

Effect of Phosphorylation on Starch Absorbency and Solubility

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Abstract: - Chemical modification is usually carried out to overcome the unstable properties of native starch and improve its physical and chemical properties during processing. In this study, phosphorylation of potato starch was carried out to determine the effect of phosphorylation on solubility and absorbency. Native potato starch was phosphorylated with sodium tripolyphosphate (STPP) at different percentage. The samples were characterized using FT-IR and SEM analyses. The FT-IR result shows a shift in absorption peak from 1342cm^{-1} in native starch to 1368cm^{-1} in the modified product due to the presence of phosphate group. While the SEM analyses shows an irregular oval shapes with smooth surface of different sizes in the native starch and rough surfaces as a result of disruption of oval shapes. The native starch appeared to be insoluble in all the solvents used, while the phosphorylated starch tend to be slightly soluble in some of the solvents used. Water absorbency initially increases with increase in the phosphate groups present on the starch backbone, however, with more phosphate groups on the backbone ($\geq 25\%$ STPP), there is a noticeable decrease in the absorbency.

I. INTRODUCTION

Starch is widely used in many industrial products due to its functional properties and nutritional value. It has been most often used in industry as thickener, colloidal stabilizer, gelling, bulking, and water retention agents in food and non-food products [1,2]. However, the applications of native starches are limited due to their storage and process instabilities. These limitations are the reasons for developing the techniques for starch modifications. Chemical modification involves the introduction of functional groups into the starch molecules, resulting in marked changes in starch physico-chemical properties. Phosphorylation of starch is an example of chemical modification of starch. Chemical modification is intended to facilitate intra and intermolecular bonds at random locations in the starch granules for their stabilization [3,4]. Pastes of phosphorylated starch are more resistant to shear and acidic conditions.

Phosphorylation is generally performed by treatment of granular starch with multifunctional reagents capable of forming either ether or ester inter-molecular linkages between the hydroxyl groups of starch molecules. The main reagents used for phosphorylation are sodium trimetaphosphate, mono-sodium phosphate, sodium tripolyphosphate, phosphoryl chloride, mixture of adipic acid, acetic anhydride, and vinyl chloride [3,5]. The type of phosphorylation agent determines the changes in functional properties of a treated starch,

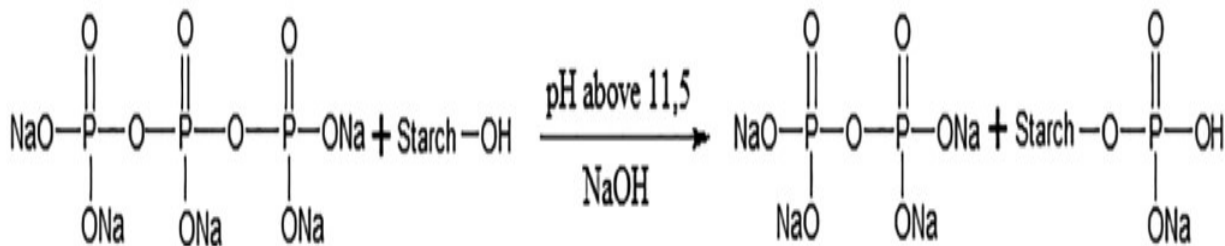
because the molecular structures of the phosphorylated starch systems produced by different phosphorylation agents are different [3,6]. Therefore, based on the reagent used for cross-linking, the final product is generally divided into three types: the first type is a mono-starch phosphate which is produced by esterification of starch with ortho-phosphoric acid, sodium or potassium ortho-phosphate, or sodium tripolyphosphate. The second type is a di-starch phosphate which is produced with sodium trimetaphosphate or phosphorous oxychloride. The third type of cross-linked starch is a phosphorylated di-starch phosphate which is produced by combined treatments of mono-starch phosphate and di-starch phosphate [6,7]. Monostarch phosphate exhibit increased paste clarity, viscosity, water binding capacity [8,9,10]. On the other hand, the formation of distarch phosphates may help to maintain the granule integrity and to make starch paste more resistant to retrogradation, high temperature, and low pH than native starch [11,12].

Starch phosphorylation with STMP has been reported and demonstrated by Sang *et al.*, (2007)[13] who concluded that the products are predominantly diesterified and may contain phosphate mono and triesters in lesser amounts. The authors also reported to have starch phosphorylation with STPP and observed predominance of monoesterified products, also with minority presence of phosphate diesters. These observations were obtained by means of ^{31}P nuclear magnetic resonance (NMR) spectroscopy, a technique that also allowed the detection of free inorganic phosphorus residues. Phosphorylated starches have been shown to be promising materials for acting as a matrix for controlled drug delivery systems [13,14]. Also, various technological applications of the starches can be improved with phosphorylated products, as the modification of various properties such as increase of paste clarity, viscosity and water absorption capacity can be achieved [15].

