

# Synthesis and Characterization of Graft Copolymer of Sago Starch- g- Poly (Acrylamide) Using Potassium Persulphate Initiator

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**Abstract:** The graft copolymerization of Acrylamide onto Sago Starch by free radical polymerization using Potassium persulphate as initiator was investigated. The optimum conditions for grafting have been evaluated by studying reaction variables, viz. polymerization time, material- to- liquor ratio and solvent. The formation of graft copolymers was confirmed by three methods namely, gravimetric estimation, FTIR spectroscopy and X- ray diffraction.

**Index Terms:** Acrylamide, Graft copolymerization, Gravimetric estimation, Potassium persulphate, Sago starch, X- ray diffraction

## I. INTRODUCTION

Starch is a natural polysaccharide having numerous repeating units joined via  $\alpha$ - D-glycosidic bonds. It is a biopolymer of great potential and is user- friendly and consumer- friendly because it is biodegradable, biocompatible, non- toxic and less expensive. The graft copolymerization of vinyl monomers onto natural polysaccharides has received widespread interest in recent years. This technique is a powerful tool which brings about substantial modification in chemical properties of starch there by widening the range of its utilization. The finished product can be reduced to particles small enough to be of minimal damage to the environment by losing its integrity in a period of time.

Though much work has been reported on the grafting of acrylamide onto various starches such as potato (Athawale V. D., 1998; Baser. K. & Lele V., 2015; Fang J. M., 2005; Lele V., 2015a, 2015b; Singh et al., 2007), maize (Abdel-Razik E. S. A., 2015; Athawale V. D. & Lele V., 1998; Samaha S. H. & Nasr H.

E., 2005), cassava (Kiatkamjornwong S., 2002; Noordergraaf I. W., 2018) comparatively less attention has been paid to the grafting of acrylamide onto sago starch. Athawale et al. (1998) have described the effect of reaction variables for the grafting of acrylamide (AM) onto maize starch using ceric ion as initiator and have established optimum conditions for grafting. Khalil et al (1993) have reported various factors affecting the grafting of AM onto maize starch using potassium persulphate system to initiate the reaction. Shrogen et al (2009) reported Horse Radish Peroxidase (HRP) - mediated grafting of AM onto. Lanthong et al. (2006) synthesized biodegradable superabsorbents based on cassava starch grafted with acrylamide and itaconic acid in presence of ammonium persulphate initiation system. In another study, Nakason et al (2010) reported the synthesis of superabsorbent polymer using cassava starch grafted with acrylamide by reactive blending. These various reports on grafting of AM onto various starches, generated interest in us to extending such study to sago starch. Lele & Savita (2018) have reported the optimization of three reaction parameters i.e. initiator concentration, monomer concentration and polymerization temperature, of sago starch grafted with acrylamide in earlier article. In view of the same, it appeared worthwhile to extend our studies over other parameters. Thus, the present work reports the effect of polymerization time, material- to- liquor ratio and presence of alcohol as solvent on the grafting of AM onto sago starch using persulphate as an initiator.

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## II. EXPERIMENTAL

### A. Materials

Pure Sago starch (SG), Food Grade was dried at 110° C in a vacuum oven for about 10 h to remove absorbed moisture which was experimentally found to be an optimum time for drying starch to constant weight. It was then stored over anhydrous CaCl<sub>2</sub> in a desiccator. Potassium persulphate (PPS) (AR Grade, Research- Lab Fine Chemical Industries, India), was used as it is. Acrylamide (AM) [LR Grade, Loba Chemie, India] was used as supplied.

