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Preparation and Partial Characterization of Sago Starch Based Graft Co-Polymers



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ABSTRACT

Sago starch is a pure carbohydrate finding its significance in many industries like textile, paper and plywood. It serves many important functions such as preparation of biofilms, adhesives, biodegradable plastic, etc. The aim of this study is to prepare sago starch sheets (SG) and sago starch co-polymerized with methyl methacrylate (SG-PMMA) sheets and compares their physicochemical and mechanical properties. The mechanical properties of the SG-PMMA sheets showed a reduced tearing strength and tensile strength equal to that of sago starch sheets without co-polymerization but had a greater elongation before breakage. The water absorption properties indicated that SG-PMMA was less prone to corrosion and absorbing less water and can effectively stay as a surface coating agent for longer durations. In conclusion we demonstrate for the first time SG-PMMA co-polymerization through a chemical reaction to produce a material that does not degrade in water consistent with the idea that this material could be used in wound dressing.

1 INTRODUCTION

Starch is a biopolymer which is naturally available, biocompatible and biodegradable. Incorporation of sago starch as a matrix produces biodegradable sheets with excellent mechanical properties [1]. Starch is one of the most abundant and cheap polysaccharide, it includes nearly 30% amylose and 70% amylopectin. Chemically modified starches with improved properties are becoming more and more important in industrial applications not only because they are cheaper but mainly because the polysaccharide portion of the product is biodegradable [2]. In starch based sheets, starch granule sizes are linearly correlated with sheet thickness and are inversely proportional to sheet strength [3]. Derivatization of starch hydroxyl groups increases the sheet flexibility and strongly reduces its tendency to form hydrogen bonds [4].

Starch can be utilized either in granular or gelatinized form as the granule architecture and size distribution of starch decides its functionality [5]. The inert granular structure of native starch is composed of macromolecules in polycrystalline state [6]. Chemical modification of starch via graft copolymerization improves its properties such as sorbancy, ion exchange capabilities, elasticity, thermal resistance and resistance to microbiological attacks with antimicrobial agent [7–9].

For biosheets preparation various plasticizers can be used such as diethylene glycol, β -lactoglobulin, dioctyl phthalate, dioctyl adipate, glycerol, MMA, Polymerized methyl methacrylate (PMMA), etc [10–12]. MMA is used in imparting hardness, flexibility, clarity, colour compatibility, toughness, internal plasticization and weatherability to the sheets. Several reports showed that MMA was grafted in co-ordination with natural rubber latex which resulted in an increase in the tear strength of sheets and improved anti ageing properties [13]. Also the grafting of MMA over cellulose nitrate by benzoyl peroxide has been reported [14]. MMA has also been reported in the formation of Photocured Chitosan/Starch blend sheets [15]. For the production of extrusion shaped products, graft copolymers of starch with methyl methacrylate (MMA) and styrene have been used [16].

In these studies we will compare the mechanical and water absorptive properties of SG and SG-PMMA; therefore the study was designed with the objective to prepare sago starch based sheets

grafted with biocompatible polymer (MMA) with the goal of developing a more water resistant material that could be used for wound dressing.

2 MATERIALS AND METHODS

2.1 Materials

Sago rice was purchased from the local retail shop and was powdered using the domestic mixer. Methyl methacrylate (MMA) was purchased from Fluka Sigma-Aldrich, USA. Potassium persulfate, Sodium metabisulfate and all the other chemicals used were of analytical grade.

2.2 Methods

2.2.1 Preparation of sago solution

50 grams of sago powder was dissolved in 500 ml of distilled water and boiled till a homogeneous solution is formed. This solution was stored and used for further experiments.

2.2.2 Preparation of sago starch sheet (SG)(Ref)

25 ml of starch solution was taken and diluted to 50 ml using distilled water. To this solution 2 ml of ethylene glycol was added and mixed thoroughly. This solution was poured into polythene tray measuring 12 x 10 cm and dried at room temperature (34 - 35⁰C). The dried sheet was stored in polythene cover for further analysis.

2.2.3 Graft co-polymerization of sago starch with MMA (SG – PMMA) (Ref)

25 ml of sago solution was taken and diluted to 50 ml using distilled water. This solution was heated to 60⁰C and 0.25 gm of Potassium persulfate and 0.25 gm of sodium metabisulfate were added. These experiments were done using a three-necked round bottom flask fitted with a condenser, thermometer and an inlet flask. After attaining 60⁰C, 5 ml of MMA was added and the contents were stirred using magnetic stirrer for 30 minutes. Later 2 ml of ethylene glycol was added and continued stirring for another two minutes. The contents were poured into a polythene tray and dried at room temperature (33-35⁰C). The dried sheet was stored in a polythene cover for further analysis.

