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RESEARCH ARTICLE

Starch/ Polyvinyl Alcohol (PVA) Blend Bioplastics: Synthesis and Physicochemical Properties

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Abstract

Starch based bioplastics are prepared from the waste of food materials and widely used as the short lived biodegradable plastic for household and food packaging application. In this work, glycerol plasticized starch (extracted from potato peels)bioplastics blended with Polyvinyl Alcohol (PVA) in various composition (wt.-%) were prepared, characterized using Fourier Transform Infrared (FTIR) spectroscopy and their physicochemical properties such as water absorption, biodegradable properties, and acid-base resistance were investigated. The FTIR spectra of starch based bioplastics blended with PVA of the peak at 2924 cm^{-1} portrayed good compatibility between starch bioplastics and PVA. The water absorption test showed that the increase in starch proportion in starch/PVA blend increases water absorption capacity. Higher weight ratio of starch in starch/PVA blend bioplastics degraded rapidly than other bioplastics. Furthermore, the bioplastics of higher starch content resist acid and base for 45 and 42 hours respectively without being dissolved.

Key Words: *Starch, bioplastic, potato peels, FTIR, PVA.*

Introduction

Petroleum-based plastics are readily available, cheaper, and possess good mechanical properties due to which they are widely used as packaging material[1]. Plastics have dominated the packaging market, due to their great combination of flexibility, strength, transparency, stability, and permeability[2]. Despite these properties, disposal of such plastics is the main challenge as it is of non-biodegradable nature[3]. However, bioplastics comprise the long chain covalently bonded polymer prepared from renewable biomass such as starch, vegetable oil, cellulose, protein, lipid etc. [4][5].Bioplastic are environmentally friendly, short lived, and widely used for the packaging, wrapping, cutlery, straws, pots, cookery etc. [6]. Likewise, starch, a natural polymer mostly found in plants, is present in a granular form[7]. Basically, plants genotype and cultural practice may differ in the morphology of starch granules which are mostly present in seeds, roots, tubers, stems and leaves[8].The starch-based bioplastic can serve as an alternative material for existing commodity plastics[9]. It can be disintegrated into glucose by microorganisms or enzymes and metabolized into carbondioxide and water [10].Similarly, Polyvinyl alcohol (PVA), a hydrolysis product of polyvinyl acetate[11][12] is water soluble polymer with excellent properties such as low permeability, high-water absorption capacity, good mechanical, and thermal properties with good transparency[13], and is widely applicable in industrial and agricultural fields [14][15][16]. The biodegradable properties of these excellent pair for blending and the water solubility of PVA makes it easy to mix evenly with starch[17]. All these led to the extensive attention of the researchers of starch/PVA blend. In many type research, starch is blended with various thermoplastic polymers likepolyethylene (PE)[18], polyvinyl chloride (PVC) [19], and polycarpolactone (PCL)[20] to improve biodegradable characteristics[21].

Moreover, the blend of starch with polylactic acid (PLA) is one of the most promising effects because starch is an abundant and cheap biopolymer and PLA is biodegradable with good mechanical properties[22]. Polyvinyl alcohol (PVA) comprises a residual group of unhydrolytic polyvinyl acetate and has strong compatibility with starch[23]. In addition, glycerol is one of the most popular plasticizers mixed with PVA/starch blends due to their close solubility parameters[13]. However,the high manufacturing cost of PVA can be reduced if PVA is blended with renewable natural resources such as starch[24].The degradability of PVA-based materials was rather limited under simulated composting and soil burial conditions. The rate of biodegradation in starch/PVA cast film was negatively correlated with PVA content[25]. In this paper, the work is focused on the extraction of the starch from the potato peels and blended with PVA in presence of glycerol. The influence on physicochemical properties of starch/PVA blend bioplastics have been investigated by varying the weight ratio of the starch and PVA.

Materials and Methods

Materials

Solanumtuberosum, (potato) was purchased from the local market of Kathmandu. Glycerol (1,2,3-propanetriol) (99%) sodium metabisulphite ($Na_2S_2O_5$), HCl (36%) and NaOH (97%) were manufactured by Thermo Scientific Company, India supplied from a local supplier at Kathmandu and used without further purification.