### B. Synthesis of Graft Copolymer

Uniform slurry of 2 g dried sago starch in 70 mL distilled water was prepared by stirring in presence of air at 400 rpm using magnetic stirrer. The slurry was treated with predetermined quantity of PPS for 10 minutes to facilitate free radical formation. Then a known amount of monomer (AM) was added to the reaction mixture and total volume was made to 100 mL with distilled water and stirred magnetically for desired time. At the end of reaction, the graft copolymer obtained in the reaction mixture was made free from homopolymer by filtering through preweighed Whatmann filter paper no. 41. This was followed by repeatedly washing with warm water, to ensure complete removal of homopolymer of Acrylamide (PAM). Finally, the resulting sago starch grafted poly (acrylamide) (S-g-PAM) was dried at 80°C in a vacuum oven for 24 hours to remove excess of water and then was weighed. Control reactions were carried out with 2g sago starch under similar reaction conditions except the addition of monomer.

### C. Grafting Parameters

The percentage grafting efficiency (%GE), percentage grafting (%G) and % Add-on were calculated using following formulae ( Athawale V. D. et al., 1998; Athawale V. D., 1998; Athawale V. D. & Lele, 1998; Lele V., 2015a, 2015b; Lele V., Savita K., & Harshada N., 2018):

$$\%GE = 100(W_2 - W_1)/W_3$$

$$\%G = 100(W_2 - W_1)/W_1$$

$$\% \text{ Add-on} = 100(W_2 - W_1)/W_2$$

Where, W<sub>1</sub>, W<sub>2</sub> and W<sub>3</sub> are the weights of starch, graft copolymer and monomer respectively. Percentage Grafting (%PG) gives graft copolymer yield with reference to weight of starch (backbone polymer), while grafting efficiency (%GE) gives yield with reference to weight of monomer in feed.

### D. Infra-Red Spectral Analysis

The IR spectra of sago starch and S-g-PAM samples were taken with Shimadzu FTIR 4200 spectrophotometer using KBr pellets in the frequency range of 4000 – 400 cm<sup>-1</sup>.

### E. X-Ray Diffraction Studies

The X- ray diffraction studies were carried out using Shimadzu- Maxima-7000. The graft copolymer and pure sago starch granules were scanned on XRD between 5° to 80°.

## III. RESULTS AND DISCUSSION

### A. Physical Appearance

All the graft copolymers synthesized in the present study were off white in color and were either amorphous powder or in the form of brittle flakes.

### B. Evidence for Grafting

All the graft copolymers synthesized in the present study were off white in color and were either amorphous powder or in the form of brittle flakes.

#### 1) Gravimetric Estimation

The graft copolymerization reactions were monitored gravimetrically which forms the confirmatory test by physical method. The homopolymer of acrylamide (PAM) is highly soluble in water, and hence was easily eliminated by repeated washings with water. In spite of extraction of homopolymers, there was a remarkable gain in weight of the residue, over control reactions, which confirmed the grafting of AM onto starch. This weight gain in starch formed the basis for the determination of %GE, %G and % Add-on. It was further observed that there was a loss 0.06 g of starch per 2 g of starch in control reactions. Hence, this was taken as a correction factor and was added to the weight of actual residue obtained in graft copolymerization.

#### 2) Infra-Red Spectral Analysis

The evidence of grafting of AM on to sago starch was confirmed by the change in the chemical structures as observed in IR spectra of pure sago starch and sago starch grafted with AM which is shown in Fig. 1. Comparison of IR spectra of pure sago starch and S-g-PAM indicates the presence of a broad band due to –OH stretching vibrations of anhydroglucose units (AGU) at 3301.60 cm<sup>-1</sup>(Fig. 1 (A)). It is observed that there is shifting of this peak from 3301.60 cm<sup>-1</sup> to 3296.91 cm<sup>-1</sup> in the spectrum of S-g-PAM (Fig. 1 (B)) indicating the participation of –OH groups of AGU in chemical reaction. Also the strong peak at around 3296.91 cm<sup>-1</sup> in grafted starch is due to merging of N-H and O-H Stretching absorption bands. In addition grafted copolymer also showed bands at 1635 cm<sup>-1</sup> due to C=O stretching of amide functional group and aliphatic C-H stretching vibration present at 2928.36 cm<sup>-1</sup>; –CH<sub>2</sub> scissoring vibration at 1335.92 cm<sup>-1</sup>; 1148.89 cm<sup>-1</sup> band due to –CN stretching vibrations of amide group; C-O stretching vibration at around 1078.13cm<sup>-1</sup>, a typical for the saccharide moiety, are common to both starch and grafted starch. This confirms

beyond doubt the existence of grafting (Athawale V. D., 1998).

