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PREPARATION AND CHARACTERIZATION OF BIODEGRADABLE POLY(VINYL ALCOHOL)/STARCH BLENDS

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ABSTRACT

Poly(vinyl alcohol) was blended with a fairly acetylated cassava starch and made into film of various percentages. Their mechanical properties, biodegradability and surface morphology were estimated and studied. The poly(vinyl alcohol)/starch blends show good modulus and biodegradability that make it suitable for disposable packaging applications in which 50 percent starch/Poly(vinyl alcohol) blends shows a modulus of approximately 199100Nm^{-2} and 59.25 percent weight lost after 18 days of standard biodegradation test.

Keywords: Starch, Acetylation, Biodegradation, Poly(vinyl alcohol), Polymer blend.

INTRODUCTION

Non-biodegradable polymers, such as polyethene, polypropane, poly(vinylchloride) etc have excellent mechanical properties such as tensile strength, tensile strain, bursting strength and tear strength (Hay and Sharma. 2000). However, they do not degrade biologically after their useful life-time and this is a major cause of environmental pollution (Rudnik. 2008). To minimize and control this environmental pollution, scientists goes into struggle to manufacture biodegradable plastics of various applications, and some with even life cycle assessment aimed at comparing a biodegradable polymer used in packaging application (Famili *et al.* 2002). Native biodegradable polymers include the polypeptides (amino acids polyamide), polysaccharides (starch, cellulose, among others), polylactide (β-hydroxy-butyrate). Lactic acid bacteria and *acetobacter* are example of bacteria capable of synthesizing polymers with gelling characteristics (Rudnik. 2008).

The first generation biodegradable polymers, which were largely commercialized in the 1980s, did not satisfy the public view of complete degradation (Tomonori *et al.* 1999). Second generation polymers have recently been introduced and promoted by the industry as fully biodegradable. However, these polymers are more costly than the commodity polymers typically used in packaging applications (Rudnick. 2008). This was achieved by blending the polymers with a relatively cheap native biodegradable polymer such as starch. The starch is sometimes modified in order to reduce its hydrophilicity before blending it with the synthetic polymer in question (Kunal *et al*. 2010).

The starch content in synthetic starch-based biodegradable plastics may range between 10% to more than 90% (Rudnick. 2008). Starch based polymers can be based on crops from which they are obtained such as corn starch (maize), wheat, cassava, potatoes among others. More than 60% of the starch is needed before any significant breakdown occurs (Lu *et al*. 2009). As the starch content is increased, the polymer composite become more biodegradable and leaves less recalcitrant residues (Kunal *et al*. 2010).

Starch/synthetic polyester blends forms biodegradable polymers that are often used to produce high quality sheet and films for packaging by flat film extrusion using chill-roll casting films methods (Rudnick. 2008). Most of these tailor made biodegradable polymers are designed to suit some specific applications such as shopping bags, bread bags, over wrap, flushable sanitary products, product backing materials and mulch films (Rudnick. 2008).

With the present public concern for preserving the environment, it has been found desirable to search for materials which, when disposed after use, will physically or biologically decompose and thereby avoid polluting the environment. In this contribution therefore blend of locally sourced cassava starch and poly(vinylalcohol) of various percentages were prepared. Results of mechanical properties and biodegradation process using soil burial method, and light microscope morphological structures are discussed.

Materials and Methods

Materials

Dry cassava starch (Kurmi Market Kano), Poly(vinyl alcohol) (BDH), Acetic anhydride (Sigma Aldrich), Sodium hydroxide (Fisher), Hydrochloric acid (Fisher), and Glycerol (Fisher).

Methods

Acetylation of starch

The cassava starch obtained was ground to fine powder and 100g of it was transferred into 500ml beaker, upon which 100ml of distilled water was added and stirred thoroughly until it became slurry. The starch slurry was stirred with continues addition of acetic anhydride at the rate of 1ml per minute and adjusting the pH to about 8 to 9 by subsequent addition of 3% NaOH. This was continued until a total of 13.1ml of acetic anhydride had been completely added and adjusted by the 3% NaOH as done earlier on. The resultant mixture was then acidified with 10% HCl to readjust the pH to about 5.2-5.6.

After vigorous stirring the mixture was allowed to settle and the reagent residue was carefully decanted, washed with distilled water, allowed to settle and decanted once again. The acetylated starch was then dried at room temperature according to the method reported by Wurzburg (1999) and Lu *et al.* (2009).