Methods

Extraction of Starch from Potato Peels

Potato peels were chopped into small pieces and soaked in a beaker containing 1% sodium metabisulphite solution (as a preservative and disinfectant) [26]for about 30 minutes and were grind to make the paste. The reaction between starch, PVA, and sodium metabisulphite is shown in the following Figure 1

The paste was put in distilled water and then filtered. The filtrate was collected in a beaker and left for about 1 hour for sedimentation and decantation of turbid brownish-white colored particles at the bottom. The particles that remained on bottom were washed with distilled water 3-4 times. Further, the collected particles at the bottom dried in an oven for 2 hours at 50 °C and white powder was obtained[27].

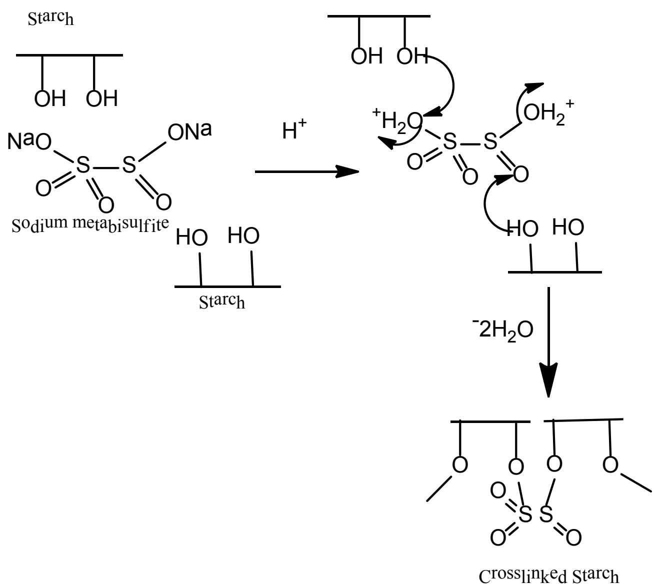

Figure 1: *Schematic representation of reaction of Starch and sodium metabisulphite.*

Preparation of Starch/PVA blend bioplastics

For the blend, pure PVA and synthesized starch from potato peels were weighted in five different weight ratios to make the total weight of mixture 2.5 g. The weight ratio of starch and PVA in five different containers were prepared as 0:100, 20:80, 40:60, 60:40 and 80:20 along with glycerol as a plasticizer. The possible chemical interaction of starch, PVA and glycerol as shown in the Figure 2

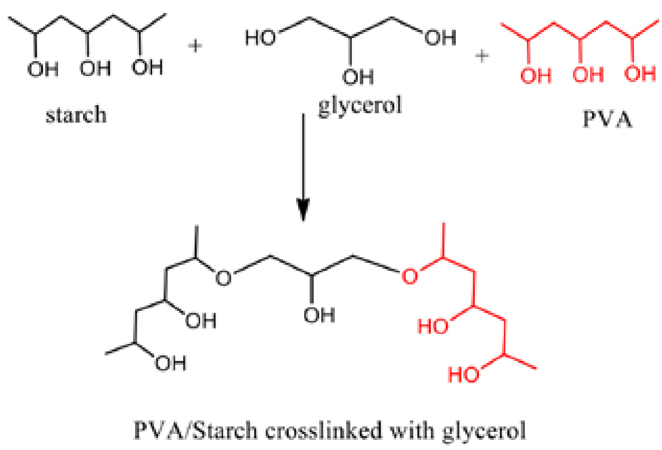

Figure 2: *Schematic representation of reaction between starch, glycerol and PVA.*

The Starch/PVA blend prepared at different compositions are shown in Table 1.

Table 1: *Weight ratio of starch/PVA blend*

S.N	Starch(g)	PVA (g)	Ratio
1.	0.0	2.5	0:100
2.	0.5	2.0	20:80
3.	1.0	1.5	40:60
4.	1.5	1.0	60:40
5.	2.0	0.5	80:20

Characterization Techniques

The analysis using FTIR represented the spectrum data that provided the information of functional groups of bioplastics. The FTIR analysis was carried out by using IR Prestige-21 model FTIR Spectrometer, SHIMADZU, Japan which identifies functional groups and vibrational modes associated with each peak. The FTIR spectrum of the sample was obtained at the wavenumber in the range of 4000-400 cm^{-1}.