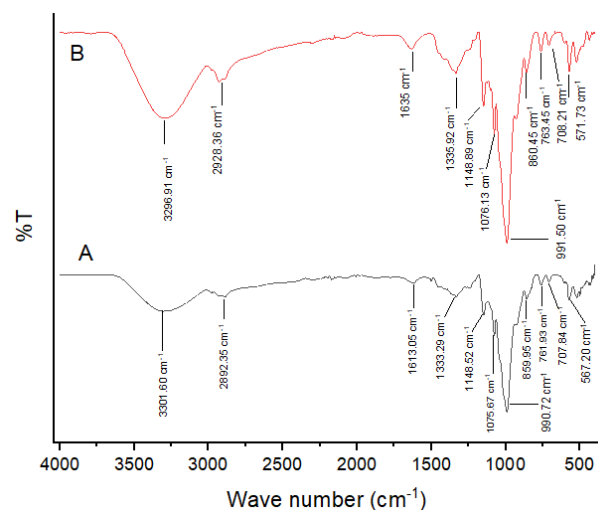


Fig. 1. IR Spectra of (A) Sago Starch (SG) and (B) S-g-PAM

### 3) X-Ray Diffraction Studies

X-ray diffraction study is another physical method of confirmation of grafting. Starch granules are semi-crystalline in nature due to amylopectin fraction that exists in it. About 20 – 25% of the total volume of the starch granule covers areas of crystallinity (Swinkles J. J. M., 1985). The

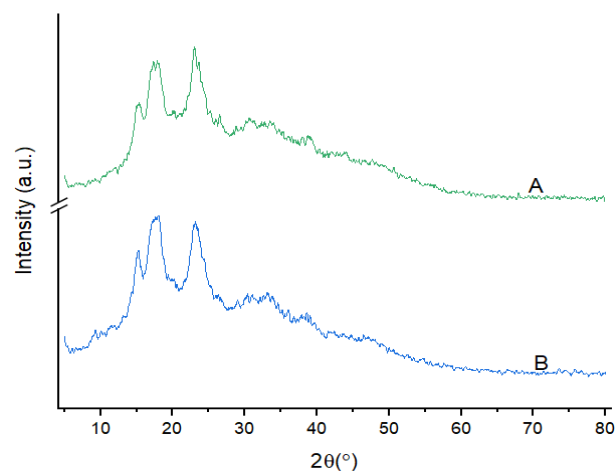


Fig. 2. XRD of (A) Sago Starch (SG) and (B) S-g-PAM wide angle X-ray diffraction pattern of pure sago starch (Fig. 2 A) comprises three more or less sharp peaks with low counts (merely up to 650) between  $2\theta$  values of  $10^\circ - 30^\circ$ . On grafting the peak counts reduced up to 370 of grafted starch (Fig. 2 B). It can therefore be concluded that there is alteration in the crystallinity of pure granular starch and hence along with the amorphous region, the crystalline region is also involved in grafting (Gao J., Tian R., & Yu J., 1994).

### C. Effect of Polymerization Time

Table I illustrates the effect of polymerization time on the grafting of AM onto sago starch. Grafting increases till 90 min., thereafter it levels off. Hence 90 min. is taken as the optimum polymerization time. Initial enhancement in grafting parameters i.e. % G, %GE and % Add-on can be due to increase in the extent of initiation and propagation of graft copolymerization with time causing addition of monomers to the growing grafted chains. However, beyond 90 min., the leveling off of the extent of grafting is perhaps a direct outcome of depletion of the monomer.

