

Full Length Research Paper

Studies in the graft copolymerization of acrylonitrile onto cassava starch by ceric ion induced initiation

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Graft copolymers of starch and acrylonitrile were synthesized in aqueous solution. Ceric ammonium ion was used to initiate the graft copolymerization. Ten grades of graft copolymers were synthesized-five by varying the initial concentration of the monomer and the other five by varying the initial concentration of the initiator. Evidence of graft copolymerization of the hydrolyzed products was obtained from the IR analyses. Some grafting parameters such as % grafting ratio and % conversion were favoured by initial increase in the monomer concentration. However, these parameters were observed to decrease at much higher concentrations (>3 M). Evidence of hydrolysis shows that the grafted copolymers could be used as flocculants.

Key words: Acrylonitrile, homopolymer, grafting initiator, starch.

INTRODUCTION

Carbohydrates comprise more than 90% of the dry weight of all biomass and more than 90% of the carbohydrate mass is in the form of carbohydrate polymer (Polysaccharides) (Zohuriaan-Mehr and Pour, 2003). Since polysaccharides are abundant from renewable sources and are relatively inexpensive, safe (non-toxic) and amenable to both chemical and biochemical modifications, it is not surprising that they find widespread and extensive use.

Graft copolymerization is a unique method among the techniques for modifying natural polymers mostly polysaccharides. Polysaccharide graft co-polymers have been prepared in order to add new properties to the natural polymer with a minimum loss of native properties (Fanta and Doane, 1986). Graft co-polymers are prepared by first generating free radicals on polysaccharides and then allowing these free radicals to serve as macro-initiators for the vinyl or acrylic monomer polymerization. Of the vinyl monomers grafted, acrylonitrile has been the most frequently used, mainly due to its highest grafting efficiency (Fanta and Doane, 1986; Athawale and Rathi, 1999; Athawale and Lele, 2000) and the subsequent alkaline hydrolysis of the grafting product to produce

starch - based water absorbent (Athawale and Lele, 2000).

In view of the growing interest and research activity in the use of renewable agriculturally derived products as extenders and replacement for synthetic petroleum - based polymers, incorporation of other monomers/ polymers into polysaccharides will not only reduce our dependence on petrochemical derivatives, but also provides improved materials which will biodegrade rapidly in the environment.

Since the last three decades, grafting of various monomers onto starch has been the most frequently attempted method to impart desirable properties on the polysaccharide without sacrificing its biodegradable nature. In the present study, acrylonitrile is grafted onto starch and the effect of varying the concentrations of the monomer and the initiator is examined.

MATERIALS AND METHODS

Materials

Acrylonitrile was extracted with aqueous sodium hydroxide - sodium chloride solution to remove inhibitor. Sodium hydroxide quinol, sodium chloride and methanol were obtained from BDH Ltd (Poole, England). Ammonium nitrate was purchased from Merck (Germany) and was used without purification. The cassava starch was

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Table 1. Grafting parameters at constant initiator concentration.

Monomer concentration (Mol/l)	Weight of Starch-g-polyacrylonitrile (g)	Weight of homopolymer + grafted polymer (g)	% Monomer conversion	% Grafting ratio (Gr)
1.00	11.01	1.01	12.67	10.01
2.00	12.06	2.06	12.93	20.60
3.00	13.87	3.87	16.19	38.70
4.00	12.64	2.64	8.29	26.40
5.00	12.56	2.46	6.43	25.60

purchased from an open market in Benin City, Nigeria and used without further purification.

Synthesis

Graft copolymerization of acrylonitrile onto starch was carried out using various amounts of the monomer and ceric ions and a constant amount of starch (10 g) dispersed in 100 ml of distilled water at 29°C. The polymerization procedure was based on the method described by Pourjavadi et al. (2006). In a typical experiment, 10 g of starch was dispersed in 100 ml of distilled water in a 250 ml flask. A given amount of monomer was added to the flask and the mixture was stirred for 10 min. Then the initiator solution was added to the mixture and continuously stirred for 3 h. The reaction was stopped by the addition of 2 ml of 5% (w/v) quinal solution to the reaction mixture. The mixture was poured into large excess of methanol with stirring to precipitate the polymer and then filtered. The residue was air dried and weighed.

