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Synthesis and Biodegradation Study of Starch/PVA/Nanoclay Blend

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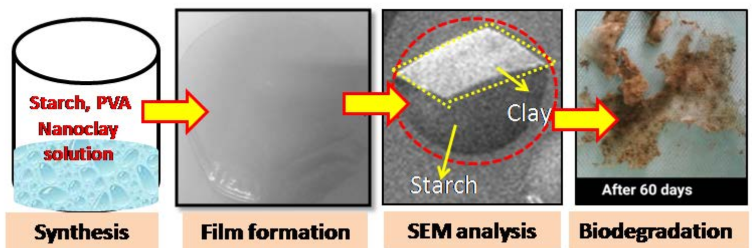
ABSTRACT



In this research work, we have synthesized blend of starch/PVA/nanoclay via solution cast method. The composition of blend was starch and PVA in 1:1 ratio by weight with citric acid as plasticizer. The amount of nanoclay was varied between 0.5 to 2 wt%. The structure elucidation of the film by Scanning electron microscopy reveals homogeneous dispersion of nanoclay into polymer matrix. The biodegradation of the films were studied by soil burial method and enzymatic hydrolysis and it was found that completely biodegradable films were produced which could serve as potential candidate for food packaging.

Keywords: Starch, PVA, Nano clay, Biodegradable, Food packaging

INTRODUCTION

Due to increase in environmental concern over few decades there is a worldwide demand for replacing currently used petroleum derived raw materials with renewable resource based raw materials for the production of polymers used for packaging.[1,2] In recent years, the dependence of various industries such as medicine, food, automobile and agriculture etc for their product packaging over petroleum based products has increased tremendously. However, the non-biodegradability of these packaging materials has led to a major problem of waste disposal and an ever-increasing landfill site.[3-5] The need of the hour is to synthesize packaging materials which provide a balance between strength, durability, and cost on one hand and environmental sustainability on the other hand.[6] The challenge of synthesizing such materials could be met by naturally occurring biodegradable materials. Among the naturally occurring biodegradable polymeric materials, starch has been considered one of the most promising because it is renewable, abundant and inexpensive.[7] Starch consists of the linear and the highly branched amylose and amylopectin polysaccharide respectively. However, low thermal and mechanical properties compared to most petroleum-based polymers restrict its industrial applications.[8-10] Therefore for the commercial production of Starch-based materials, it is blended or mixed with synthetic polymers such as polyvinyl alcohol (PVA). PVA is a biodegradable synthetic polymer which has the advantages of good film forming, high tensile strength, and high thermal stability.[11,12] In this paper, Starch-PVA film has been prepared by mixing them in 1:1 ratio by wt%.[13] To reduce the strong interactions between PVA and starch, citric acid was added as plasticizer.[14] It has been observed that citric acid improves the flexibility of starch/PVA blend by forming inter and intra molecular H-bonds.[15] In order to use these films for food

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packaging applications, these should be less permeable to environmental conditions like humidity and air so that shelf life of food can be enhanced.[16-20] It is known in literature that incorporation of nanoclay, montmorillonite (MMT) into polymer matrix provide barrier for water and oxygen molecules by increasing or altering the path length which these molecules have to travel while diffusing through the film.[21] In current project starch/PVA/nanoclay (MMT) blend has been prepared by solution casting method. Different blends has been synthesized in which amount of MMT was increased from 0.5 to 2 wt%. The characterization of the film has been done by Infra red spectroscopy (IR) and Scanning electron microscopy (SEM). The biodegradability of the films was checked by soil burial method and enzymatic hydrolysis.

EXPERIMENTAL

Materials

Starch (potato starch), polyvinyl alcohol (PVA) and citric acid were obtained from Loba Chemicals India. PVA was 80% hydrolysed with average molecular weight of 99,000–1,000,00. Enzyme Amylase was purchased from SD fine chemicals Ltd. and is stored in refrigerator. Montmorillonite (MMT) was purchased from Alfa Aesar. All the chemicals have purity above 99% and were used without further purification. Doubly distilled water was used throughout the experiment.