Table I. Effect of polymerization time on the grafting of AM onto sago starch in presence of PPS

Time (minutes)	%G	%GE	% Add On
15	1.15	2.30	1.14
30	1.70	3.40	1.67
60	2.40	4.80	2.34
90	5.85	11.70	5.52
120	5.80	11.60	5.48
150	5.80	11.60	5.48
180	5.75	11.50	5.43

Reaction conditions: Sago starch = 2g, [PPS] = 0.004 mol/L, [AM] = 0.141 mol/L at  $40^\circ\text{C}$ ; total volume made to 100mL of distilled water.

### D. Effect of Material to Liquor Ratio

The desired material- to- liquor ratio was achieved by altering the volume of water in the reaction medium. It can be seen from Table II that reduction in the volume of water to less than 100 mL, results in enhancement in the rate of grafting.

Table II. Effect of material – to – liquor ratio on the grafting of AM onto sago starch in presence of PPS

Material to liquor ratio	Volume of liquor (mL)	%G	%GE	% Add On
1:33.33	100	5.50	11.00	5.21
1:26.66	80	8.30	16.60	7.66
1:20	60	8.65	17.30	7.96
1:16.66	50	6.90	13.80	6.45
1:13.33	40	5.85	11.70	5.52
1:6.66	20	3.40	6.80	3.28

Reaction conditions: Sago starch = 2g, [PPS] = 0.004 mol/L, [AM] = 0.141 mol/L, for 90 min., at  $40^\circ\text{C}$

This can be attributed to:

1. Better orientation of monomers in the reaction medium with respect to free radical sites on starch backbone
2. Greater kinetic probability of collision between them

Nevertheless, the ratio of 1:20 was taken as the optimum ratio for the grafting of AM onto sago starch. Further decline in the quantity of liquor led to decline in %G which can be ascribed to the restricted motion of the monomer molecules.

#### E. Effect of Solvent

Acrylamide (AM) is highly soluble in water. Hence, it was decided to study the effect of presence of various alcohols having different dielectric constants (Table III) on the grafting parameters.

Table III. Dielectric constant values of different solvents

Solvent	Dielectric constant
Water	81.0
Methanol	32.7
Ethanol	24.5
Isopropanol	17.9

Reaction conditions: Sago starch = 2g, [PPS] = 0.004 mol/L, [AM] = 0.141 mol/L, for 90 min., at 40°C

Water and alcohol were taken in the ratio of 4:1 keeping the total volume of the reaction to 100 mL. Table IV illustrates the effect of solvent on graft copolymerization of AM onto starch.

Table IV. Effect of solvent on the grafting of AM onto sago starch in presence of PPS

Solvent	Dielectric constant of medium	%G	%GE	% Add On
Water	81.0	5.50	11.00	5.21
Water : Methanol	71.3	4.40	8.81	4.21
Water : Ethanol	69.7	3.96	7.93	3.81
Water : Isopropanol	68.4	3.60	7.20	3.47

Reaction conditions: Sago starch = 2g, [PPS] = 0.004 mol/L, [AM] = 0.141 mol/L at 40°C; total volume made to 100mL of distilled water. Water: Alcohol = 4:1 (v/v)

Both %G as well as %GE decreases from methanol to isopropanol as:

1. Molecular weight of alcohol increases
2. Size of non – polar hydrocarbon group increases
3. Miscibility of alcohol with water decreases
4. Dielectric constant decreases

So it can be said that high dielectric constant in turn the polarity of the medium favors the grafting reaction. This is because both starch & AM are polar. Hence, pure water was the most suitable medium for grafting of AM onto sago starch.

#### CONCLUSION

It is possible to graft acrylamide onto sago starch in presence of persulphate as an initiator. In the present study, the optimum conditions for effective grafting of [AM] = 0.141 mol/L on to 2g of sago starch using 0.004 mol/L of PPS at a temperature of 40°C has been established as: Polymerization time = 90 min., Material- to Liquor ratio = 1:20, preferable in an aqueous medium.

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