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PREPARATION OF WHITE STICKY RICE STARCH-CLAY NANOCOMPOSITE FILMS AND ITS APPLICATION

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Abstract

Plastic materials are not easily degradable and produce hazardous waste, causing environmental problem. In order to solve this problem, the uses of biodegradable polymers from renewable sources were generated. In this study, polymer films of polyvinyl alcohol (PVA)–white sticky rice starch were prepared by casting method. White sticky rice starch was extracted from white sticky rice grains collected from Myothit Township, Magway Region, and yield percentage was 64 %. Physicochemical properties such as pH, moisture percent, true density and bulk density and porosity of sticky rice starch were determined as 7.10, 10.51 %, 3.85 g mL^{-1}, 2.41 g mL^{-1} and 37.50 %, respectively. Semi-crystalline nature of the sticky rice starch with the average crystallite size of 51.65 nm was shown by XRD. Nanoclay was prepared from volcanic mud of Nagarpwak Taung in Minbu Township, Magway Region and the crystallite size was 30.79 nm. Nanocomposite films of PVA – starch – clay- glycerol were prepared by varying the ratios of nanostarch and nanoclay, i.e., 50:50 and 75:25. PVA – starch – clay- glycerol (75:25) film was found to have more flexible and plasticizing effect than the film with the ratio of 50:50. Biodegradability of these films was tested by soil burial method and the film with nanostarch and nanoclay with the ratio of 75:25 completely degraded after 18 days. For fruit coating application tomato fruits were dipped in prepared nanocomposite film and the tomato fruits were still fresh after 25 days compared to 8 days of non-coated tomato fruit.

Keywords: White sticky rice starch, clay, nanocomposite films, polyvinyl alcohol

Introduction

Plastics are widely used packaging materials for food and non-food products due to desirable material properties and low cost. However, the merits of plastic packaging have been overshadowed by its non-degradable nature, thereby leading to waste disposal problems. The public is also gradually coming around to perceive plastic packaging as something that uses up valuable and scarce non-renewable natural resources like petroleum. Moreover, the production of plastics is relatively energy intensive and it results in the release of large quantities of carbon dioxide as a by-product, which is often believed to cause, or at least contribute to global warming. Some recent research findings have also linked plastic packaging to some forms of cancer (El Amin, 2005; Kirsch, 2005). In order to solve problems generated by plastic waste many efforts have been done to obtain an environmental friendly material. Most of the researches are focused on substitute starch - based plastics by biodegradable materials with similar properties (Cyras *et al.*, 2008). Starch is known to be completely biodegradable in soil and water, and due to its cheap sources is one of the best candidates for replacing current synthetic plastics including packaging materials (Park *et al.*, 2003).

Packaging materials based on polymers that are derived from renewable sources may be a solution to the above problems. Such polymers include naturally existing proteins, cellulose, starches, and other polysaccharides, with or without modifications. These renewable polymers are not only important in the context of petroleum scarcity, but are also generally biodegradable under normal environmental conditions. Interest and research activity in the area of biopolymer packaging films have been especially intensive over the past 10 years (Krochta *et al.*, 1997; Tharanathan, 2003).

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Materials and Methods

Extraction of Starch from Sticky Rice (White) Grain

The sticky rice (white) grains were collected from Myothit Township, Magway Region. Starch was extracted from sticky rice (white) grains. White sticky rice powders (200 g) were ground and the powder was passed through 250 mesh screen. Distilled water (250 mL) was added to the powder, stirred manually for 30 min and allowed to settle overnight. The supernatant was decanted off and this starch was subjected to a second washing and settled overnight. The supernatant was then decanted off and filtered through a double-layered cotton cloth. Then the starch obtained was dried in air for 48 h at room temperature. The starch lumps were powdered before it was stored in polyethene bag prior before use and the yield percent of sticky rice (white) starch powder was calculated. The yield percentage of starch powder was found to be 74.00 %.