Phosphorylation is usually done by a dry heat reaction in the temperature range $140\text{--}160^\circ\text{C}$. The phosphate diester starches have the phosphate esterified with two hydroxyl groups, very often from two neighboring starch molecules. This leads to the formation of a covalent bridge or cross-linking. Phosphate cross-linked starches show resistance to high temperature, low pH, high shear and leads to increased stability of the swollen starch granule. Moreover it improves viscosity and textural properties of the starch. As a thickener and stabilizer, starch phosphate diesters are superior to unmodified starches. They

also provide resistance to gelling and retrogradation, and do not synerise on storage. Starch phosphate can substitute gum arabic (at ~ 0.5% level) in sugar syrups, ice cream mixes, salad dressing, and pudding. Efforts have been made to replace the conventional processes for the production of starch phosphates with an extrusion cooking process. Phosphorylation of rice starch by extrusion cooking showed that increased barrel temperature (120 – 180 °C) resulted in

greater phosphorus incorporation into the starch. Phosphorylation at low levels of substitution resulted in greater solubility, swelling power, paste viscosity and clarity for rice starch. Starch granule size has impact on the effect of phosphorylation on the properties of rice starch. Phosphorylated rice starch has been reported to exhibit a reduced degree of hydrolysis by acid or amylase. Scheme 1 shows the reaction of starch with phosphorylating agents.



Scheme 1. Starch Phosphorylation with STPP in alkaline medium

II. MATERIALS AND METHODS

Starch of high purity was extracted from potato; sodium triphosphate and other chemicals used in this experiment were purchased from sigma-aldrich.

2.1 Synthesis of Phosphorylated starch

Phosphorylation of starch was carried out using the procedure reported by Blennow *et al.*, (2002) [16] with some modifications. 1.26g of sodium triphosphate (STP)/10g of starch (d.b.) were added to 150 mL of distilled water with constant stirring. The mixture was cooled and placed in 100 mL of 50% aqueous methanol, and stirred for 30 minutes. Filtering and washing three times with 50% methanol recovered the product. The product was re-slurried in 50% methanol and washing step was repeated. The solid product was dried in an oven at 45-50°C for 48h, milled using a hammer mill, then placed in a sample container for further analyses.

2.2 Water Absorbency

A gravimetric method was applied whereby a polymer sample (1g) was immersed in water (250 g), or 0.9% saline solution

(150 g) for 10h at room temperature. The swollen polymer was separated using a 100mesh sieve and weighed. The water absorbency (Q) was calculated from the relation:

$$Q(\text{g/g}) = (w_2 - w_1)/w_1 \quad (1)$$

Where Q is the water absorbency, w_1 and w_2 are the weights of dry sample and swollen gel respectively. The absorbency under load (AUL) of the sample was tested using a standard gravimetric procedure reported by (Mohammed *et al.*; 2014)[17]. A macro-porous sintered glass filter plate (porosity # 0, d $\frac{1}{4}$ 80mm, h $\frac{1}{4}$ 6mm) was placed in a petridish (d $\frac{1}{4}$ 118mm, h $\frac{1}{4}$ 12mm). One gram of the sample was uniformly placed on the filter paper in the sintered glass and a load of 500 g in a glass cylinder was placed on the dry sample of the polymer. A 0.9% NaCl solution was added till the liquid reached the height of the filter plate (around 6mm). The swollen particles were weighed again after 60 min. and the AUL was calculated from Equation 1. In each case, three runs were carried out and the average values obtained were used in calculating the water absorbency

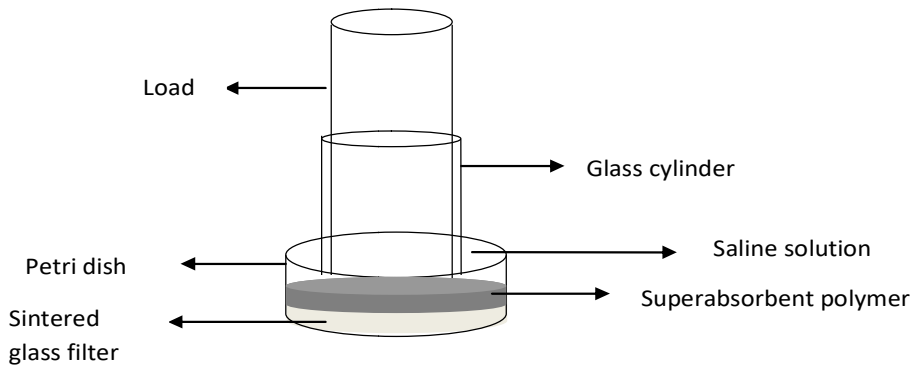


Figure 2.1 showing absorbency under load [17].