Water Uptake Analysis

The samples were cut in size approximately 30×10 mm, dried in an oven at about 50 °C for 4 hours and their weight was taken. The specific sized samples were deep in distilled water. Each sample was weighed every 2-hour time interval. By following the standard procedure described elsewhere[28]. Their weight was recorded for 50 hours. The water absorption property was calculated as a percentage of initial weight[28]. The water uptake properties were calculated by using the following equation:

$$water\ uptake = \frac{W_w - W_d}{W_w}$$

Where, W_w = wet weight (after absorption) W_d= dry weight (before absorption).

Soil Burial Test

Soil burial test was done by decomposing the small section of the bioplastic in the soil in a beaker with little amount of water sprinkling. The test was performed according to the standard procedure described elsewhere[29] with slight modification. The experiment was performed in the laboratory by taking the soil from flower nursery, Jhor, Kathmandu in a 250 mL beaker. For the test, the sample was made in 30×30 mm size and their weight was recorded. Weighted sample was buried in soil at about 4 cm in depth. The degradation of samples is inspected at regular 5 day time intervals. The soil burial test was evaluated by the weight loss of the film over time. The weight loss was determined every five days from the starting date and was calculated by the help of following equation[29].

$$Weight\ loss(\%) = \frac{W_i - W_d}{W_i}$$

Where W_d= dry weight of film after being washed with distilled water W_i= initial dry weight of specimen.

Acid-Base Resistance Test

For the acid resistance test, 0.5N HCl solution had been prepared and every prepared bioplastic was the same in dimension and in weight. The weighed bioplastics were kept in the beaker containing HCl. In every three hours interval the weight of each sample was taken out to find the amount of acid it can resist or absorb. For the base resistance test, a similar procedure was carried out using 0.5 N NaOH solution. The acid-base resistance properties of each sample were measured by using the following equation[30].

$$A(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

$$B(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

Where, W_1= initial weight of sample film. W_2= weight of sample after absorption.

Result and Discussions

FTIR Analysis of Starch Based Bioplastic of Different Weight Ratio of PVA

The FTIR spectra of pure PVA, Starch:PVA (St:PVA)=1:4 and starch:PVA(St:PVA)=3:2 bioplastic are shown in Figure 3.

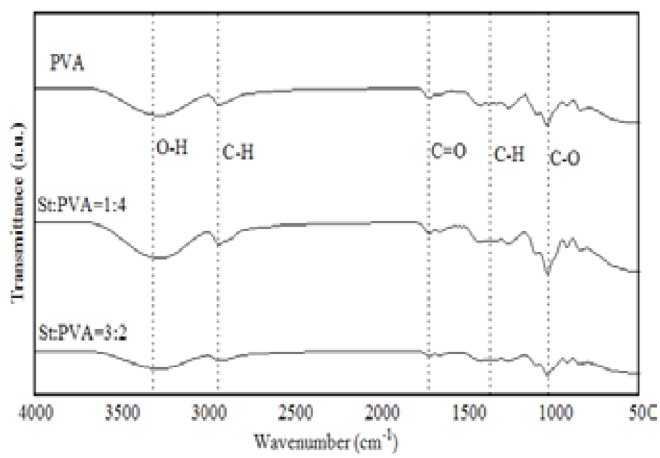

Figure 3: *Comparison on the FTIR spectra of different starch/PVA blend bioplastics.*

The peak around 3271 cm^{-1} represented hydrogen interaction due to the presence of hydroxyl group (-OH) in the plasticizer and 2931 cm^{-1} represented –CH bond stretching. The peak around 1651 cm^{-1} and 1250 cm^{-1} indicated the C=O stretching and C-H stretching respectively[31]. And the peak at 1081 cm^{-1} assigned the presence of characteristic of an anhydro-glucose ring of C-O stretch[31]. Starch-based bioplastic synthesized from banana/corn was also assigned with similar peaks as Sultan *et. al.* also observed the broad peak at 3271cm^{-1} was due to the -CH stretching[32]. As a result, the creation of the -OH and C-H stretching group indicates strong compatibility of bioplastics with PVA at various wt.-% ratios.

Water absorption test of Starch/PVA blend bioplastics

The weight gain by starch/PVA blend bioplastics against time is shown in following Figure 4.