Determination of Some Physicochemical Properties of Sticky Rice (White) Starch pH

Sticky rice (white) starch (1.0 g) was made into mucilage with 100 mL of distilled water and it was determined for pH with a pH meter (Oyster-15), which was previously calibrated with standard buffers of pH 4 and 7.

Moisture content

Moisture content of the white sticky rice sample was determined by using moisture analyzer (USA, MB-23) at Research Center, Magway University.

True density

The true density (D_t) of sticky rice (white) starch powder was determined by the liquid displacement method using xylene as the immersion fluid (Hasan *et al.*, 2014). Density bottle (10 mL) was filled with xylene solvent and then weighed and recorded. Sticky rice (white) starch powder (2 g) was added into the above bottle and weighed and recorded. True density of sticky rice (white) starch was calculated by the following formula:

$$D_t = \frac{W_p}{\left[\left(a + W_p\right) - b\right]} \times SG$$

where, D_t = true density

W_p = the weight of starch powder

SG = specific gravity of solvent (xylene, 0.962)

a = weight of bottle and solvent

b = weight of bottle, solvent and starch powder.

Bulk density

A clean dry 10 mL graduated cylinder was weighed. It was then filled with the dry white sticky rice sample to the 10 mL mark and reweighed. The graduated cylinder was placed in a tapping box and the cylinder was tapped gently until there is no more reduction in volume. The minimum volume was recorded and the bulk density was calculated.

$$\text{Density} = \frac{\text{Weight of sample (g) x 6.24}}{\text{Final volume of sample (mL)}}$$

Porosity

The porosity is related to the true density and bulk density. So, the porosity of starch was calculated by the method of Ohwoavworhua *et al*. (2007) as:

$$\text{Porosity} = \left(1-\frac{\text{bulk density}}{\text{true density}}\right) \text{x } 100$$

Preparation of Starch Nanoparticles

Starch nanoparticles were prepared by hydrolyzing starch with H_2SO_4.The prepared starch powder of white sticky rice was suspended in 3 M H_2SO_4 at a concentration of 5% (w/v) and incubated in a shaker at 37°C and 100 rpm for 5 days. Then, the resultant solution was filtered using Whatman filter paper. The obtained H_2SO_4 hydrolyzed starch nanoparticles were dried at 60°C to constant weight.

Extraction of Nanoclay from Volcanic Mud

Nanoclay was extracted from volcanic mud of Nagarpwak Taung in Minbu Township. Firstly, 60 g of volcanic mud are placed into the first plastic container. Next, 8.4 L of distilled water was poured into the container. After keeping still a mixture of volcanic mud and water for 24 h, the mixture was stirred for 20 min and became liquid along with some solid precipitate. The mixture was then kept still for 48 h and precipitate was found at bottom of the first container. The liquid of the first plastic container was decanted into the second plastic container. The liquid was kept still in the second plastic container for 7 days, and precipitate was found at the bottom of the second container. The liquid of the second plastic container was decanted into the third plastic container. After 2 L of the liquid was taken from the third plastic container, the liquid was baked and heated on sand-bath. Then the remaining liquids were dried in an oven at 250 ^{o}C for 48 h and dried nanoclays were ground up to be powder.

Characterization of Nanostarch and Nanoclay

Surface morphology of nanostarch and nanoclay were examined by Scanning electron microscope (SEM), EVO– 18, ZEISS, Germany at Research Center, Magway University and structural property by XRD at Universities' Research Center, Yangon.

Preparation of Film

PVA-starch was taken in water in different composition (50:50 v/v and 75:25 v/v). The reaction mixture was stirred at 70ºC and 100 rpm until uniformity appeared. After cooling the solution at 35 ºC, all the solutions are mixed and modified with 30 % glycerol. A specified amount of Nano Clay (0.3 % by wt. of PVA-starch) was dissolved in the PVA-starch solution. The starch solution containing the clay was stirred at 70 °C and 100 rpm, held at that temperature for 20 min and then cooled to 50 °C. Then the solutions were poured into casting mold and dried in the oven at 75ºC to remove water contents. After complete drying, the films were stored in moisture free environment.