III. RESULT AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM)

Images of unmodified and phosphorylated starch are shown in Figure 3.1. The native starch (Fig. 3.1 a) shows an irregular oval shapes with smooth surface of different sizes. However

in the phosphorylated starch, (Fig.3.1 b), the surface morphology changes to a rough surface and there is disruption of the ovular shapes observed in the native starch. This is as a result of the presence of phosphate groups being attached to the starch backbone.

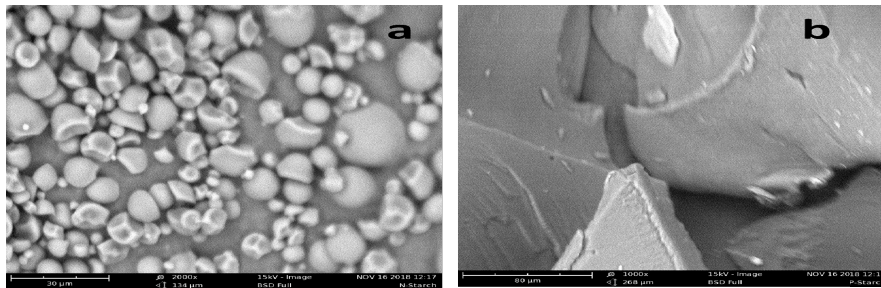


Figure 3.1. SEM Image of a Starch and b Phosphorylated starch

3.2 FTIR Analyses

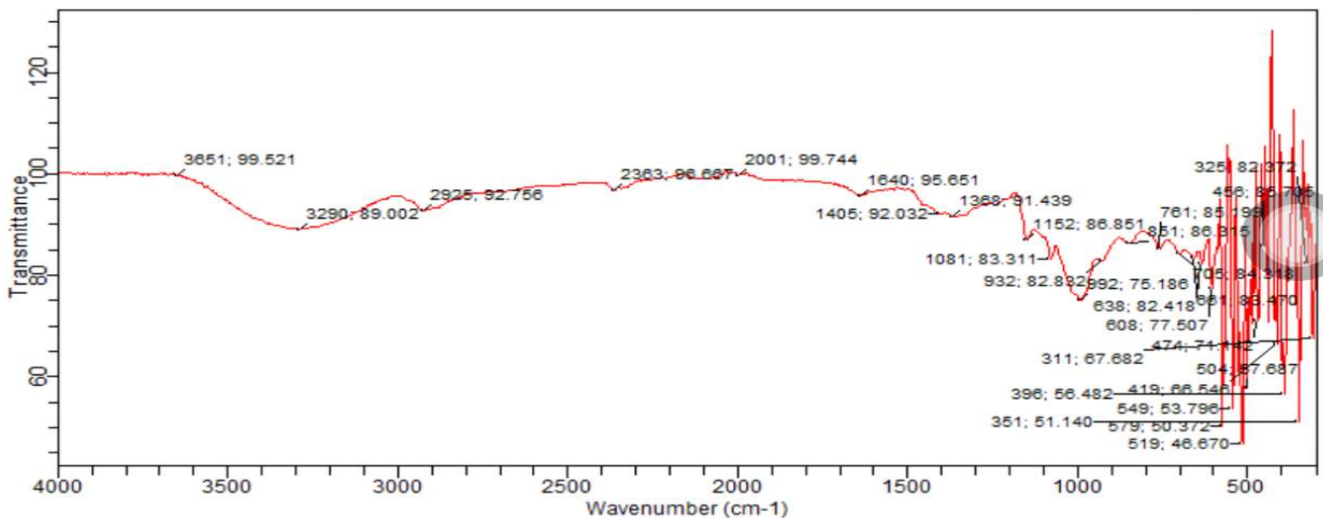


Figure 3.2: FTIR spectrum of Starch

The FT-IR Spectrum is shown in figure 3.2 and 3.3. The native starch (Fig. 3.2) shows absorption peak at 3290 cm^{-1} and 2929 cm^{-1} due to OH and CH stretching vibration

respectively. There is also another absorption peak at 1640 cm^{-1} which is assigned to OH bending bond and 1081 cm^{-1} due to C-O-C vibration modes.

