Short Communication

Selective metal adsorption by chemically modified novel biopolymer

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Abstract

Starch as a natural biopolymer is extensively used in paper, food, adhesive, medicines, nano films and many other industries. Biopolymers are sustainable, carbon neutrals and are always renewable. Starch is the second most abundant natural biopolymer on the earth. In order to improve the performance of starch, crosslinking is often carried out either in the processes of starch modification or during the application processes. By controlling the degree of crosslinking, the water retention capacity of starch-based hydrogel can be well controlled. In addition, the adsorptivity and binding strength of starch on a substrate can be significantly improved. Chemically modified biopolymers can be used as selective metal chelators. They have applications in waste water management. In the present study chemical crosslinking of starch using Ethanedial (glyoxal) was carried out to judge its adsorptivity towards Copper. The novel crosslinked biopolymer is characterized by IR, NMR, XRD. Surface chemistry of metal-biopolymer was studied using SEM.

Keywords: Potato Starch (PS), Crosslinked Potato Strach (CPS), Glyoxal, FTIR, XRD.

Introduction

In nature, growth cycles of organisms lead to form biopolymers, therefore they are also known as natural polymers. Activated monomers are the monomers which are formed in the cells by complex metabolic processes. Enzyme catalyzed chain growth polymerization reactions of activated monomers are involved in the synthesis of biopolymers. Biodegradable polymers and plastics were introduced in 1980s. Since last few decades, environmental concerns and realization of finite petroleum resources have attracted an increasing amount of attention. The common purposes of starch modifications are to change adsorption capacity, reduce viscosity of pastes, improve resistance to processing conditions (acids, heat, mechanical shear, etc) and add desirable functional groups. Many crosslinkers have been developed in the past for crosslinking purpose. This study focuses on the fundamental study of modified biopolymer in an aqueous solution and its applications in diverse fields. Adsorption of metal ions on modified starch can be studied from application point of view.

Literature Survey: Glucopyranose units bonded in α -linkages forms polysaccharide starch. Starch as a polysaccharide has two forms in nature: i. Amylose (linear molecule of $(1 \rightarrow 4)$ linked α -D-glucopyranosyl units with very few $(1 \rightarrow 6)$ - α -linkages¹), ii. Amylopectin (a highly branched molecule - chains of α -D-glucopyranosyl linked majorly by $(1 \rightarrow 4)$ -linkages and $(1 \rightarrow 6)$ linkages at the branch points).

Starch being an abundant natural polymer, has many attractive properties such as biocompatibility, biodegradability and low

cost. Due to which it has been widely used in food and non-food applications. Starch as a non-toxic biodegradable natural polymer having a good chemical reactivity, is also widely used in non-food applications including adhesives, coating, cosmetics and pharmaceutical products, additives for papermaking and plastics.

Increasing prices and decreasing availability of conventional film-forming resins² have introduced wide use of starch as a raw material in film production. Production of disposable food packagings, food service ware, purchase bags, composting bags are the potential applications of starch films³.

Materials and methods

Glassware used were all made of corning glass. The burettes, pipettes, volumetric flasks used were of 'A' grade. An analytical balance Shimadzu, Japan of 0.1 mg sensitivity was used for weighing.

All chemicals were A.R. grade. Deionised distilled water was used to prepare all aqueous solutions. Hydrochloric acid and sulphuric acid or acetic acid used were SD Fine (A.R.) grade. Sodium acetate required for preparing buffer solution was also of A.R. grade (SD Fine).

Instruments: Following instruments were used during the study. pH meter: LI 120, Elico, Hyderabad,

Balance: ATX 124 Shimadzu, FTIR: Frontier PE, USA, XRD: Maxima7000S, Shimadzu, Japan

NMR: Avance 300 MHz, Bruker, Germany.

CPS preparation: Polycondensation method of polymerization was undertaken for the reaction of Glyoxal and Potato starch in 2:1 molar ratio. Sodium chloride and Boric acid were used to keep the pH weakly acidic. In round bottom flask the reaction mixture was heated upto 80°C for 3-3.5 hours with occasional stirring. The reaction mixture was cooled and was kept at RT for 2-3 days. A slight yellowish white colored highly viscous product was obtained. Viscous product was then dried under vacuum. The yield of the final product obtained was Eighty five percent. Slow solubility was found in distilled water and insoluble in organic solvents like chloroform, ethanol, methanol etc.

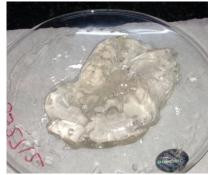


Figure-1: CPS – Before drying.