Investigation of Biodegradability of Films by Soil Burial Test

The biodegradability of the prepared PVA and PVA - starch - clay - glycerol films were investigated by soil-burial test. Firstly, composted soil under tamarind tree was collected and put into the different plastic boxes. The films (4″ × 6″ dimensions) were layered on the soil and then the films were covered with the same soil, the depth being 10 cm. The boxes were placed in the laboratory and the moisture of the soil was maintained by sprinkling water at regular time intervals. The excess water was drained through a hole at the bottom of the box. The degradation of the samples was determined at regular time intervals (4 days) by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film. They were taken out from the soil at an interval of 4 days until entirely degraded. Sample geometry on degradation was also recorded by photograph.

Study on Food Coating of Tomato Fruits

PVA-starch-clay-glycerol (75:25) mixture solution was prepared. Then tomato fruits were dipped in this solution for film coating and kept at room temperature. For control, these fruits were not treated with the PVA-starch-clay-glycerol mixture solution. The appearances of the fruits were observed daily.

Results and Discussion

Physicochemical Properties of White Sticky Rice

The physicochemical properties such as pH, moisture percent, true density and bulk density of white sticky rice starch were 7.1, 10.51 %, 3.85 gmL^{-1} and 2.41 gmL^{-1}, respectively. Porosity of starch was calculated to be 37.50 %. All data are shown in Table 1.

Table 1 Physicochemical Properties of White Sticky Rice Starch

No.	Parameter	Experimental values
1	pH	7.10
2	Moisture content (%)	10.51
3	True density (g mL^{-1})	3.85
4	Bulk density (g mL^{-1})	2.41
5	Porosity (%)	37.50

Characterization of Nanostarch and Nanoclay

Scanning electron microscopic (SEM) analysis of nanostarch

The surface morphology of nanostarch sample was examined by SEM micrograph as described in Figure 1. The sample was observed as polygonal shape for the starch granules with ununiform sizes.

X-Ray Powder diffraction studies on nanostarch

XRD pattern (Figure 2) of sticky rice starch shows strong diffraction peaks at 16.5°, 21.0°, and 23.09° of 2θ. For the presence both sharp and diffuse diffraction in this XRD, sticky rice starch was observed to have semi-crystalline nature. Parallel double amylopectin molecules result in the formation of crystalline regions, while amylose molecules result in the formation of amorphous regions in the starch structure. The average crystallite size of nanostarch sample was calculated based on Sherrer formula and it was found to be 51.65 nm.