Preparation of Starch/PVA film

In a typical procedure, 1 g starch, 1 g PVA and 0.4 g citric acid were dissolved in 50 mL of water and stirred at 80-90°C till a homogeneous solution was obtained. To this required amount of MMT (nanoclay) was added and stirred for 60 minutes. The solution was poured into clean and dry glass petriplates, and dried at room temperature for 24-48 hours followed by drying in vaccum oven at 70°C for 1 hour. The dried film was carefully peeled off from petriplate. The concentration of nano clay was varied from 0.5 to 2 wt% and four films were prepared by same procedure.[22, 23] Table 1 summarizes the composition and sample codes of various films.

Table 1: Composition of nano clay in 1:1 starch/PVA blend

Sample code	Starch (g)	PVA (g)	Citric acid (20 wt%) (g)	MMT (wt%)
SP1	1	1	0.4	0.5 (0.01g)
SP2	1	1	0.4	1.0 (0.02 g)
SP3	1	1	0.4	1.5 (0.03 g)
SP4	1	1	0.4	2.0 (0.04 g)

CHARACTERIZATION

Scanning electron microscopy (SEM) and EDAX measurements were performed with a JEOL JSM 6610 at 20 kV, width distance 10 mm and spot size 30. EDAX was performed at a resolution of 135.2 eV. FT-IR spectra of as prepared samples were recorded directly in a Perkin Elmer FT-IR 2000 spectrophotometer.

RESULT AND DISCUSSIONS

FTIR spectrum of the film was shown in Figure 1. The film shows broad peak at 3200-3300 cm^{-1} which is attributed to the strong inter and intra molecular hydrogen bond between starch-PVA matrix and MMT.[12] The peak at 2880 cm^{-1} corresponds to C-H stretching vibrations. The absorption peak at 1016 cm^{-1} is attributed to the stretching vibration of Si-O-Si bond. Characteristic peaks of C-O and C-C vibration bands of glycosidic bonds appear in 1200-800 cm^{-1}.[12]

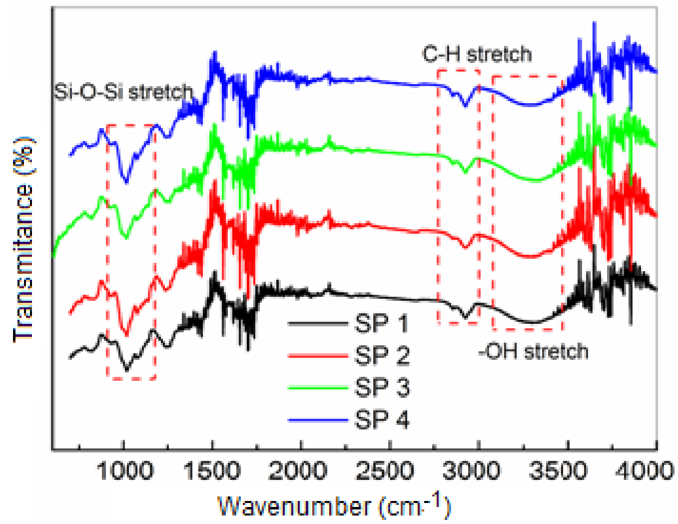


Figure 1. FTIR analysis of as- synthesised films with various concentration of MMT (see Table **1 f**or composition of **SP1- SP4**)

The as-prepared Starch/PVA/nanoclay blends were analyzed by scanning electron microscopy (SEM), as shown in Figure 2. SEM analyses helps in study of morphology, anatomy and crystallinity content of starch, PVA and nanoclay. From the SEM it was found that starch and PVA forms a homogenous mixture as only dark globules (spheres) were observed in SEM image panel "a" of Figure 2, as in this case synthesis has been performed in absence of clay. Whereas the second component that is nanoclay (MMT) were clearly observed in the exfoliated rectangular layer over the starch matrix. From the SEM image panel "b" starch matrix sphere were measured around 8 µm in diameter having nanoclay sheets of cross section 4 µm x 7 µm (panel c of Figure 2). SEM investigations showed a homogeneous dispersion of the components in all the examined samples. A homogeneous surface is observed for starch/PVA/nanoclay blend indicating that nanoclay was dispersed in the starch/PVA matrix.

