

Graft Copolymerisation of Acrylic Acid onto Starch and A Study of its Grafting Parameters

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Abstract: The graft copolymerisation of sago starch with acrylic acid was initiated by using persulphate as chemical initiator. The effects of reaction variables such as material to- liquor ratio and presence of alcohol in reaction medium, on grafting parameters such %G,%GE and % Add on, were studied. The optimum reaction conditions were obtained. The conclusions were drawn on the basis of observations made. The formation of graft copolymer of starch was confirmed by the gravimetric estimation and infra-red spectroscopy study.

Index Terms: acrylic acid, graft copolymerisation, infra-red spectroscopy, persulphate, sago starch.

I. INTRODUCTION

Starch is one of the mostly abundantly available source of bio-polymer. It is present in various parts of plants such as roots, leaves, tubers and trunks. Sago starch is present in the pith of sago palm stems *Metroxylon Sago* (Abbas., 2008; Takeda Y. et al., 1989) and can be considered as one of the important available starch for present and future study.

The modified starches are found to have better physico-chemical properties as compared to pure starches. Hence we decided to study different methods of modification of starch. Modified starches show enhanced applicability in various fields (Bertolini, 2010) such as preparation of thermoplastics (Fang J.M., et al., 2002), thickeners (Bayzeed, et al., 1989), in the preparation of bio adhesives grafted starch copolymers as platforms for controlled drug delivery (Geresh S., et al., 2002)

Starch can be modified by grafting it with vinyl monomers using either range of chemical initiators or by employing physical methods such as U.V./gamma irradiation of starch, mastication, milling or freezing and thawing cycle methods for generating free radicals at the starch backbone (Zenash T.,

1969). Physical methods like mastication, milling and freezing and thawing cycle methods have many disadvantages and hence not preferred. Thus, chemical initiation method becomes the most viable one.

Pure sago starch constitutes the major diet component of South East Asian countries and is devoured in the form of vermicelli, biscuits, crackers and bread (Karim A.A. et al., 2008). It is also used for making adhesives for textiles, plywood, ethanol (Bandaru V.V.R., 2006), and paper industries as well as stabilisers in pharmaceuticals.

Modified sago starch with improved physical properties has wide applications (Abbas, 2008). Graft copolymerisation of sago starch with acrylic acid results in range of applications in its hydrogels in medical (Al-Karawi, 2010) and hygiene products, construction of buildings and in food packaging. (Inderjeet K., 2012). Hence we found it interesting to study the effects of factors such as polymerization time, material- to-liquor ratio and presence of alcohol in reaction medium on the grafting parameters of Sago starch-g-acrylic acid. (Mostafa, Kh. M. 1995; Chen Y., Liu S., Wang G., 2007).

II. MATERIALS AND METHODS

Sago starch in pure powdered form was made available from Yiak Say Hang Food Industries(S) PTE Ltd., Singapore. It was dried at 70° C for approximately 10 h to constant weight to make it free of any moisture. It was then cooled and kept in a desiccator. Potassium persulphate (AR) and acrylic acid (AR) were procured from S.D. Fine Chemicals, India. Acrylic acid was refrigerated and was brought to room temperature before use. Dried starch and potassium persulphate were kept in a desiccator containing anhydrous calcium chloride to avoid moisture absorption.

2g of sago starch was weighed and mixed and stirred for 10 minutes with 70ml of distilled water to obtain a uniform slurry.

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To the starch slurry a predetermined amount of potassium persulphate was added and then again stirred for 10 minutes to ensure the formation of free radical sites on starch substrate. This was followed by addition of certain quantity of acrylic acid and then the total volume was made to 100 mL using distilled water.

The reaction mixture was stirred continuously at a constant rate for a fixed time period. It was then filtered through a dried and pre-weighed Whatmann filter paper number 41. The residue obtained was washed thoroughly with water to extract the homopolymer of AA as it is soluble in water. The residue obtained is the graft copolymer of our interest which is then dried in a vacuum oven.

A control reaction was also carried out under similar conditions except the addition of monomer.

The same procedure was repeated by varying reaction period, material to- liquor ratio and solvent medium.

A. Grafting Parameters

The percentage grafting efficiency (%GE), percentage grafting (% G) and % Add on were calculated as follows (Eromosele, 1994)

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

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

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

Where W_1 , W_2 and W_3 correspond to the weights of pure sago starch, graft copolymer and monomer charged respectively.

The average loss in weight based on control reactions was added while calculating grafting parameters.

B. Infra-red Spectroscopy

The insoluble sago starch and graft copolymer i.e. S-g-AA samples were run in the form of KBr pellets on Shimadzu FTIR 4200 spectrophotometer in the frequency range of 4000 – 400 cm^{-1} to obtain the Infra-red spectra.

III. RESULT AND DISCUSSION

In the present study, sago starch is modified by grafting acrylic acid onto it using persulphate as a chemical initiator by varying one factor at a time to understand its effect on grafting.

The formation of graft copolymer was confirmed using gravimetric estimation method. A sizeable difference in the weights of grafted starch and pure starch was obtained. The correction factor based on control reactions compensates for the loss of starch during grafting. Needless to say, the increase in weight of starch is due to grafted acrylic acid. (Witono J.R., et al., 2012).