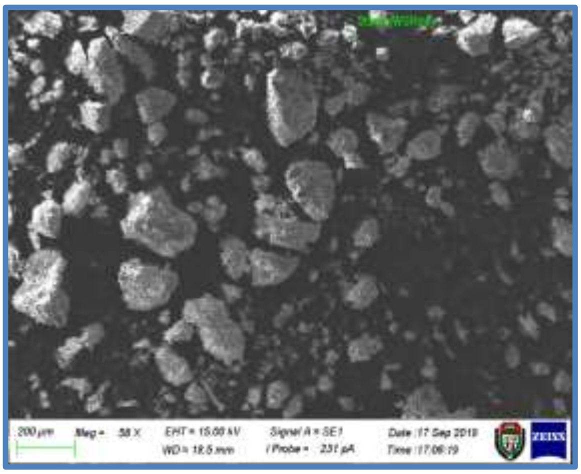


Figure 1 Scanning electron micrograph of nanostarch from white sticky rice

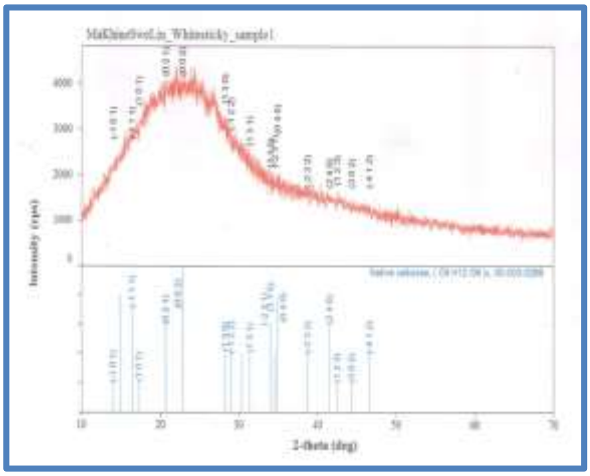


Figure 2 X-ray diffractogram of nanostarch from white sticky rice

Scanning electron microscopic (SEM) analysis of nanoclay

Nanoclay was extracted from volcanic mud of Nagarpwak Taung in Minbu Township. The surface morphology of nanoclay sample was examined by SEM micrograph as shown in Figures 3. From SEM micrograph, the sample was disordered pore system.

X-Ray powder diffraction studies on nanoclay

Crystalline nature of nanoclay was observed in X-ray powder diffractogram (Figure 4) because of the presence of sharp peaks. Nano - clay sample showed strong diffraction peaks at 12.45°, 18.72°, 20.79°, 25.12°, 26.57°, 31.63° and 45.40° of 2θ. The average crystallite size of nanoclay was determined from XRD pattern by using Scherrer equation. The average crystallite size of nanoclay was 30.79 nm.

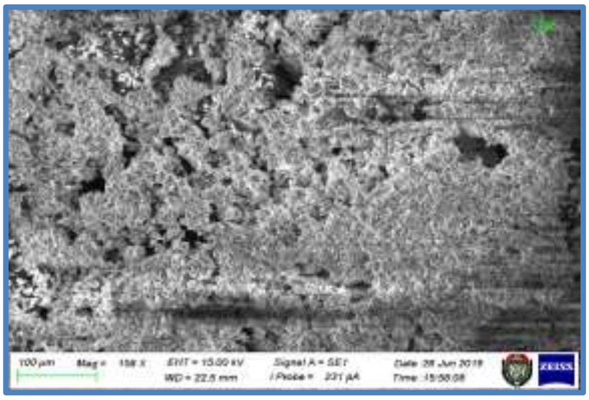


Figure 3 Scanning electron micrograph of nanoclay

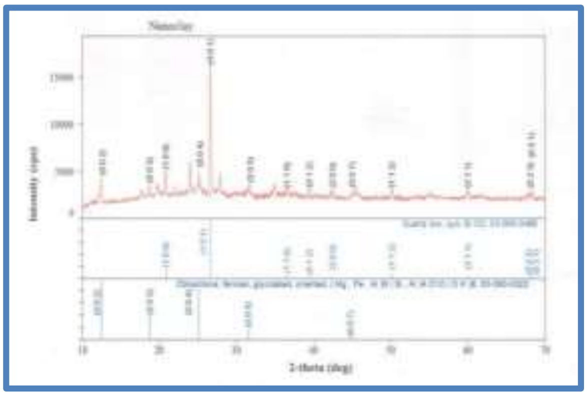


Figure 4 X-ray diffractogram of nanoclay

PVA-Starch- Clay – Glycerol Films with Different Concentrations

Nanocomposite films of PVA - starch - clay - glycerol were prepared by casting method. Different ratios (50:50 and 75:25) of nanocomposite films were made. Film with PVA – starch – clay- glycerol (75:25) was found to be flexible and plasticizing effect than the film with the ratio of 50:50 (Figure 5).