Furthermore, the SEM analysis has also performed with various concentration i.e 0.5 to 2.0 wt% (stochiometric composition is shown in Table 2.) has been performed, as shown in Figure 2 b-f. It was found that the clay agglomeration occurs on increasing its concentration (see panel d-f). The clays show some orientation and this is due to the clay alignment during compression molding also the distortion of spherical starch matrix has been observed on increasing nanoclay concentration. Low amount of clay seems to be fairly compatible with polymer matrix resulting in well-dispersed nanocomposites.[24] It is well explained in literature that presence of layered silicate nanoclay significantly improves the thermal and mechanical and barrier properties of the films.[25,26]

The plate like structure of the MMT increases the diffusive path length for air and water vapours thereby provide stability to oxidation and decrease the permeability for solvent and water molecules.[27] The presence of nano clay improves the strength of the blends because of high aspect ratio of silicate nanolayers and high surface area.[28] With the increase in amount of nano clay the transparency of the films decreases which provide optical barrier to light and the extent of photo degradation decreases and hence shelf life of packaged food may increase.[28]

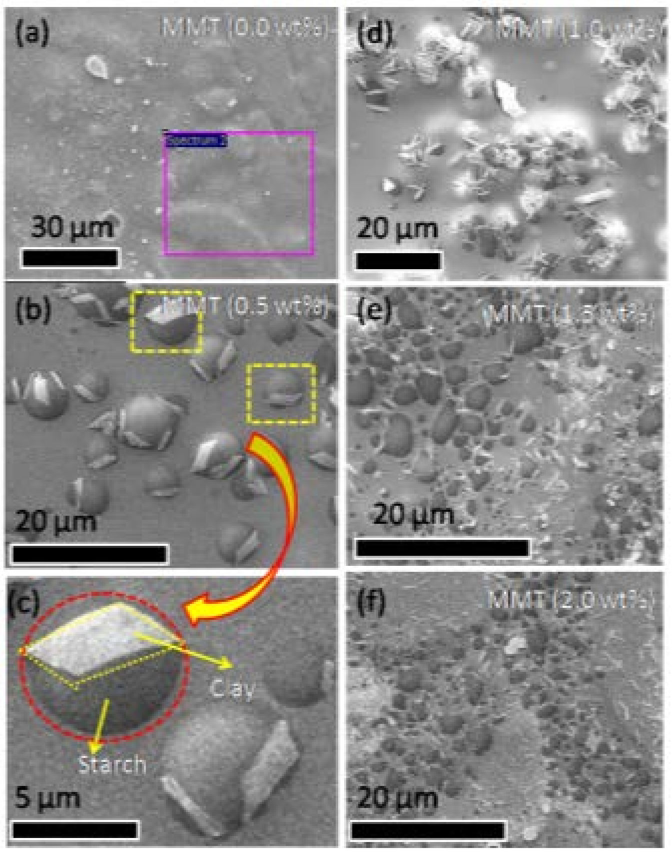
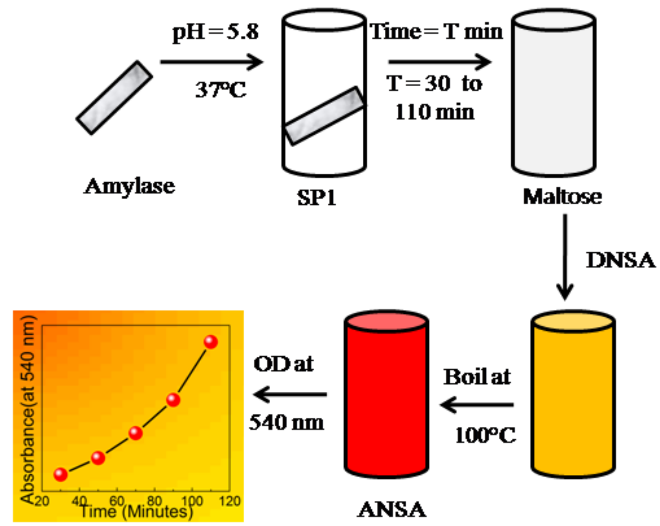