A. Infra-red Spectroscopy

On comparison of IR spectra of pure and grafted sago starch, a broad absorption band between 3450-3200 cm^{-1} which is characteristic of the glucosidic ring is noted. A slight increase in intensity of two peaks one between 2892.35 to 2922.08

cm^{-1} and another 1613.05 to 1634.90 cm^{-1} forms the basis of confirmation of grafting (Fig. 1).

Based on our earlier study, the effect of initiator & monomer concentration and reaction temperature for the grafting of AA on sago starch, the optimum conditions for the same are [AA] =

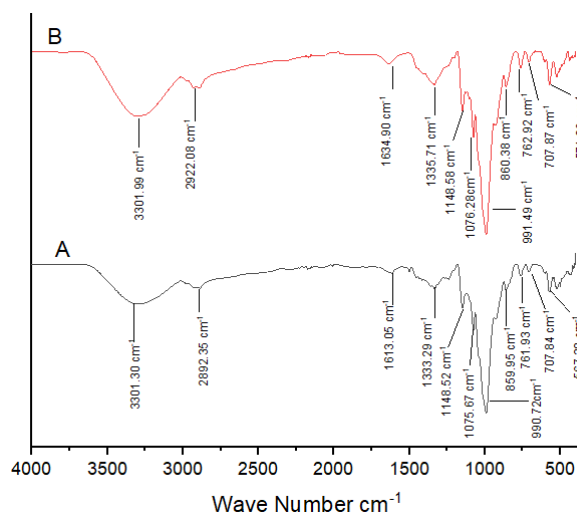


Fig. 1. IR Spectra of (A) Sago Starch (SG) & (B) S-g-AA 0.2775 mol/L; [PPS] = 0.002 mol/L at 40°C (Vidyagauri L. & Harshada N., 2018)

B. Effect of Material-to-liquor ratio

Table I reveals the effect of material-to-liquor ratio on the grafting parameters. The material-to- liquor ratio was changed by decreasing the quantity of water in the reaction mixture. It can be seen that the decrease in volume of water to less than 100 mL, leads to enhancement in extent of grafting (Athawale, V.D. & Lele V., 1998). This can be explained on the basis of improved orientation of the monomer molecules towards the active sites on starch backbone and also increase in the kinetic probability of collision between the two. The maximum grafting parameter values were obtained at material-to-liquor ratio of 1:25. Further decrease in the volume of liquor leads to decline in the %G, %GE and %Add on, maybe because of the restricted movement of the monomer molecule in comparatively lesser

Table I. Effect of material to liquor ratio on the grafting of acrylic acid on sago starch

Total Volume (mL)	Material-to- liquor ratio	% G	% GE	% Add on
80	1:40	5.75	5.48	5.44
70	1:35	5.70	5.43	5.39
60	1:30	6.50	6.19	6.10
50	1:25	7.50	7.14	6.98
40	1:20	5.30	5.05	5.03
20	1:10	5.40	5.14	5.12

Starch = 2g; [AA] = 0.275 mol/L; 0.001 mol/L PPS, Reaction temperature 40°C; Polymerisation time = 60 minutes.

volume of the reaction mixture. Hence, a material-to-liquor ratio 1:25 is most suitable.

C. Effect of Presence of Alcohol

Acrylic acid is slightly miscible with alcohol. Thus, it was decided to study the effect of presence of various alcohols on the

Table II. Effect of presence of solvent on grafting of acrylic acid on sago starch

Solvent	Dielectric constant of medium	% GE	%G	% Add on
Water	81.0	8.63	8.21	7.94
Water : Methanol	71.3	4.55	4.34	4.35
Water : Ethanol	69.7	3.88	3.69	3.73
Water : Isopropanol	68.4	2.58	2.45	2.51

Starch = 2g; [AA] = 0.275 mol/L; 0.001 mol/L PPS, Reaction temperature 40°C; Polymerisation time= 60 minutes, Alcohol 25mL; distilled water 75 mL; Total volume = 100mL

grafting parameters. Alcohol and water were added in the ratio 1:4 maintaining the total volume of the reaction to 100mL. The effect of presence of alcohol in the medium on the grafting parameters is shown in Table II.

The presence of alcohol in the reaction medium leads to decrease in the values of %G, %GE and %Add on from methanol to isopropanol. This can be attributed to the following reasons (Lele V., 2015)

Table III. Dielectric constant values of solvents

Solvent	Dielectric Constant
Water	81.0
Methanol	32.7
Ethanol	24.5
Isopropanol	17.9

1. Increase in the molar mass of alcohol
2. Increase in the size of non – polar hydrocarbon group
3. Decrease in miscibility of alcohol with water
4. Decrease in dielectric constant (Table III).

Thus, it can be interpreted that grafting reaction is favoured by the high dielectric constant and the polar nature of both the solvent and monomer. Nevertheless, one can prefer pure water over other solvents for grafting of AA onto sago starch as a reaction medium.

CONCLUSION

The grafting of sago starch with acrylic acid using persulphate as an initiator is possible. The study of effect of reaction variables such as polymerisation time, material-to-liquor ratio and

presence of alcohol in the reaction medium was successfully carried out. The optimum conditions were as follows

- 1) Material to liquor ratio = 1:25
- 2) In presence of pure water as reaction medium.

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