2.3 Characterization

The prepared sheets were characterized by mechanical properties, water absorption studies, IR, SEM and EDX.

2.3.1 Mechanical Studies

Three dumbbell-shaped specimens of 4 mm wide and 10 mm length were punched out from the prepared sheets using a die. Mechanical properties such as tensile strength (MPa), tearing strength and percentage of elongation at break (%) were measured using a universal testing machine (INSTRON model 1405). The results given are average of three specimens.

2.3.2 Infrared Spectroscopy

IR spectroscopy of SG and SG-PMMA was taken using Nicolet impact 400 FTIR spectroscopy by preparing a 500 mg KBr pellet containing 2-6 mg of the sample.

2.3.3 Water absorption capacity

Estimation of water absorption capacity was done by the method explained by Rao et al [17]. The water absorption capacity of samples prepared was determined by swelling small pieces of each sample of known weight in distilled water at room temperature. The weights of the samples after swelling were determined by first blotting the samples with filter paper followed by accurately weighing the sample. The weights of the swollen pieces were recorded every 1 h, 2 h, 3 h and after 24 h. Percentage swelling of the samples at a given time was calculated from the formula:

$$ES = \frac{W_s - W_o}{W_o} \times 100$$

Where W_s is the weight of the sample (moist) at given time, W_o is the initial weight of the sample and E_s is the percentage of swelling at a given time. The results given are average of three samples.

2.3.4 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX)

SEM measurements were carried out on a Leica stereo scan-440 scanning electron microscope equipped with phoenix EDX attachment. The EDX spectrum was recorded in the spot profile mode by focusing the electron beam onto the specific regions of the sheet.

3 RESULTS AND DISCUSSION

3.1 Tensile strength

Tensile strength of the SG and SG-PMMA sheets are given in the Table 1. The tensile strength of the SG-PMMA sheet was found to be around 0.85 MPa and that of control was 0.89 MPa, where as the extension at break of the polymerized sheet was less. The brittleness may be due to the plastic nature of the polymer MMA.

3.2 Tearing strength

Tearing strength of the SG and SG-PMMA are given in the Table 1. The tearing strength of control sheet (SG) was very high that is 9.33 N in comparison to the polymerized sheet (SG-PMMA) showing 5.80 N. The hydrogen bonding between the two hydroxyl groups of the natural starch sheet (SG) gives good tearing strength, whereas in the polymerized sheet (SG-PMMA) the hydroxyl groups are graft co-polymerized & exhausted. This may be the reason for the elastic reduction in the tearing strength of polymerized sheet.

3.3 Water absorption capacity

The water absorption capacities of the samples are given in Table 2. In the SG sample there is a gradual increase in the percentage of water absorption. Similar trend was observed in the polymerized sheets but the percentage of water absorption was much less when compared with those of the control sheets. The PMMA was graft co-polymerized through -OH groups of sago starch. As the hydroxyl groups are blocked by the polymer the number of hydrophilic (-OH) are reduced and there by reduction in the water absorption capacity was observed in the SG-PMMA samples. This property may be useful when the modified starch solutions are used as coatings on the surface of the materials. When they are used as surface coatings they may absorb less water and hence prevent corrosion.

3.4 IR spectroscopy

IR spectrum of SG and SG-PMMA sheets are shown in Figures 1 and 2. The typical carbohydrate spectrum was shown in SG sheet. The -OH broad band was observed between 3200-3500 cm^{-1} with very sharp intensity. Similarly -OH in plane deformation vibration was observed between 1435-1378 cm^{-1} . The finger print region between 1182-1023 cm^{-1} confirms the nature of carbohydrate. The -CH₂-CH₂ stretching vibration was found at 2925 cm^{-1} . This IR spectrum conforms to that of typical carbohydrate spectrum. In the polymerized sheet we can observe the ester carbonyl (-C=O) group at 1734 cm^{-1} which confirms the polymerization of PMMA onto sago starch. The broadness of the -OH peak in SG-PMMA is also reduced indicating that the graft copolymerization of PMMA was occurred through -OH groups of the sago starch. The water absorption study also confirms these results.

3.5 Scanning electron microscopy

Scanning electron microscopy of SG sheet and SG-PMMA sheets are shown in Figures 3 and 4. The surface morphology of control sheet has shown a discontinuous sheet with some breakages. The polymerized sheet has shown continuous sheet. The graft copolymerization of PMMA has helped in the bondage of the starch molecules through -OH groups. Hence, the continuous sheet was observed in the electron micrograph of polymerized starch sheet.