Hydrolysis of the grafted copolymer

The grafted copolymer produced was hydrolyzed by adding 2M NaOH to the product in a 100 ml flask immersed in thermostated water bath fitted with magnetic stirrer and a reflux condenser. The hydrolysis was on for about 1½ h at 60°C. The pasty mixture was allowed to cool to room temperature and neutralized to pH8 by the addition of 10 wt% aqueous acetic acid solution. The mixture was poured into excess methanol to precipitate out. The precipitate was filtered and air dried.

GRAFTING PARAMETERS (Jideonwo and Okieimen, 2000)

The percent grafting ratio (Gr) is reported as the ratio of the weight of the grafted polymer to the weight of the substrate (starch) multiplied by 100.

$$\text{Gr}\% = \frac{\text{weight of grafted polymer}}{\text{weight of starch}} \times \frac{100}{1} \quad (1)$$

The percentage conversion is taken as the ratio of the weight of the grafted polymer to the weight of the monomer.

$$\% \text{ Conversion} = \frac{\text{weight of grafted polymer}}{\text{weight of monomer}} \times \frac{100}{1} \quad (2)$$

SPECTRAL CHARACTERIZATION

The graft copolymer before and after hydrolysis were characterized

by IR spectroscopy using KBr pellets on Shimadzu FTIR 4200 spectrophotometer.

RESULTS AND DISCUSSION

The backbone polymer (starch) was grafted with acrylonitrile monomer. The effects of monomer concentration on the level of conversion and quantities of grafted acrylonitrile on starch were investigated. Experiments were performed in the monomer concentration ranges of 1.00 - 5.00 mol/l. The initiator (ceric ammonium ion) concentration of 2M at a reaction temperature of 29°C for 3 h was used. The grafting parameters obtained are given in Table 1.

The results show that the grafting parameters increased initially with increase in monomer concentration and then decreased thereafter 3 M concentration. It has been established that the extent of graft copolymer formation depend on the amount of monomer complexed (Jideonwo and Okieimen, 2000). The increase in grafting ratio and percentage monomer conversion may be probably due to increasing supply of monomers to starch macroradicals and the nonexistence of homopolymer on acrylonitrile (Nayak and Singh, 2001). Maximum values of 38.70 and 16.9% were obtained for percentage grafting ratio and percentage monomer conversion respectively at 3 M monomer concentration. At higher monomer concentration (>3 M), the decrease in grafting parameters may be due to increasing trend of side reaction such as chain transfer to excess molecules in the vicinity of growing ends of grafted chains (Labet et al., 2007). Moreover, large amounts of homopolymer deposits may block the way of monomer molecules to the starch macroradicals resulting in further decrease in percentage monomer conversion and yield. Therefore 3 M was taken as the maximum concentration at which monomer (acrylonitrile) can be complexed. The effect of monomer concentration on the percentage monomer conversion is shown in Figure 1. Table 2 indicates the effect of varying the initiator concentration on some grafting parameter.

The result in Table 2 showed that, the percent grafting ratio and monomer conversion increased initially with an increase in the ceric ion concentration up to 3 M and decreased beyond this initiator concentration. The initial

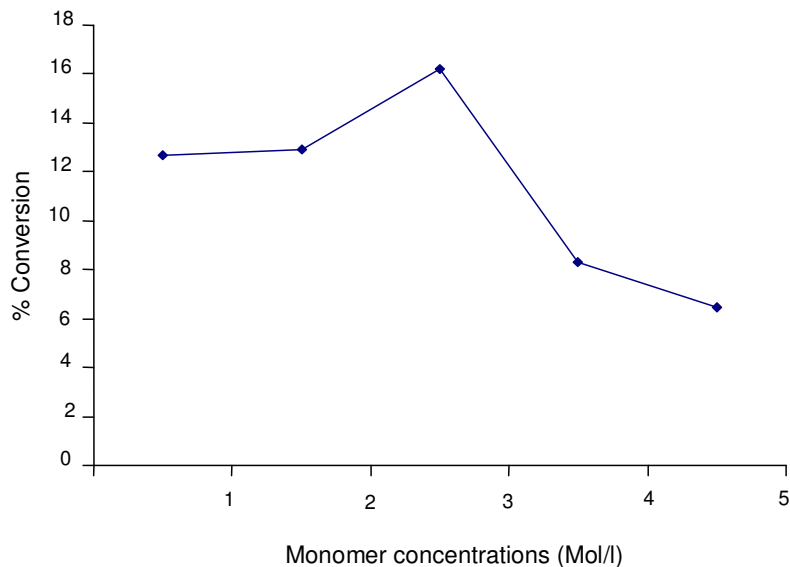


Figure 1. Effect of Monomer concentration on % monomer conversion.