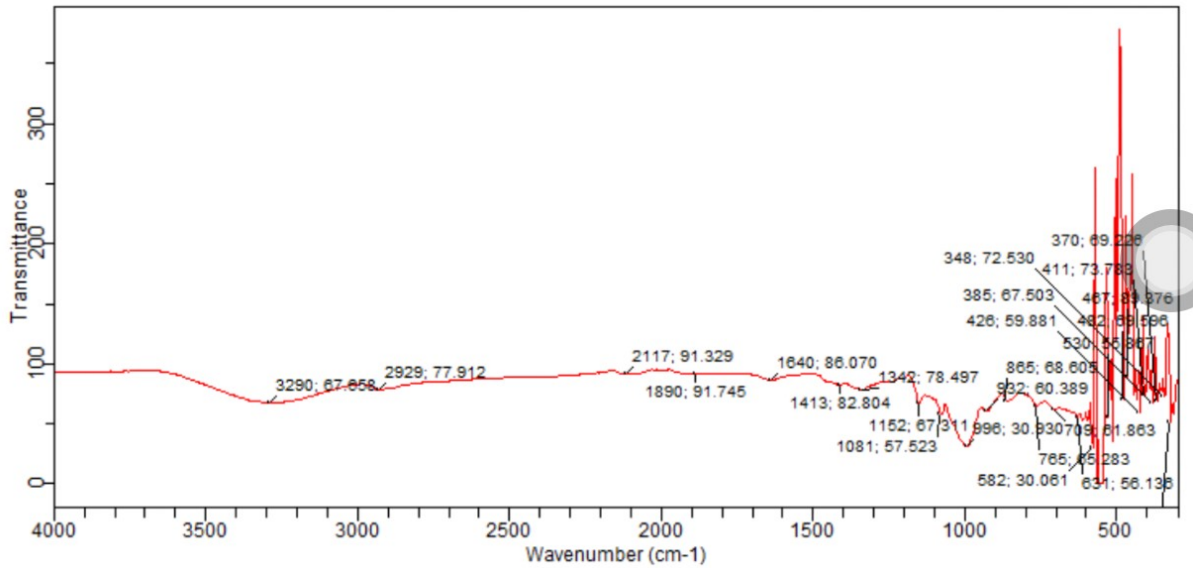


Figure 3.3: FTIR spectrum of phosphorylated starch

However, in (Fig. 3.3) of the phosphorylated starch, there is a shift in absorption peak from 1342 cm^{-1} in native starch to 1368 cm^{-1} in the modified product. This is ascribed to the presence of P=O and P—O stretching vibration at around 1380 cm^{-1} .

3.3 .Water Absorbency

The water absorbency of phosphorylated starch is shown in Table 3.1. The water absorbency initially increases with increase in the phosphate groups present on the starch

backbone, however, with more phosphate groups on the backbone ($\geq 25\%$ STPP), there is a noticeable decrease in the absorbency. The decrease in absorbency could be associated with more phosphate groups around the backbone, which form clusters and pose serious hindrance for the aqueous substance to pass down and become trapped in the network. On the other hand at moderate degree of phosphate group, (20% phosphorylating agent), there wasn't such hindrance. Hence, the oxygen atoms in the phosphate group readily form hydrogen bonds with water molecules.

Table 3.1: Water absorbency of phosphorylated starch

S/No	Phosphorylating agent (% by weight of starch)	Water absorbency in grams	Absorbency under load	Saline solution absorption	Retention percentage (%) of water
1	0.00	1	1	1	100
2	12.6	102	54	58	99
3	20.0	180	57	62	97
4	25.0	168	50	60	98
5	30.0	90	44	55	100
6	35.0	60	39	48	100

3.4 Solubility Test

In table 3.2 , it is shown that native starch is insoluble in all the solvents used in the solubility test. However, the phosphorylated starch shows an increase in solubility because it is slightly soluble in some of the solvents used. This is due to the presence of phosphoryl group attached on the starch

backbone. The interaction between phosphate groups and solvents' molecules coupled with the structural changes on the starch molecules could facilitate a certain degree of solubility to the phosphorylated starch.

Table 3.2 : Solubility of modified and unmodified starch in different solvents

S/N	Solvent	Native Starch	Phosphorylated starch
1.	Methanol	Insoluble	Insoluble
2.	Dimethyl sulfoxide	Insoluble	Slightly soluble
3.	Ethyl acetate	Insoluble	Insoluble
4.	N-hexane	Insoluble	Insoluble
5.	Acetone	Insoluble	Insoluble

IV. CONCLUSION

Starch phosphorylation process has been successfully performed using sodium tripolyphosphate (STPP). SEM analyses shows an irregular oval shapes with smooth surface of different sizes and a rough surface due to disruption of the oval shapes in native and modified starches, respectively. and FTIR absorptions were observed, where it shows a shift in absorption peak from 1342cm^{-1} in native starch to 1368cm^{-1} in the modified product due to the presence of P=O and P—O stretching vibration at around 1380cm^{-1} . The phosphorylated starch presented increased solubility in some of the solvents used while the native starch appears to be insoluble in majority of the solvents.

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