Figure-2: Dry Film Prepared using Viscous CPS product.

Properties of CPS: i. CPS is observed to exhibit hydrophobic property, when a piece of known weight was added to water its weight was found to be unchanged upto 5-6 hours. Later it starts swelling to form gel. ii. Comparative dissolution of 100 mg PS and CPS into acidic and alkaline medium at various concentrations of sulphuric acid and Sodium hydroxide showed that PS dissolves completely within 10 min whereas CPS takes about 3 hours to dissolve in 9 N H₂SO₄. On the other hand PS requires 15 min to dissolve in 1 N NaOH while CPS takes 40-50 min. iii. CPS was also found to show electrical conductance. A 0.02 M CPS showed electrical conductance of 0.789 millisiemens.

Formation of Cu-CPS complex: Equal volumes (10 ml) of 1% aqueous soln of crosslinked potato starch and 0.1 M Cu were mixed at pH 7, this precipitated a blue colored product was obtained which was washed using distilled water and filtered. The product was dried in vacuum desiccator on calcium chloride.



Figure-3: Cu-CPS Complex.

Results and discussion

IR and XRD for Potato Starch, Crosslinked Potato Starch and Cu-Crosslinked Potato Starch Complex.

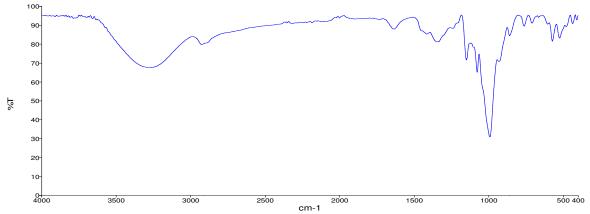


Figure-4: Potato starch.

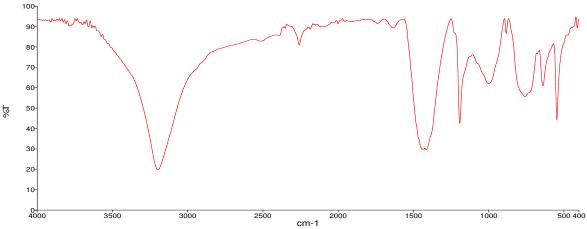


Figure-5: Crosslinked Potato starch.

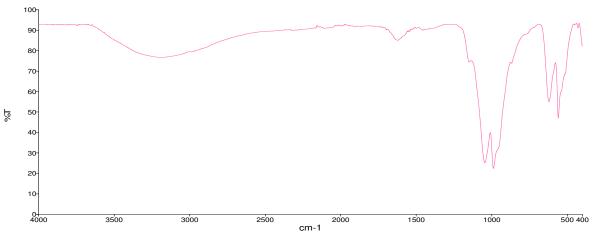


Figure-6: Cu-Crosslinked Potato starch.

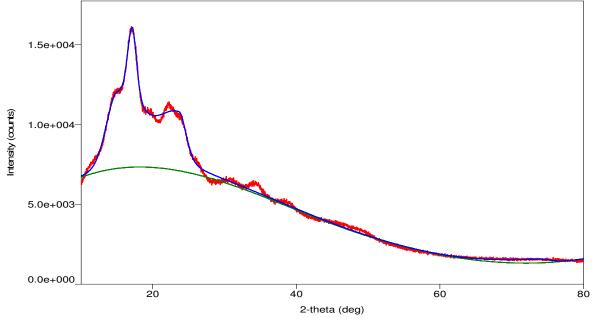


Figure-7: XRD for Potato Starch.

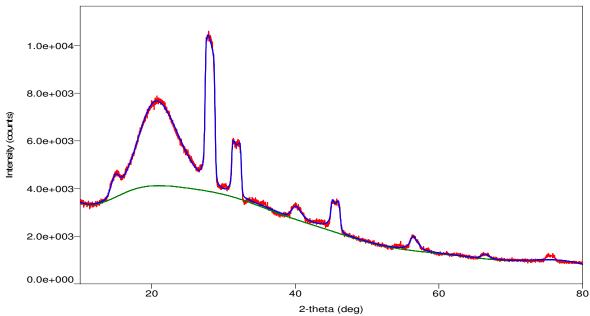


Figure-8: XRD for Crosslinked Potato Starch.

Conclusion

Chemically modified starch shows improved properties which can be capitalized to search for novel applications. The modified biopolymer has remarkable porosity to adsorb metal ions, optimum electrical conductivity, well defined acid and base resistance, biodegradability. The finished product can be reduced in thickness so as to prepare thin films for substrate.

References

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