industrial areas. Therefore, it is thought that the future of bioplastics shows great potential. Nevertheless, the cost of the bioplastics produced from microbial resources is still higher than produced from renewable resources. For this reason, most of bioplastics manufactures have focused on the producing via renewable resources. In this study, the overall purpose was to investigate the utilization of the waste newspaper in bioplasics production. To achieve this objective, the production of bioplastics from waste newspaper was investigated. In addition, some properties of the produced bioplastics such as water absorption capacity biodegradability, physico-mechanical properties, thermal properties and morphological were analyzed (Ezgi Bezirhan Arikan & H . Duygu Bilgen. ,2019)

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Materials and Methods

Materials and Equipments

The materials used in this study were waste newspaper, glycerol, hydrochloric acid, sodium hydroxide and rice starch, polyvinyl alcohol. The tools used in this research were glassware, hotplate, blender and magnetic stirrer, FEI Quanta 250, USA (SEM), Perkin Elmer (FT-IR) spectrophotometer, NSK micrometer and DTG-60, Shimadzu, Japan (TG-DTA).

Methods

Preparation of Waste Newspaper Pulp

The waste newspaper (10g) was cut in small pieces and added enough water (100L). This mixture was boiled for 15 min and filtered the solution. Then it was blended until it became mush. The wet waste newspaper pulp was obtained and it was ready for use as a bioplastic feedstock.

Extraction of Starch

The extraction of the starch from rice was done manually. First, 100g rice was washed and boiled with water for an hour. Rice was ground in a motor with 100 ml purified water. The mixture was filtered and the remaining solid mass was put into the motor. This procedure was repeated five times and more starch was obtained. The blend was allowed to settle in the beaker for 5 min. Then, 100 ml of purified water was added and was agitated softly. The water was removed after repeating the above process 3-4 times and the starch, white in color, was obtained. (Ammar & Hemini. , 2018)

Qualitative Iodine Test for Starch

Iodine (3.0g) and potassium iodine (93.0g) were ground and the mixture was dissolved in 60ml of distilled water. The solution was diluted to 100ml with distilled water in a volumetric flask. The prepared rice powder was qualitatively examined by iodine staining method. Rice powder(1g) was added into a beaker containing 10ml of boiled distilled water and then boiled for 10 minutes. The solution was cooled down to room temperature. Two drops of iodine solution was added in the solution. The color changes were examined. (Bemiller, 1986)

Figure1. Rice starch powder Figure 2.Color development of iodine test for rice starch

Bioplastic Production

Bioplastic production was performed by weighing wet waste newspaper pulp (2.5g) and rice starch (2.5g). Distilled water (50ml), HCl (3ml), NaOH (3ml) and glycerol (3ml) were added to the wet waste newspaper pulp. This mixture was heated on a hotplate till to (60-65 ºC) and kept waiting at the temperature for 20 min while stirring with a magnetic stirrer. After the sample begins to form the gel, the sample put into Petri dish and dry to air for about 48h and plastic films were obtained. The PVA blended bioplastics was produced similarly as the above procedure. (Ezgi Bezirhan Arikan & H. Duygu Bilgen. , 2019)

(a) (b)

Figure 3. Bioplastics of (a) rice starch PVA newspaper waste (b) rice starch newspaper waste

Measurements of Water Absorption

Bioplastics having the same surface-area and weight were dried in an oven at 50 ºC for 24h and cooled in a desiccator before weighing. Bioplastics were submerged in distilled water at 25 °C. For the determining of water –soluble content of the sample during soaking the sample was dried at 50 ºC for 24 h. At the end of 24 h, sample was weighed again and weight loss of the sample was calculated. The sum of the weight again following soaking plus the weight loss after drying is defined as the total absorbed water. All water absorption measurements were performed in three replications.

Biodegradability Analysis

The biodegradability of sample was investigated in different controlled environments. After weighing the sample was buried in soil for one month. Bioplastics samples, whose initial masses were known, were weighed after burying weekly. All experiments were performed in three replications. Biodegradation is a degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of a material. Also, the weight loss measurement is a standard method for biodegradation of polymer. Amount of biodegradation was calculated by the following equation.

$$WL (\%) = (W_0 - W) / W0 \times 100$$

W_0 and W are the initial and final weight of bioplastic samples, respectively. Also WL refer to the weight Loss. (Ezgi Bezirhan Arikan & H. Duygu Bilgen., 2019)

Determination of Physico-Mechanical Properties of Prepared Bioplastics

Determination of Thickness

Thickness of the prepared newspaper waste bioplastics was measured by using NSK micrometer. The thickness of the blended bioplastics was measured at five locations (center and 4 corners) using, micrometer. (Chandra, 1995 and website 1)

