

## GRAFT COPOLYMERISATION OF VINYL MONOMERS ON TO SAGO STARCH

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### Introduction

Graft copolymerisation of vinyl monomers onto a starch is an excellent method for preparing composites of starch with synthetic polymers (Athwale and Rathi, 1997; Bazuaye et al. 1989; Mostafa, 1995). Depending on the type of monomers used in the copolymerisation 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 used for food and food related products. Alteration of starch properties by graft copolymerisation widens the scope of its utilisation which consequently increases its economic important. The objective of this study was to synthesise and characterise of several graft copolymers prepared from several vinyl monomers and sago starch.

### Materials and Methods

All the monomers (styrene, acrylonitrile and methyl acrylate) are purified by passing them through an activated alumina column. Graft copolymerisation of these monomer onto sago starch was carried out by a batch method using a 250 ml three neck flask equipped with a mechanical stirrer, reflux condenser and thermostatic water bath. Initiation process for the copolymerisation was carried out using ceric ammonium nitrate. To optimise the reaction conditions, effect of initiator concentration, reaction period, reaction temperature, monomer concentration and preswelling on the percentage of grafting and grafting efficiency were investigated. Removal of homopolymer from the grafted product was carried out by solvent extraction. The presence of functional groups on the polymer samples is analysed by FTIR spectroscopy. Thermal behaviour of the polymers was examined by TGA and DSC. The morphology of the polymer surface was observed by the scanning electron microscope.

### Results and Discussion

Optimum conditions for grafting acrylonitrile onto sago starch are as follows: concentration of ceric ammonium nitrate,  $9.52 \times 10^{-3} \text{ mol}^{-1}$ ; concentration of acrylonitrile,  $0.50 \text{ mol}^{-1}$ ; reaction temperature,  $50^\circ\text{C}$  and reaction period, 90 min. FTIR spectrum of poly acrylonitrile grafted starch clearly showed a sharp absorption peak at  $2244 \text{ cm}^{-1}$  which indicates the presence of nitrile group in the copolymer suggesting that polyacrylonitrile was 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 was obtained when methyl acrylate is grafted onto sago starch. It was 130% that 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 were as follows: concentration of ceric ammonium nitrate,  $8.77 \times 10^{-3} \text{ mol}^{-1}$ ; concentration of the monomer,  $0.80 \text{ mol}^{-1}$ ; reaction temperature,  $50^\circ\text{C}$  and reaction period, 60 min. FTIR study of the purified copolymer clearly indicated the presence of carbonyl group suggesting that polymethyl acrylate was 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 was successfully carried out. The grafting efficiency for methyl acrylate onto sago starch under the optimum reaction conditions is 82%.

Although polystyrene can also be grafted onto this starch, its percentage of grafting was only 54%, which was lower than the percentages for grafting polyacrylonitrile and polymethyl acrylate. The optimum conditions for obtaining the above percentage of grafting were: concentration of ceric ammonium nitrate,  $8.00 \times 10^{-3} \text{ mol}^{-1}$ ; concentration of styrene,  $1.75 \text{ mol}^{-1}$ , reaction temperature,  $50^\circ\text{C}$  and reaction period, 120 min. The presence of the styrene component on the grafted product was 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 was successfully grafted onto the sago starch. The grafting efficiency of this copolymerisation is 73%.

### Conclusions

Acrylonitrile, methyl acrylate and styrene were successfully grafted onto sago starch by free radical copolymerisation using ceric ammonium nitrate as an initiator. Experimental conditions (temperature, reaction period and concentrations of the monomers, the backbone polymer and the initiator) were important parameters to determine the percentage of grafting and grafting efficiency. The grafting percentages of grafting acrylonitrile, methyl acrylate and styrene onto sago starch under optimum reaction conditions were 82, 130 and 54% respectively.

### References

- Athwale, V.D. and Rathi, S.C. 1997. Synthesis and characterization of starch-polymethacrylic acid) graft copolymer. *J. Appl. Polym.Sci.* 66: 1399-1403.
- Bazuaye, A., Okiemen, F.E. and Said, O.B. 1989. Graft copolymerization of acrylonitrile on starch. *J.Appl. Polym.Sci.* 38: 433-436.
- Mostafa, K.M. 1995. Graft polymerization of acrylic acid onto starch using potassium permanganate acid (Redox system). *J. Polym.Sci.* 56: 263-269.