3.6 EDX

The EDX spectrum is shown in Figure 5. In the EDX spectrum of SG sheet the presence of Magnesium, Calcium and Phosphorus were observed. These peaks represent the elements in the sago starch. In the grafted SG spectrum apart from Magnesium, Calcium and Phosphorous the Sulphur and Potassium peaks were also observed. The presence of these elements is due to the presence of initiators in the sheet.

4 CONCLUSIONS

The graft co-polymerization of PMMA over sago starch has attributed a continuous sheet forming nature. The continuous polymerized sheets can act as a good substitute for the discontinuous conventional sago starch sheets. Polymerized sheets possessed a substantial tensile

strength and much lower tearing property with least % elongation at break. Hence the SG-PMMA sheets when used as surface coating agents will absorb less water and avoid corrosion.

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Table 1. Mechanical properties of SG and SG-PMMA sheets

S. No.	Sample	Tensile Strength (MPa)	Elongation at break (%)	Tearing Strength (N)
1.	SG	0.89 ± 0.05	25.83 ± 1.5	9.33 ± 0.08
2.	SG-PMMA	0.85 ± 0.03	54.83 ± 0.9	5.80 ± 0.03

Values are expressed as mean ± SD for six individual experiments. Within a line, values without a common letter are significantly different from the control group at $p < 0.05$ as determined by ANOVA.

Table 2. Water absorption capacity of SG and SG-PMMA sheets

S. No.	Sample	1 hour (%)	2 hours (%)	3 hours (%)	24 hours (%)
1	SG	281.4 ± 7.3	359.94 ± 9.1	479 ± 10.3	493.18 ± 10.5
2	SG-PMMA	77.5 ± 3.3	84.29 ± 3.9	94.93 ± 4.4	98.73 ± 4.8

Values are expressed as mean ± SD for six individual experiments. Within a line, values without a common letter are significantly different from the control group at $p < 0.05$ as determined by ANOVA.

Legends to the figures

Figure 1: IR spectrum of SG sheet shows finger print region between 1182–1023 cm^{-1} confirming carbohydrate nature.

Figure 2: IR Spectrum of SG-PMMA sheet shows ester carbonyl ($-\text{C}=\text{O}$) group at 1735 cm^{-1} confirming the polymerization of PMMA onto sago starch.

Figure 3: SEM image of SG sheet shows discontinuous nature with some breakages.

Figure 4: SEM image of SG-PMMA sheet shows continuous nature.

Figure 5: EDX spectrum of SG-PMMA sheet shows peak of elements such as Magnesium, Calcium, Phosphorous, Sulphur and Potassium indicating the presence of initiators in sheet.