Determination of degree of acetylation

Two weeks after the acetylated starch had completely dried, 10g of it was measured and transferred into a conical flask and 65ml of water was added, and stirred until it formed a uniform suspension. Few drops of 0.01M NaOH was added in the presence of phenolphthalein indicator until the pale pink colour was maintained according to by Wurzburg (1999). Thereafter, 25ml of 0.5M NaOH was added and stirred for about 35 minutes. The resulting mixture was titrated against 0.5M HCl. After reaching the end point, the mixture was decanted and the residue was washed with distilled water before drying in a dessicator. The weight of the completely dried mass of starch was taken as 8.67g.

Preparation of the Starch/PVA blends

The following weights in grams (5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 and 0.0) were measured separately and each was heated to about 80 ^{0}C in a beaker containing 100ml of water for about 12 minutes with stirring until the starch was gelatinized. Exactly 25ml of glycerol was measured and transfer into a 250ml beaker and the corresponding weights in grams of PVA (5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0 9.5 and 10.0) were added and heated gently until the PVA completely mixed with glycerol by stirring with a glass rod. This was followed by the addition of the corresponding weights of starch gel while, stirring. The temperature was raised to about to about 105^{0}C in order to remove the remaining water in the mixture. The mixture was transferred into a blender and blended for 10 minutes after which it was heated again to ensure that all the water content has completely evaporated. This was notice by the change of the smell of the evaporating vapour. The thick viscous mixture was spread on a flat sheet material and allowed to dry for 2 days at room temperature. A transparent flexible material was obtained.

Estimation of modulus of the blend

A thin length of the Starch/PVA blend material was cut with a scissors. The original length of the thin film was determined and so was the rectangular width and height of the thin length material was taken at different positions and their averages were determined, which were used in calculating the cross sectional area of the material. The sample was fixed at one end by a retort stand filling the gap by a divided cork, cut at it diameter in order to hold the thread like material. At the other end, slotted mass was attached using a thread. The extension caused by this mass was recorded and other mass combinations of 10g, 20g, 50g, and 100g were attached and, the extension recorded. The results are shown in table 1

Biodegradation test (Soil Burial Method)

A rich loamy soil was obtained from farmland behind Biological Sciences Department, Bayero University Kano, Nigeria. The soil was mixed properly with some sand in a container and leveled out. Sample of the materials were prepared and buried after taking their weight. After 18 days of burial, the samples were brought out to observe the physical changes, and any loss of weight as a result of microbial activity according to the method reported in ASTM D 5988-96.

RESULTS AND DISCUSSIONS

Starch was gelatinized in order to disintegrate granules and overcome the strong interaction of its molecules in the presence of water and the plasticizer which lead to well dispersion. Raw pure starch materials were reported to show low resilience, high moisture sensitivity and high shrinkage. These problems were overcome by adding materials such as PVA, Poly(caprolactone) (PCL) to starch matrix even at low concentration (Lu *et al.* 2009).

The degree of acetylation was calculated according to Wurzburg (1999) and was found to be 18.6%

Percent acetylation = (25-X) 0.043 x 0.5 x 100/a i

Where X = the amount of 0.5M HCl used to titrate the sample, and a = weight of dry Starch recovered. The titre value `x` was found to be 12.3ml and the total mass of starch recovered was 4.72g. The modulus `G` for the various percentages (% Starch content with respect to corresponding PVA) blends was determined according to Wurzburg (1999).

The initial length of the material was L = 0.035M. The area of cross section of the thin length was A = 2.93 X 10^{-5}. A plot of extension `e` against the force exerted `F` was plotted and the slope was found to be 0.006N/M^2,

From

$$e = FL/AG \quad \text{ii}$$

The Stress = Force/Area F/A (NM^{-2}) iii

Strain = Extension/Length = e/L iv

The stress and strain were calculated for each force exerted over a given cross-sectional area and for each extension produced per unit length by the material at given concentration, and hence the average stress and strain was deduced. The measurement of mechanical properties can be a tool to investigate the compatibility in blended system. Generally the mechanical properties are expected to depend mainly on the composition of the blends (Lu *et al.* 2009).

Table 1: Modulus of the material in relation to Percent Starch content

S/NO	The PVA/Starch Blends (%)	Modulus `G` (NM^{-2})
1.	50	199089.88
2	45	229873.22
3	40	247684.32
4	35	467857.14
5	30	564358.56
6	25	939849.60
7	20	1273459.29
8	15	1395734.67
9	10	1498563.56
10	5	1663404.06
11	0	1798745.46

Table 1 shows the estimated tensile strength as a function of blends composition for series of ten blends. Because of the hydrophilicity of PVA and its tendency to absorb water, its tensile strength and puncture resistance are reduced in high humidity environments, particularly above 60% relative humidity, and by immersion in water (Follain *et al*. 2005). The addition of modified starch with PVA decrease tensile strength due to probably poor adhesion between the two materials and the tensile strength of the blend decrease following a linear relationship (See Table 1). The good mechanical properties exhibited by the blend is believed to be due to the strong interaction among the hydroxyl groups on the PVA and starch polymer chains and because both starch and PVA are polyols, starch will form a continuous phase with PVA during blending (Choi and Kang. 1999).