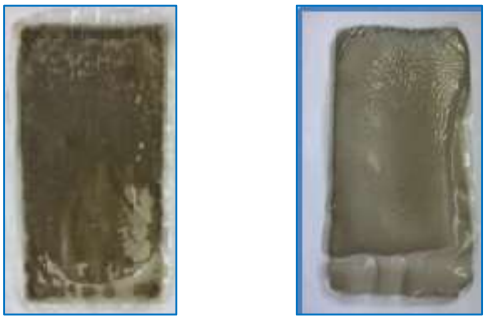
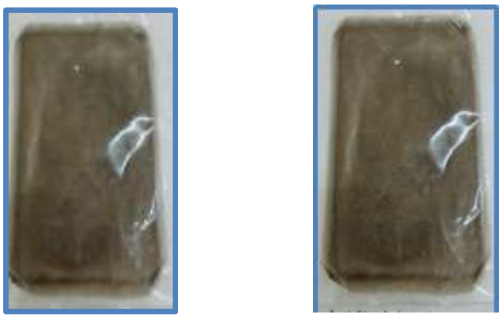


Figure 5 Prepared PVA-starch- clay - glycerol films with different concentrations

Soil Burial Test for Prepared Films

The natural biodegradation of these films in the soil environment were observed in soil burial method during 20 days. After 18 days, PVA – starch – clay – glycerol (75:25) film was completely destroyed.

PVA PVA+S+Cly+ Gly



Before burial test

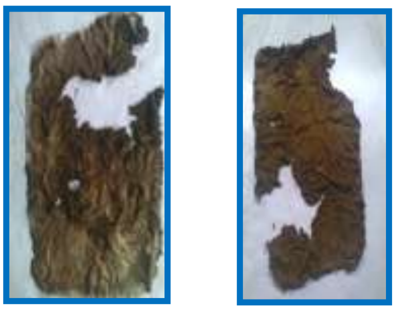
PVA PVA+S+Cly+ Gly

After four days

PVA PVA+S+Cly+ Gly

After eight days

PVA PVA+S+Cly+ Gly



After twelve days

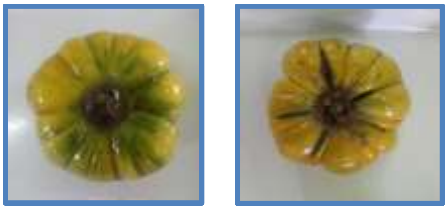
PVA PVA+S+Cly+ Gly

After sixteen days

Figure 6 Soil burial tests for prepared films

Study on Food Coating of Tomato Fruits

Figures 7 to 9 show the physical appearances of tomato fruits. After 8 days, the tomato fruit without coating started to decay. The tomato fruit with coating was still fresh after 25 days. It was observed that PVA – starch – clay – glycerol (75:25) blended solution retreated ripening and decay.



Coating Non-coating

Figure 7 Coating and non-coating tomato fruits (after 1 day)

Coating Non-coating

Figure 8 Coating and non-coating tomato fruits (after 4 days)

Coating Non-coating

Figure 9 Coating and non- coating tomato fruits (after 8 days)

Conclusion

Polymer films of polyvinyl alcohol (PVA) - starch - clay - glycerol were successfully prepared by casting method. White sticky rice starch extracted from white sticky rice grains and prepared nanoclay from volcanic mud of Nagarpwak Taung in Minbu Township, Magway Region were used to prepare films. They were polygonal in shapes for the starch granules with non-uniform sizes and disordered pore system for nanoclay. XRD confirmed the nanosize of both sticky rice starch (51.65 nm) and nanoclay (30.79 nm). PVA - starch - clay- glycerol nanocomposite films with clay. PVA - starch - clay- glycerol (75:25) ratio showed to have more smooth and plasticizing effect than the film with the ratio of 50:50. The prepared film it was completely degraded after 18 days. In the study on food coating, the tomato fruit coated by PVA - starch - clay- glycerol (75:25) film was still fresh after 25 days whereas non-coating fruit started to decay after 8 days.

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