Table 2. Grafting parameters at constant monomer concentration.

Ceric ion concentration (Mol/l)	Weight of starch-g-polyacrylonitrile (g)	Weight of homopolymer + grafted polymer (g)	% Monomer conversion	% grafting ratio (Gr)
1.00	11.65	1.16	2.91	11.60
2.00	12.56	2.56	6.43	25.60
3.00	14.23	4.23	10.62	42.30
4.00	14.20	4.20	10.55	42.00
5.00	11.83	1.83	4.59	18.30

increase may be explained in terms of the mechanism of ceric ion initiation which involves the formation of chelate complex that decomposes to generate free radical site on the polymer backbone (Athawale and Rathi, 1999). As the ceric ion concentration increased, the active free radicals on the starch backbone at which the monomer can be grafted also increased and these active free radicals in the presence of monomer generate graft copolymers (Nakason et al., 2004). The average number of grafting sites per backbone molecule depends on the concentration of the ceric ion, and the substrate (Pourjavadi and Zohuriaan-Mehr, 2002; Zohuriaan-Mehr and Pourjavadi, 2003). The results also showed that the grafting ratio reached the maximum value of 4.32% at 3 M ceric ion concentration which indicates the reduction equivalent of the polymer backbone (Nakason et al., 2004). The decrease in grafting ratio at 4 M ceric ion concentration may be attributed to the solubility limitation of the starch at higher ceric ion concentration. It may also be due to the termination of the growing grafted chains by excess of ceric ions. The reaction of free radicals on starch backbone to produce oxidized starch is incapable

of initiating polymerization. Figure 2 showed the trend in the percentage monomer conversion with change in ceric ion concentration.

Hydrolysis of the grafted polymer

Starch, on hydrolysis transforms to glucose which is soluble in water and does not precipitate with methanol. However when a solution of the grafted starch was poured in excess of methanol, the precipitate of the hydrolyzed grafted starch was obtained. This shows that the grafted starch could be used as flocculants.

SPECTRAL CHARACTERIZATION

The grafted copolymer and the non grafted starch were characterized by IR spectrophotometer. The spectra of the grafted copolymer showed the existence of a moderate peak at 2240 cm^{-1} as observed in Figure 3 which is an evidence of grafting. This absorption band