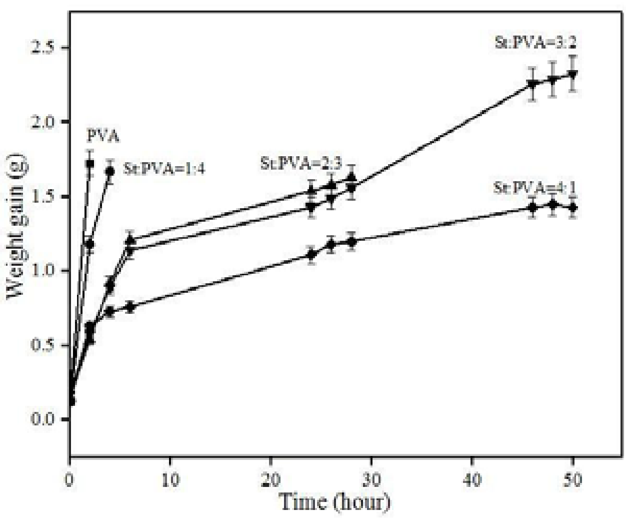

Figure 4: *A plot of water absorbability of starch/PVA blend bioplastic.*

Pure PVA-based bioplastic has very low water resistance capacity, which completely dissolves after 2 hours. The St: PVA=1:4 bioplastic got completely dissolved after 4 hours. Whereas, the St: PVA=2:3 bioplastic disintegrated after 28 hours. Bioplastic of St: PVA=3:2 as well as St: PVA=4:1 absorb water till 50 hours without being dissolved in water but the weight gain was higher in St: PVA=3:2 bioplastic. Hence, with an increase in starch proportion in starch/ PVA blend bioplastics the water absorption capacity also increases. When the weight of starch was higher than that of the PVA, the rate of water absorption by bioplastic was slower and hence bioplastic can resist water for a long time.The plot shows that the PVA has a high water solubility than that of PVA/Starch bioplastics. Because PVA contains a lot of hydroxyl groups, which form hydrogen bonds with the water molecules. Whereas in PVA/Starch bioplastics the polysaccharide chain of starch and –OH group of PVA were mostly occupied with a glycerol molecule. So, there was little chance for the water molecule to be associated or absorbed with the film. Starch is mainly responsible for the water absorption of the blend due to its hydrophilic nature[33].

Soil burial test of starch/PVA blend bioplastic

Soil burial test of the starch/PVA blend bioplastic was analyzed using the weight loss against the time (days) plot as shown in Figure 3.

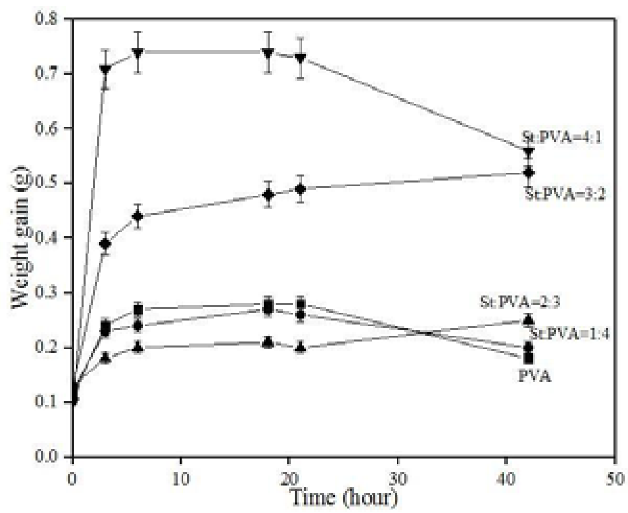

Figure 3: *Soil burial test of starch/PVA blend bioplastic.*

In Figure 3, the weight of each sample increased rapidly up to 10 days after being buried in the soil. After 16 days the weight loss was noticed gradually and the sample broke down into small pieces after 28 days. The bioplastic of St: PVA=4:1 almost decayed completely in 40 days. St: PVA=3:2 sample decayed in 44 whereas, St: PVA=2:3 degraded in 52 days. Pure PVA bioplastic and St: PVA=1:4 bioplastic were almost degraded in 56 days. The plot showed that the degradation of all the samples followed a similar pattern. The decomposition pattern of different samples with different compositions of starch and PVA wasSt: PVA =4:1 > St: PVA=3:2 > St: PVA=2:3 > St: PVA=1:4 > PVA.

At initial hours, the rapid gain in weight was due to the absorption of moisture contained in the soil. From this plot, it was clear that the absorption of water was higher for the bioplastic made from pure PVA. The biodegradability of PVA increased with the presence of starch so they degraded more quickly as compared to PVA bioplastic. Starch/PVA blends were biodegradable as PVA was the only petrochemical polymer to be synthesized with a backbone containing–OH bonds due to which starch blending with PVA was biodegradable[34]. Hence, the higher weight ratio of starch in starch/PVA blend bioplastics degraded more rapidly than other bioplastics.