Figure 2. SEM images of as-synthesized starch/PVA/nanoclay nanocomposites. (a) SEM image of starch/PVA homogenous mixture, when reaction performed without nanoclay. (b-c) starch/PVA/ nanoclay blend synthesized with 0.5 wt% of nanoclay. (d-f) are SEM images of starch/PVA/nanoclay blend with 1.0, 1.5. and 2.0 wt % of nanoclay, respectively, (f) show most agglomerated starch/PVA/nanoclay blend sample with 2.0 wt% of nanoclay.

The enzymatic hydrolysis of **SP1** (see table 1) film sample was done by α-amylase. Amylase is an enzyme that catalyses the hydrolysis of starch into sugars. All amylases are glycoside hydrolases and act on α-1,4-glycosidic bonds.[29,30] 3,5-Dinitrosalicylic acid (DNSA) method is used for quantitative estimation of reduced sugars. DNSA is an aromatic compound that reacts with reducing sugars and other reducing molecules to form 3-amino-5- nitrosalicylic acid (ANSA), which strongly absorbs light at 540 nm. On reduction to ANSA, yellow colour of DNSA changes to orange red colour. Amylase breaks starch into maltose and the extent of hydrolysis of starch with time can be followed colorimetrically by measuring absorbance of ANSA at 540 nm. The graph was plotted between time and optical density (OD) at 540 nm (as shown in **Figure 3**) and it was found that concentration of maltose produced increases with time and there is linear increase in OD value with time. The observations are listed in the Table 2. The OD value increases from 0.18 to 0.34 after keeping the film for 110 min in enzyme solution. These results clearly suggest that film can be easily degraded by enzymatic hydrolysis and therefore will not pose any problem in disposal. Scheme 1 shows the schematic for the enzymatic hydrolysis.



Scheme 1. Schematic diagram for hydrolysis of **SP1** by α-amylase (composition of **SP1** has been given in Table 1)

Table 2: OD values for **SP1** kept in enzyme solution for specified time intervals

<table>
<tr><th>Time (minutes)</th><th>Enzyme (mL)</th><th>DNSA (mL)</th><th></th><th>OD at 540 nm</th></tr>
<tr><td>30</td><td>1</td><td>1</td><td rowspan="5">Kept in boiling water for 10 minutes</td><td>0.18</td></tr>
<tr><td>50</td><td>1</td><td>1</td><td>0.20</td></tr>
<tr><td>70</td><td>1</td><td>1</td><td>0.23</td></tr>
<tr><td>90</td><td>1</td><td>1</td><td>0.27</td></tr>
<tr><td>110</td><td>1</td><td>1</td><td>0.34</td></tr>
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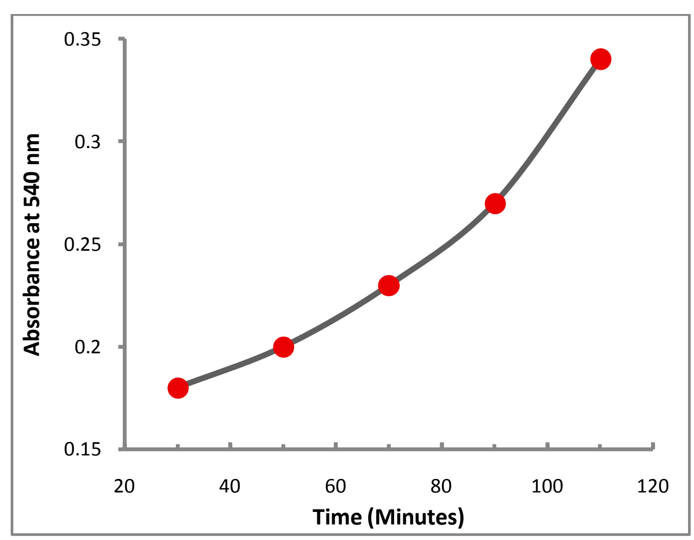