Determination of Tensile Strength and Percent Elongation at Break

Dog bone shaped test specimens were cut from the prepared bioplastic. Both ends of the test pieces were firmly clamped in the jaw of the test machine. One jaw was fixed and the other was moveable. The rate of moveable jaw was hold 100mm/min. The recorder of the machine showed the tensile strength in Mpa. This procedure for tensile strength was repeated for three times. (website 2)

Tensile strength (MPa) = Loaded Weight (N)/ Cross sectional area (mm^2)

Elongation at break (%) = (L x100)/L

Where, ΔL=Different Length, L= Original Length

Determination of Tear Strength

Test specimen was cut off by a die from the above prepared bioplastics. Specimen was cut with a single nick mm) at the entire of the inner concave edge by a special cutting device using a razor blade. The clamping of the specimen in the jaw of test machine was aligned with travel direction of the grip in 100mm/min. The recorder of the machine was shown the highest force to tear from a specimen nicked. The recorder of the machine was shown the highest force to tear from a specimen nicked. The procedure was done in triplicate. Tear strength can be calculated according to the formula. (Long –Cheng Tang & Jin Ping Peng , 2019)

Tear strength = (kN/m) = Force at break /Thickness

Functional Groups Identification of Prepared Bioplastics

FT- IR spectra of prepared bioplastics were measured at the Department of Chemistry in Monywa University. The prepared bioplastics was analyzed using Perkin Elmer RX1 FT-IR spectrophotometer. The FT-IR spectrum of the samples were obtained at the wavelength in the range 450-4000cm^{-1}.

Thermo Gravimetric-Differential Thermal Analysis (TG-DTA) and Examination of Surface Morphology of Prepared Bioplastics

Thermo Gravimetric-Differential Thermal Analysis and Surface Morphology of prepared bioplastics were measured at the Department of Chemistry in Yadanabon University.TG-DTA (DTG-6OH) thermal analyzer, Shimadzu, Japan and Scanning electron microscope (Quanta 250, Thermo

Fisher Scientific, USA) were employed. TG-DTA thermograph and SEM images were obtained by using Aluminum as reference and photographed at 1000X magnification. The measurements thermograph were carried out at a heating rate of 20.0 $kJmin^{-1}$ and were run at 36.48 ℃ to 600.92 ℃. (M.E. Brown, 2007 & Bangwei Zhang, 2016)

Results and Discussion

Results of the Water Absorption Capacity and Biodegradability of Prepared Bioplastics

Results of the water absorption capacity and biodegradability of prepared bioplastics were shown in Table1 and Table2.

Table 1. Results for Water Absorption Capacity of prepared Bioplastics

No	Bioplastics	Results
1	Newspaper waste-rice starch based bioplastics	78.5%
2	Newspaper waste -PVA-rice starch based bioplastics	63.7%

Table 2. Results for Biodegradability of Prepared Bioplastis

No	Bioplastics	Results
1	Newspaper waste-rice starch based bioplastics	85.3%
2	Newspaper waste -PVA-rice starch based bioplastics	45.6%

According to table1 and table 2, the rice starch based bioplastics gave the higher value then the PVA- rice starch based bioplastics.

Figure 4 .Newspaper waste-rice starch

Figure 5.Newspaper waste -PVA-rice starch

Results of Physico –mechanical properties of Prepared Bioplastics

Physico-mechanical properties, such as, thickness, tensile strength, elongation at break and tear strength of prepared bioplastics were investigated. These results were described in Table 3 and Figure 4.

Table 3. Physico-Mechanical Properties of Prepared Bioplastics

□	Rice Starch Bioplastics	Rice starch –PVA Blended Biopiastic
Thickness(mm)	0.20	0.20
Tensile Strength (MPa)	3.7	1.33
Elongation at break (%)	35	20
Tear Strength (kN/m)	20.8	11.5