Acid-base resistance test of starch/PVA blend

The plot of acid and base resistance test of starch/ PVA blend bioplastics is shown in Figures 4 and 5 respectively.

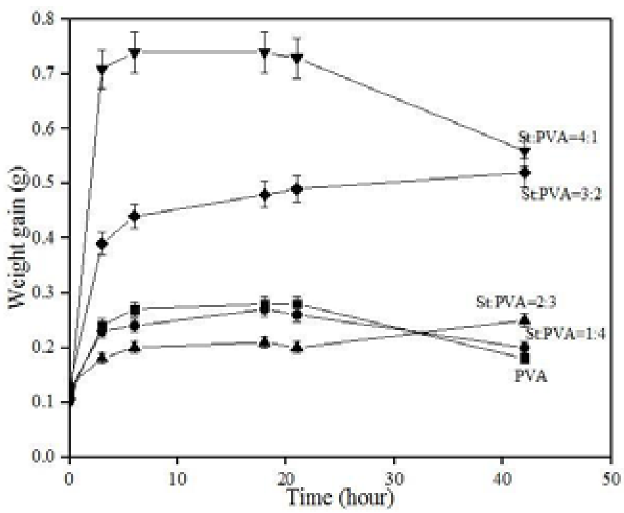

Figure 4:*Acid resistance test of starch/PVA blend.*

Bioplastic of pure PVA and St: PVA=1:4 disintegrate within 6 hours which was followed by St: PVA=2:3 and disintegrated within 21 hours.The bioplastic with the higher concentration of starch disintegrates after 45 hours. Hence, the bioplastics prepared from starch/ PVA blend having higher concentration of starch or higher weight ratio shows higher acid resistance.

Figure 5 describes the resistance pattern of starch/ PVA blend bioplastic in the basic medium. There was a sharp increase in weight at initial hours and then decreased successively. During this test, bioplastics were stable up to 42 hours and after that bioplastics dissolved in basic solution.

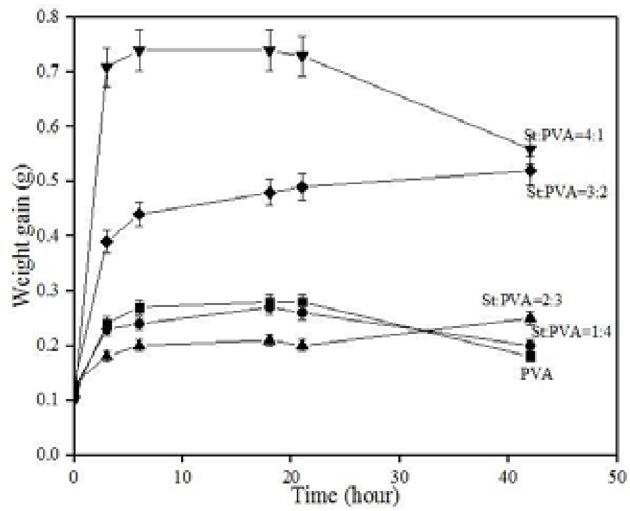

Figure 5:*Base resistance test of starch/PVA blend.*

PVA is a petrochemical polymer with a backbone containing the -OH group. Due to this the condensation reaction takes predominantly in acidic medium with removal of water molecules. This H_2O molecule is again absorbed by the bioplastics that is why the weight gain of PVA is higher than 0.5 g whereas it is not higher than 0.3 g in case of basic medium. Thus, the resistance of bioplastic increases with increase in concentration of starch. Those bioplastics having higher wt.-% of starch than that of PVA have comparatively higher resistance capacity towards base. Comparative study showed that the starch/PVA bioplastic resisted acid more than base.

Conclusion

Starch/PVA based bioplastics have been prepared by varying the weight ratio of starch and PVA using glycerol as a plasticizer. The prepared starch/ PVA bioplastics were characterized by using FTIR spectroscopy. After that, different physicochemical properties such as water absorption, soil burial test, andacid base resistance test were investigated. In water absorption, soil burialtest and acid-base resistance test, higher amount of starch containing blend showed higher weight containing primarily due to the hydrophilic nature of starch and also degradability and resistance properties showed higher weight ratio of starch in starch/PVA blend bioplastics.

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