Figure 3: Graph between time and OD at 540 nm for enzymatic hydrolysis of film (**SP1**)

Soil burial studies have been performed with **SP1** film. After exposure of films from soil it eventually became hard and diminished in size as evident from the digital photographs of the films which are shown in figure 4. After burying in soil the films have undergone microbial degradation to a large extent.[31, 32] Therefore it can be concluded that completely biodegradable film has been obtained by the proposed methodology.

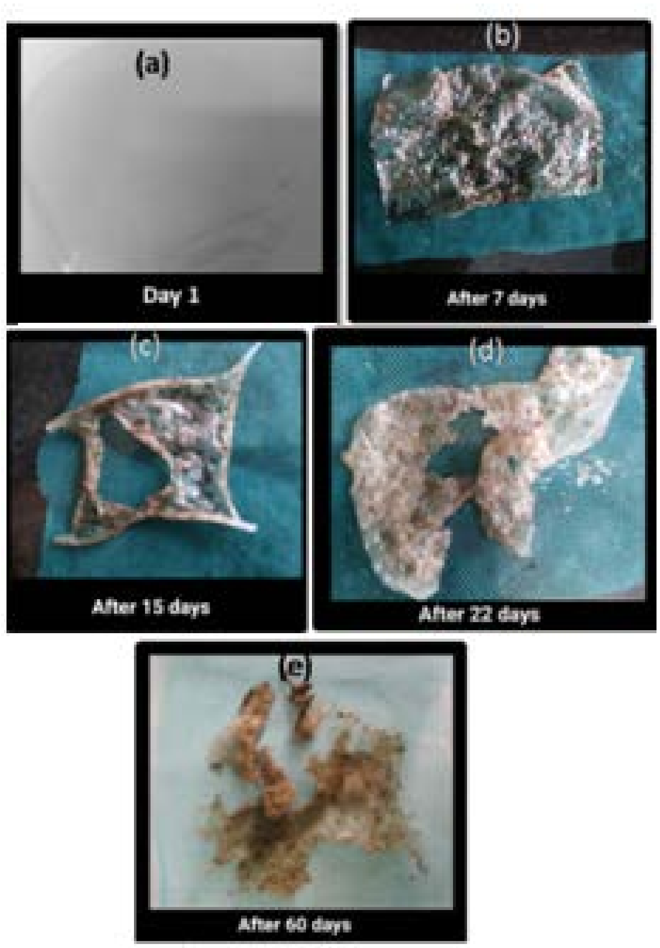

Figure 4: Digital photographs of the films after taking out from soil in specified time.

BIODEGRADATION STUDY

The enzymatic testing was done at pH 5.8 maintained by monosodium phosphate buffer saline prepared by mixing monosodium and disodium phosphate. To carry out the test, 20 mL buffer solution and 0.5 mL enzyme solution were added into a conical flask containing pre weighted film. The film was kept in the enzyme solution for specified period of time (See table 2) after which 1 mL DNSA was added and solution was boiled for 10 minutes on water bath. During this time solution acquire orange red colour which was measured colorimetrically by taking absorbance at 540 nm[33] (preparation of enzyme and buffer solutions have been given in notes.) Soil burial degradation was done by burying the test samples for 60 days in a pot containing soil at a depth of 6 cm. The pot was 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 pot. The degradation of the samples was determined at regular time intervals (5 days) by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film.