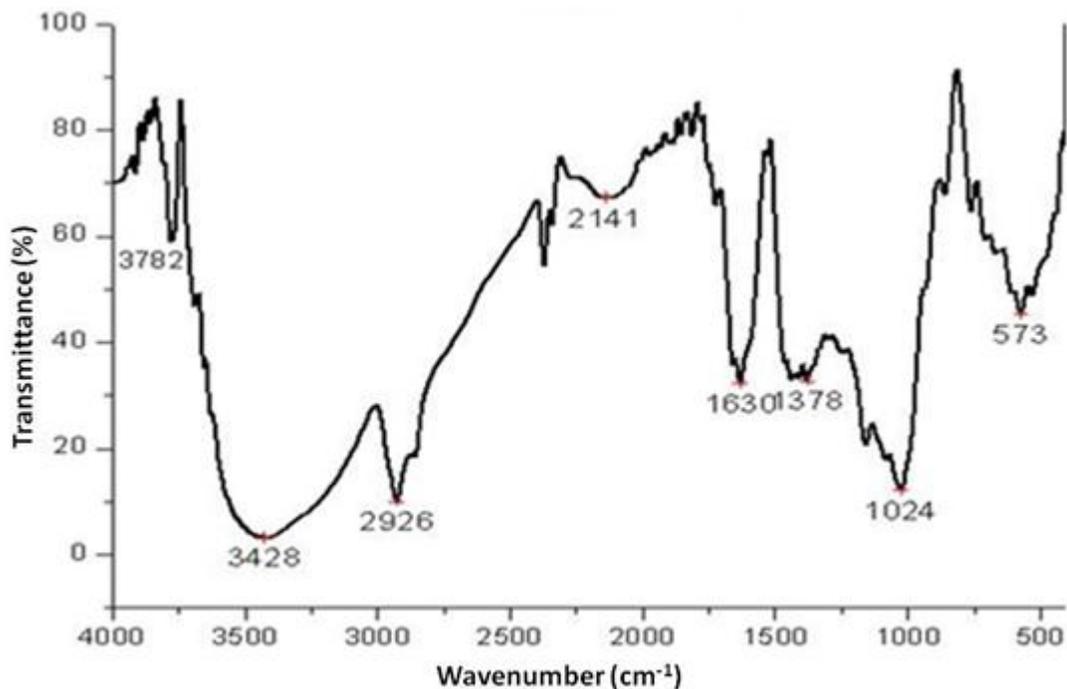


Figure 1

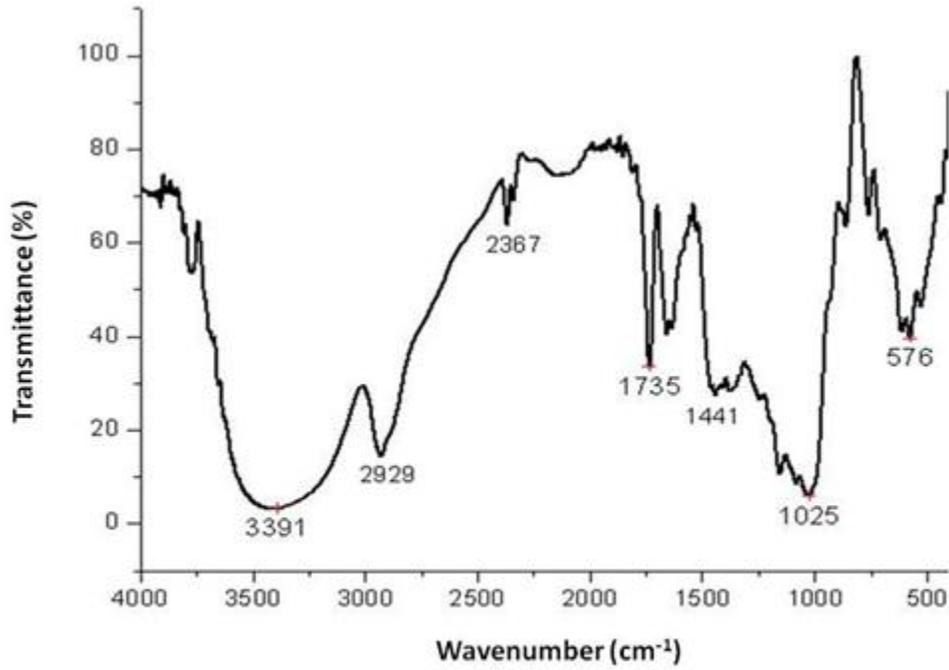


Figure 2

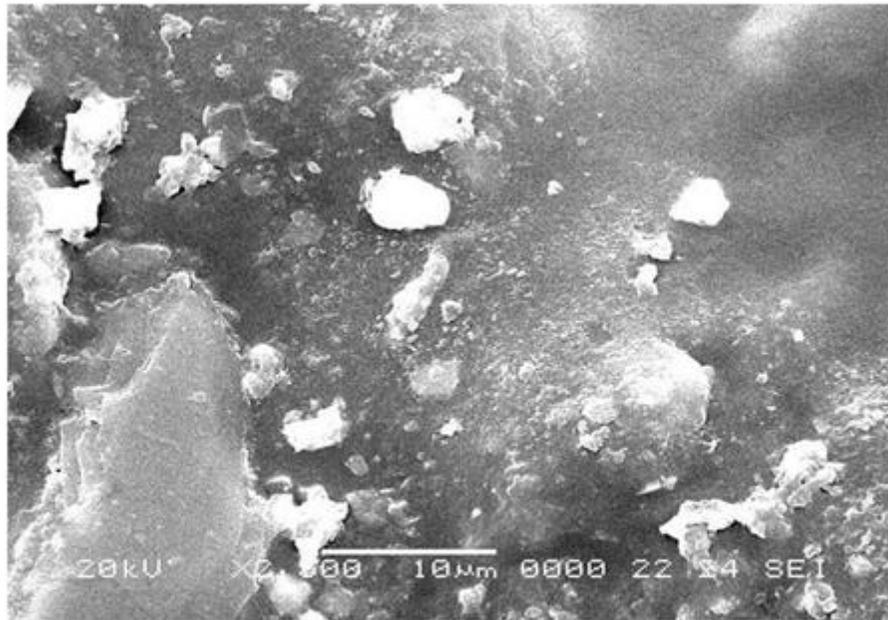


