

## Graft Copolymerization of Vinyl Monomers onto Sago Starch

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### Introduction

Graft copolymerization of vinyl monomers onto a starch is an excellent method for preparing composites of starch with synthetic polymers<sup>1-3</sup>. Depending on the type of monomers used in the copolymerization reaction the products may be used as thickeners, absorbents, sizes, adhesives, flocculants, resins and plastics. Although various monomers, such as methyl acrylate, acrylic acid, hydroxyethyl methacrylate, acrylamide etc., have been successfully grafted onto starch from various sources (for example corn and potatoes) there apparently no study in this area has been done on sago starch. Sago starch is one of our commodities and is currently mainly used for food and food related products. Alteration starch properties by graft copolymerization widens the scope of its utilizations which consequently increase its economic important. The objective of this study is to synthesize and characterize of several graft copolymers prepared from several vinyl monomers and sago starch.

### Materials and Methods

All the monomers are purified by passing them through activated alumina columns. Graft copolymerization of these monomers onto sago starch is carried out by a batch method using a 250 mL three neck flask equipped with a mechanical stirrer, reflux condenser and thermostated water bath. Initiation process for the copolymerization is carried out using chemical techniques. To optimize the reaction conditions, effect of initiator concentration, reaction period, reaction temperature, monomer concentration and preswelling on the percentage of grafting and grafting efficiency are investigated. Removal of homopolymer from the grafted product is carried out by solvent extraction. The presence of functional groups on the polymer samples

is analyzed by FTIR spectroscopy. Thermal behavior of the polymers is examined by TGA and DSC. The morphology of the polymer surface is observed by the scanning electron microscope. Conversions of poly(methyl acrylate)- and poly(acrylonitrile)-grafted sago starches into poly(hydroxamic acid) and poly(amidoxime) chelating ion exchange resins are carried out by treating these starting polymers with hydroxylamine solutions.

### Results and Discussion

Optimum conditions for grafting acrylonitrile onto sago starch are as follows: concentration of ceric ammonium nitrate,  $9.52 \times 10^{-3} \text{ molL}^{-1}$ ; concentration of acrylonitrile,  $0.50 \text{ molL}^{-1}$ ; reaction temperature,  $50^\circ\text{C}$  and reaction period, 90 min. FTIR spectrum of poly acrylonitrile grafted starch clearly shows a sharp absorption peak at  $2244\text{cm}^{-1}$  which indicates the presence of nitrile group in the copolymer suggesting that polyacrylonitrile is successfully grafted onto the starch. This conclusion is also supported by TGA and DSC data. The percentage of grafting and grafting efficiency under the optimum conditions are 82 and 96% respectively.

Higher maximum percentage of grafting is obtained when methyl acrylate is grafted onto sago starch. It is 130%, which is about 50% higher compared with the percentage for the polyacrylonitrile-sago starch system. The experimental conditions to obtain the maximum percentage of grafting of methyl acrylate are as follows: concentration of ceric ammonium nitrate,  $8.77 \times 10^{-3} \text{ molL}^{-1}$ , concentration of the monomer,  $0.80 \text{ molL}^{-1}$ ; reaction temperature,  $50^\circ\text{C}$  and reaction period, 60 min. FTIR study of the purified copolymer clearly indicates the presence of carbonyl group suggesting that polymethyl acrylate is successfully grafted on the backbone polymer as

carbonyl group is only originated from the monomer. The different thermal behaviour of the original polymer and the graft copolymer, observed from DSC and TG thermograms, also supports that the grafting reaction is successfully carried out. The grafting efficiency for grafting methyl acrylate onto sago starch under the optimum reaction conditions is 82%.

Although polystyrene can be also grafted onto this starch, its percentage of grafting is only 54%, which is lower than the percentages for grafting polyacrylonitrile and polymethyl acrylate. The optimum conditions for obtaining the above percentage of grafting are: concentration of ceric ammonium nitrate,  $8.00 \times 10^{-3} \text{ molL}^{-1}$ ; concentration of styrene,  $1.75 \text{ molL}^{-1}$ , reaction temperature,  $50^\circ\text{C}$  and reaction period, 120 min. The presence of the styrene component on the grafted product is very difficult to detect directly from its FTIR spectrum, probably due to the insufficient amount of the styrene to be detected. The FTIR spectrum of the hydrolysed (to remove the starch component from the copolymer) product is identical to the pure polystyrene spectrum. This indicates that the styrene is successfully grafted onto the sago starch. The grafting efficiency of this copolymerization is 73%.

Studies on the preparation of 2-hydroxyethyl methacrylate(HEMA) grafted sago starch are conducted using ceric ammonium nitrate(CAN) and potassium persulphate(PPS) as the free radical initiators under a nitrogen atmosphere. The optimum conditions for HEMA grafting onto sago starch using CAN as an initiator are as follows: reaction period, 3h; reaction temperature,  $40^\circ\text{C}$ ; HEMA amount, 0.17 mol; CAN amount, 1.00 mmol. Meanwhile the conditions for the copolymer preparation using PPS an initiator are as follows: reaction period, 2h; reaction temperature,  $40^\circ\text{C}$ ; amount of PPS,

5.00 mmol and amount of HEMA, 0.05 mol. The percentage of grafting and grafting efficiency under optimum conditions for CAN initiation are 200% and 46% whereas for PPS initiation are 406% and 63% respectively.

Acrylic acid and methyl acrylate are also grafted onto sago starch using PPS as the initiator. The graft yields for both copolymerisations were reaction conditions dependent. Optimum conditions are: reaction temperature, 40°C; reaction period, 1.5h; amount of initiator, 10mmol and amount monomer, 0.02 mol for poly(acrylic acid) grafted sago starch and reaction temperature, 50°C; reaction period, 1.5h; amount of the monomer, 0.09 mol and amount of PPS, 8.33mmol for poly(methyl acrylate) grafted sago starch. TGA studies show that the grafted sago starches exhibit different thermal behavior as compared to gelatinised sago starch. SEM micrographs indicate that both acrylic acid and methyl acrylate are homogeneously grafted onto the starch. Poly(hydroxamic acid) and poly(amidoxime) chelating ion-exchange resins are successfully prepared from poly(methyl acrylate)- and poly(acrylonitrile)- grafted sago starches. Both resins show high binding metal ion capacities and rapid rate of metal ion extraction. The sorption of these resins towards metals ions were pH dependent and together with their high capacity and good kinetics of extraction, this could be used for metal ion extractions and separations. The water absorbency study of poly(hydroxamic acid) resin indicates that its water absorption capacity is poly(methyl acrylate) content dependent. The water absorbency of 192g/g is obtained at 69% of poly(methyl acrylate).

### Conclusions

Acrylonitrile, methyl acrylate, HEMA, acrylic acid and styrene are successfully grafted onto sago starch by free radical copolymerizations. Experimental conditions (temperature, reaction period and concentrations of the monomers, the backbone polymer and the initiator) are important parameters to determine the percentage of grafting and grafting efficiency. Poly(methyl acrylate)- and poly(acrylonitrile)- grafted sago starches were successfully converted into poly(hydroxamic acid) and poly(amidoxime) chelating ion-exchange resins.

### Benefits from the study

Polyacrylonitrile, polymethyl acrylate, poly(HEMA), poly(acrylic acid) and poly(styrene) grafted sago starches are new materials produced from sago starch. These copolymers are potential raw materials for many industrially important applications. This study also indicates that poly(methyl acrylate)- and poly(acrylonitrile)- grafted sago starches can be used to prepare chelating ion exchange resins and hydrogels.

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None.

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