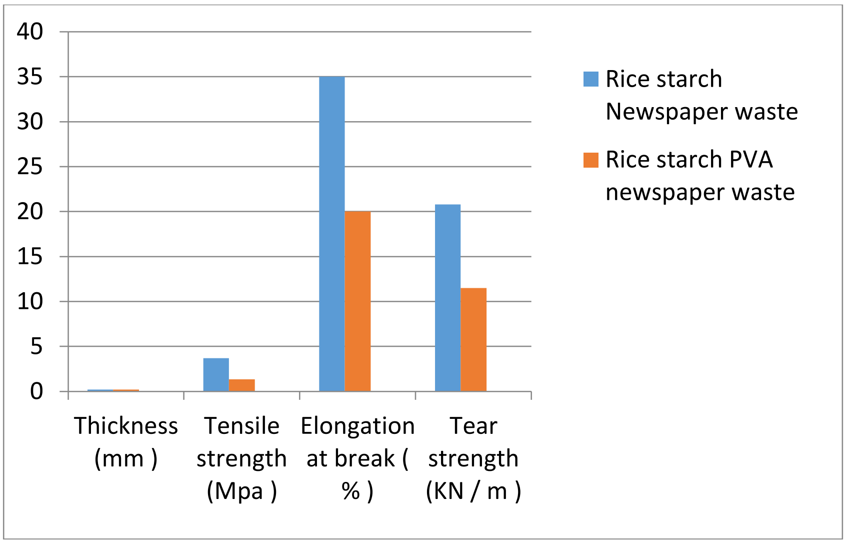
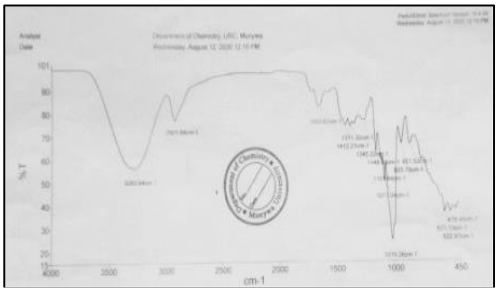


Figure 6 . Histogram of physico-mechanical properties of rice starch –PVA blended bioplastics.

According to this table, newspaper waste rice starch bioplastics gave the highest values than the newspaper waste rice starch PVA blended bioplastics. Because,the addition of PVA into the cellulose based bioplastics to decrease mechanical properties and moisture sensitivity.

Characterization of Blended Bioplastics by FT-IR

FT-IR spectra were measured at Department of Chemistry in Monywa University. The resulting functional groups of blended bioplastics were described in Table 6 and Figure 5.



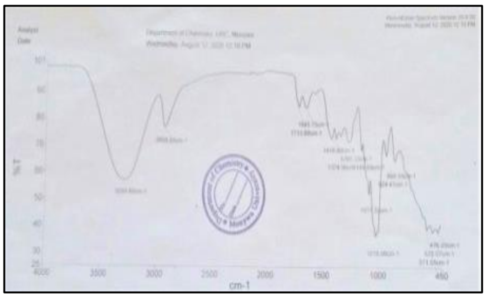


Figure 7.FT-IR spectra of rice starch based bioplastics and PVA blended starch based bioplastics

In accordance with the FT –IR spectrum of blended bioplastics, the band which appear at 3293.84cm^{-1}and 3293. 80cm^{-1} shows the O-H stretching vibration of hydroxyl group. The peak at 2925.68 cm^{-1}and 2935.22cm^{-1} are due to asymmetric and symmetric stretching vibration of sp^{3} hydrocarbons. In addition, the band which appears at 1650.67cm^{-1} and 1645.75cm^{-1} are –OH bending vibration of water. C-H in plane bending vibration of hydrocarbon indicates at 1412.21cm^{-1}and 1416.60cm^{-1}. The peak at 1245.22cm^{-1} and 1260.33cm^{-1} showed C-O stretching vibration of C-OH groups. This spectrum also represent the C-O-C stretching vibrations at 1000-1110cm^{-1}. The peak at 925.70cm^{-1} and 924.47cm^{-1} illustrates C-O stretching vibration of glycosidic bonds.

Table 4 .FT-IR Assignments of Rice Starch Based of Prepared Bioplastics

No	Wave number(cm^{-1})	Remarks
1	3293.84, 3293.80	O-H stretching vibration of alcohol group
2	2925.68 ,2935.22	Asymmetric and symmetric stretching frequency of sp^3 hydrocarbon
3	1650.67 , 1645.75	-OH bending vibration of water
4	1412.21 , 1416.60	C-H bending vibration of CH_2
5	1245.22 , 1260.33	C-O stretching vibration
6	1077.04 , 1077.33	C-O stretching vibration in C-OH
7	925.70 ,924.47	C-O stretching vibration in glycosidic bond

Results of Thermo Gravimetric –Differential Thermal Analysis (TG-DTA) of Prepared Bioplastics

TG-DTA has been done for all the samples to understand the thermal stability and its behavior at high temperature. The bioplastics with and without PVA undergo three steps and two steps degradation. The results are tabulated in Table 5,6 and Figure 7.These results generally confirm to thermal degradation events of most starch based films. Maximum amount of weight loss has occurred in the first step of degradation. The mass loss at this stage can be due to the removal of surface water in the bioplastics and degradation of polymer. The second stage of the thermal degradation at 317.28 °C, and313.17 °C the weight losses correspond to complete evaporation of polymer. The third stage of thermal degradation of bioplastics occurred at 411.09 ºC. The weight loss in this temperature range corresponds to complete degradation of saccharide ring. Moreover, the weight losses based on initial weights of the bioplastics were observed as 17.48%, 5.72%, 5.38% and 12.51 %,7.84% respectively.