Figure 3

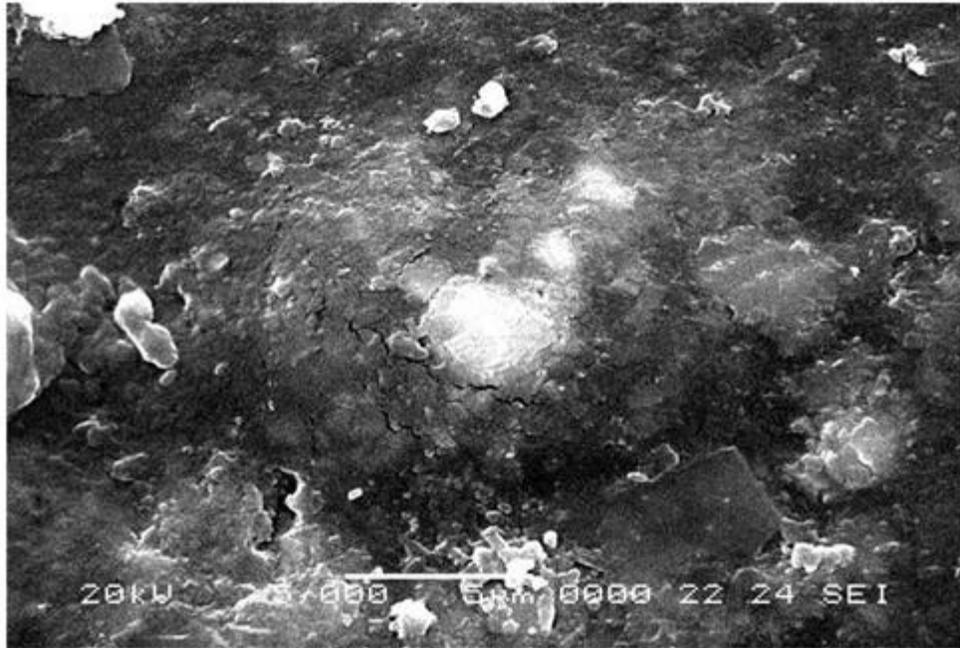


Figure 4

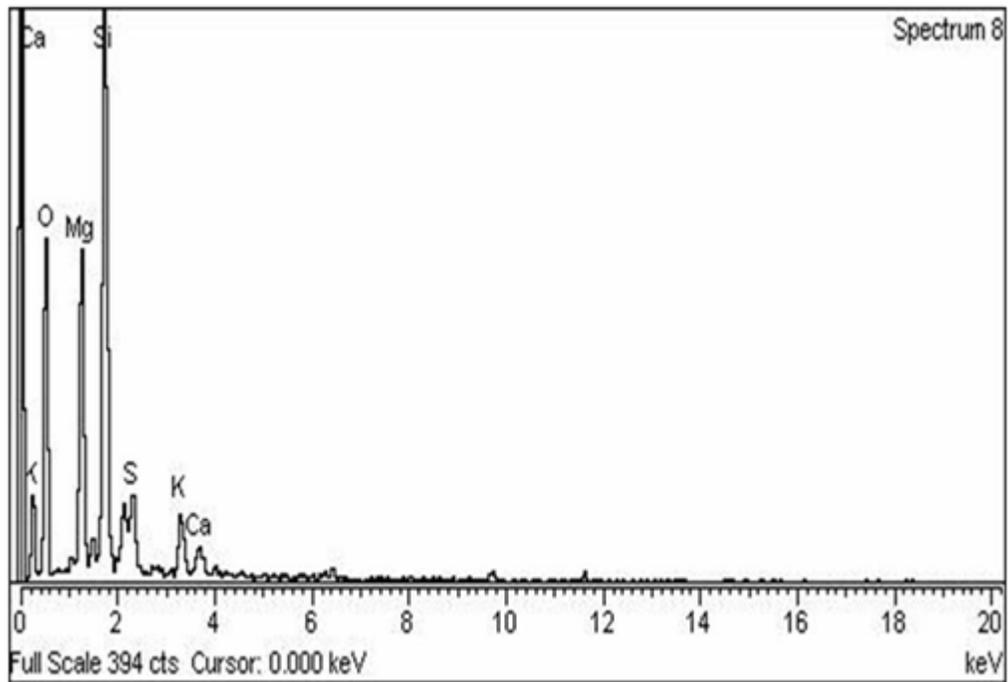


Figure 5