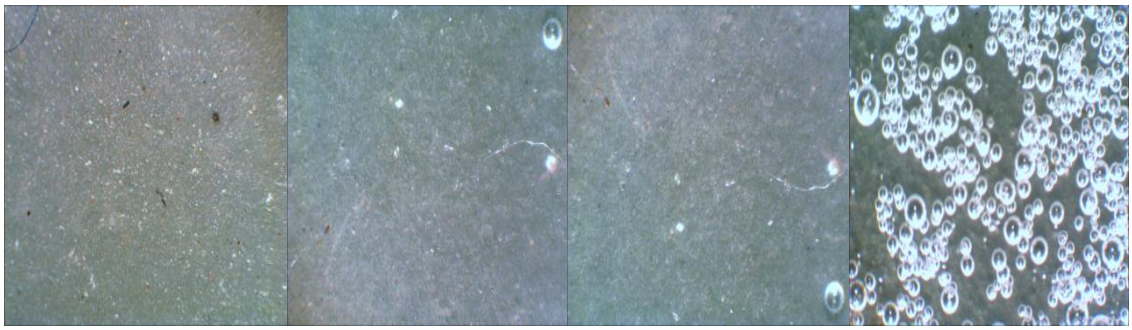
Table 2: Biodegradation Test (Soil burial test) results

S/NO	Percent Starch in the blend	Initial mass of blend (g)	Final mass of blend (g)	Weight lost by the blend (g)
1	0	22.01	19.58	2.43
2	5	22.38	18,81	3.62
3	10	22.16	17.54	4.62
4	15	20.26	17.2	3.06
5	20	21.2	16.84	4.36
6	25	20.69	15.43	5.26
7	30	22.54	14.34	8.20
8	35	21.47	12.34	9.13
9	40	20.65	11.53	9.12
10	45	22.03	10.45	12.02
11	50	20.8	8.95	11.85

From table 2 above it can be seen that all the blends exhibit some form of reduction in weight after 18 days of standard soil burial biodegradation test. The blend shows appreciable fall in weight lost in the biodegradation test as the concentration of starch content decreases. The increase in the weight lost by the blend is evidence that the microorganisms in the soil had consumed the starch and the amorphous regions of PVA, and the plasticizer component as compared to the report for isolated fungi and bacteria in the literature (Lu *et al.* 2009). Starch/PVA blend is assumed to be biodegradable in various microbial environments. The biodegradability of blends consisting of starch/PVA glycerol was performed by bacteria and fungi isolated from the activated sludge of a municipal sewage plant and landfill, which indicate that microorganisms consumed starch and the amorphous regions of PVA as well as the plasticizers (Lu *et al.* 2009). Biodegradation is dependent on a number of factors such as microbial activity of the environment, and the exposed surface area, moisture, temperature, pH, and molecular weight.

Morphology

Figure 1 shows the image taken with digital microscope camera (Amscope MD 900E) of the surface scanned under light stereo microscope for the blends containing different starch/PVA weight % at the increasing ratio of the PVA content. Blend with 5g starch/5g PVA shows a clear and smooth surface texture without presence of any air bubbles.



(a) (b) (c) (d)

Figure 1: Photomicrograph of starch/PVA film at different concentrations of starch/PVA (a) 5g/5g (b) 4.5g/5.5g (c) 4.0/6.0g (d) 1.5g/8.5g respectively

Samples with 4.5g starch/5.5g PVA to 3g starch/7g PVA blend ratio exhibited one or two air bubbles with clear surface texture. The appearance of the air bubbles indicated some form of in compatibility of the blend. As the ratio of starch decreases with increasing PVA content there was observed much more air bubbles and rough surfaces as can be evidently see in figure 1 above. These shows that the compatibility of the blend decreases as the percent starch content decreases in the blend and this is in agreement with soil burial biodegradation test (table1). These properties exhibited by the starch based biodegradable polymers can be possible alternative for food packaging to overcome the problem of environmental pollution and plastic disposable problem.

CONCLUSION

A new polymer material consisting of starch/PVA blends has been prepared and the mechanical properties, biodegradability and morphological structures were studied. Addition of modified starch with increasing PVA content decreases the mechanical properties. Result of soil burial exhibited an appreciable weight lost under standard test conditions and the compatibility of the blend decreases with increase in the PVA content. The new material could be use as a disposable packaging film.

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