Table 5 . TG-DTA Thermograph of rice starch based bioplastics

No	Peak nature	Initial Weight(mg)	Loss in Weight(mg)	Weight loss (%)
1	Small and broad exothermic peak at 148.92 °C	2.969	0.519	17.48
2	Very long and sharp exothermic peak at 317.28 °C	1.03	0.17	5.72
3	Small exothermic peak at 411.09 °C	0.86	0.16	5.38

Table 6. TG-DTA Thermograph of PVA blended starch based bioplastics

No	Peak nature	Initial Weight(mg)	Loss in Weight(mg)	Weight loss (%)
1	Small and broad exothermic peak at 219.63°C	2.549	0.319	12.51
2	Very long and sharp exothermic peak at 313.17°C	1.00	0.20	7.84

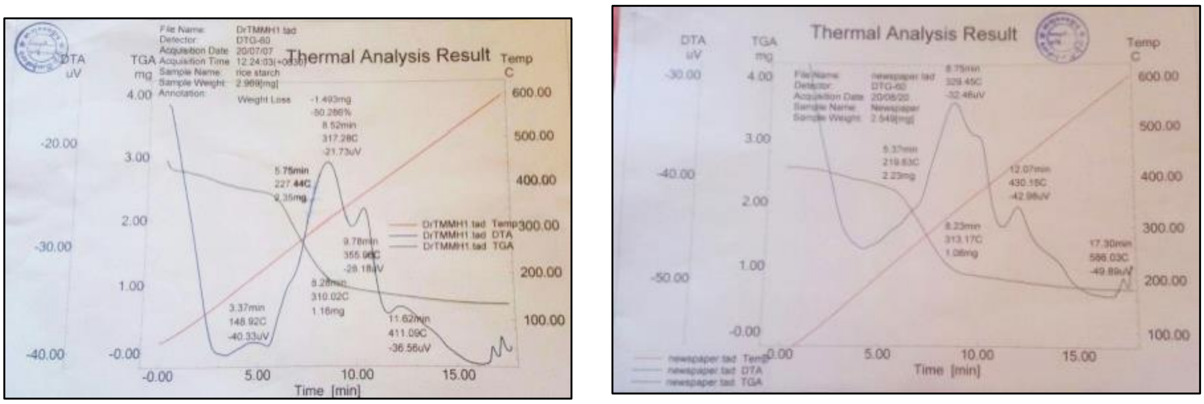


Figure 8. TG-DTA Thermograph of rice starch based bioplastics and PVA blended starch based bioplastics

Results of Surface Morphology of Blended Bioplastics

SEM images of starch based PVA blended bioplastics were shown in figure 9 and figure 10. Based on the SEM images, it was found that the surface of the bioplastics were found to be uniform, homogenous and smooth without any cracks and pores.

Figure 9.SEM Images of rice starch based bioplastics and PVA blended starch based bioplastics

Conclusion

A courting to the results, it was found that the newspaper wastes could be used for bioplastics production. In the study of water absorption capacity and biodegradability of bioplastics from waste newspaper were analyzed. The water absorption capacities of rice starch based bioplastics and polyvinyl alcohol rice starch base bioplastic were found to be 78.5% and 63.7% respectively. The biodegradability of rice starch based bioplastics was found to be 85.3% and that of polyvinyl alcohol rice starch based bioplastics was 45.65%.

And then, the physico mechanical properties of rice starch based bioplastics gave higher value than the PVA blended bioplastics. Moreover, the functional groups identification of blended bioplastics were identified by FT–IR spectroscopic method. All prepared bioplastics contains alcohol group, sp^3 hydrocarbons, asymmetric and symmetric deformation glycosidic bond respectively.

From the TG-DTA analysis, the blended bioplastics gave the highest weight loss at about 148.92°C of rice starch base bioplastics and 219.63°C of PVA rice starch based bioplastics. The SEM images of blended bioplastics were uniform and homogeneous. Therefore, the higher contents water absorption capacity of bioplastics cannot be used in the food service industry but can be used as packing materials. Thus, paper waste newspaper can be used in bioplastics production. In this way, petroleum-based plastic pollution of the environment might be decreased.

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