CONCLUSIONS

Environment friendly polymeric blends of Starch/PVA/nano clay have been synthesized by solution cast method. The amount of nano clay has been successively increased from 0.5 to 2 wt%. The dispersion of nanoclay into starch PVA matrix has been confirmed by IR spectroscopy. The surface morphology of the films has been elucidated by SEM and it was found that at low concentration nanoclay was found to be completely miscible with starch PVA matrix but on increasing concentration above 1.5 wt% it agglomerates. The biodegradability of the film has been checked by soil burial test, and enzymatic hydrolysis. Enzymatic hydrolysis of film was done by alpha amylase and it was found that films on hydrolysis by amylase produced maltose which was confirmed by colorimetric assay using DNSA method. Extent of hydrolysis of the films increases with time which is evident from linear increase in OD value from 0.18 to 0.34 at 540 nm. The biodegradability of the films was checked by soil burial method and it was found that films have undergone biodegradation by soil microbes. The mechanical testing of these films and its applications in food packaging is currently underway. In nutshell biodegradable films of starch and PVA and nanoclay were synthesized which could serve as potential candidate for food packaging applications.

ACKNOWLEDGEMENT

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To prepare 250 mL of buffer solution of pH 5.8, 117 mL (0.2 M) of mono sodium phosphate and 8 mL (0.2 M) of di sodium phosphate were mixed and diluted with 125 mL distilled water. The pH of the buffer was checked by pH meter. To this 2.25 g sodium chloride was added and the solution was mixed properly. Amylase solution was prepared by dissolving 2 mg enzyme in 50 mL buffer solution. DNSA reagent was prepared by adding 1 g DNSA, 1.6 g NaOH and 30 g sodium potassium tartrate in 100 mL distilled water. All the reagents were freshly prepared.

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Dr. Himani Chauhan obtained her Ph.D. in inorganic chemistry from the University of Delhi (India) in 2017. She had worked in PCI, Institute for Physical Chemistry and Electrochemistry, Leibniz University of Hannover, Germany during DST-DAAD Indo-German project. In 2017 she was appointed as assistant professor, by the Chemistry Department of Gargi College University of Delhi, India. Her scientific interests involve the synthesis of semiconductor nanocrystals, nanocomposites and hybrid nanoparticles, their applications as catalyst in various catalysis reactions, energy storage devices (supercapacitors). During her research she broadly worked on synthesis of quantum dots, core/shell and there gold hybrid nanostructures and for energy storage devices. She worked on graphene nanocomposites of various semiconducting nanostructures. Dr. Chauhan has published over 12 scientific papers in reputed journals.

Aeshna Gupta is an undergraduate student, currently pursuing BSc.(Hons.) Microbiology (III year) from Gargi College, University of Delhi. She has undergone summer training at B.R. Ambedkar Centre for Biomedical Research, North Campus, University of Delhi, completing a project on gene cloning. Her areas of interest include molecular biology, genetic engineering and biochemistry and how they can be applied for approaching environmental problems like waste disposal, handling non-biodegradable polymers like plastic, wastewater treatment etc. Furthermore, she wants to continue research on improving the properties of the biodegradable Starch:PVA polymeric blend.

Disha Gangotia is pursuing BSc.(H) Microbiology from Gargi College ,University of Delhi. She is currently in the third year of her bachelors program. She has been awarded a trophy of excellence for securing the highest marks in the 1st two years of her course and has 2 months of work experience as an intern. She has an inquisitive mind and her research interests include microbial ecology and bio-degradation, molecular biology and immunology .Further she wishes to continue research on improvising the polymeric films of starch:PVA.