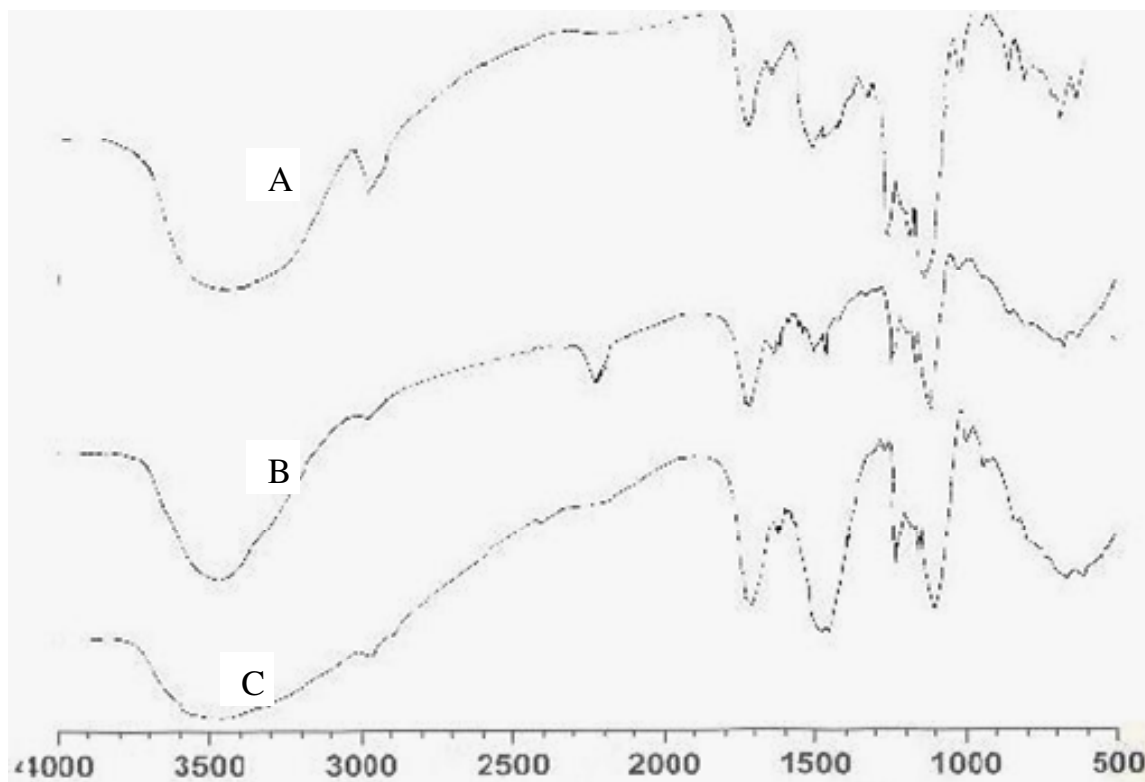


Figure 3. IR spectra of Starch (A), Starch-g- polyacrylonitrile (B) and Hydrolyzed Starch-g- acrylonitrile (C).

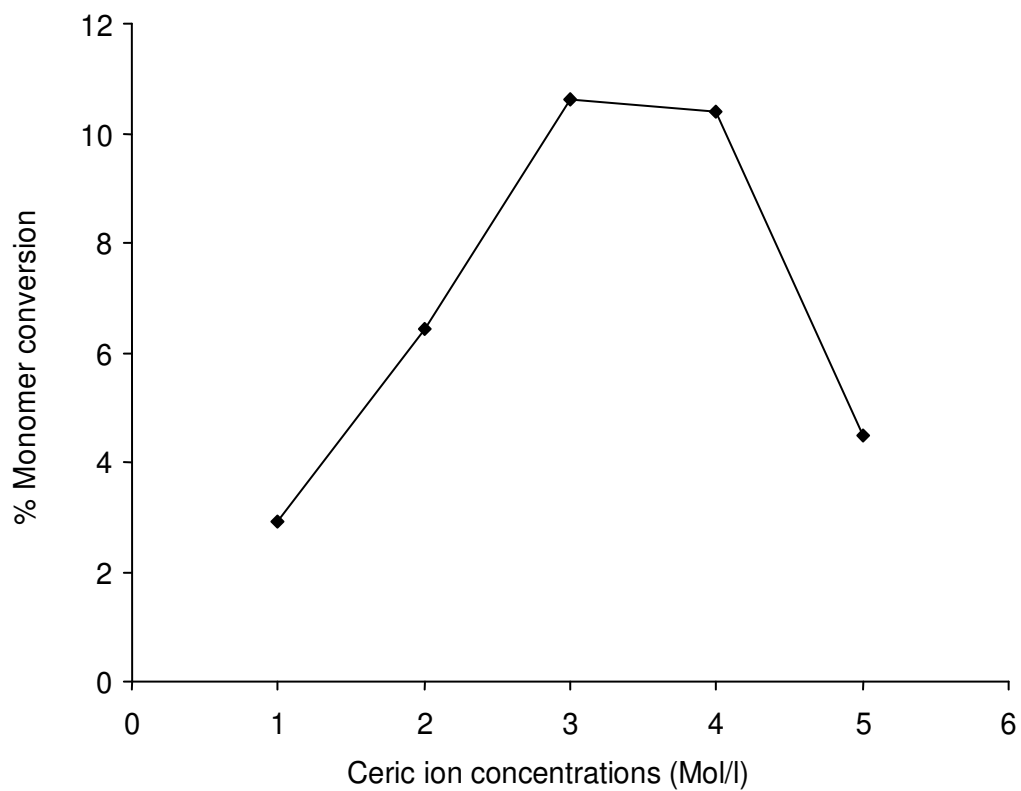


Figure 2. Effect of ceric ion concentration on the % monomer conversion.

arises from the stretching vibration mode of the nitrile groups (B). There is also a small characteristic peak at 2340 cm^{-1} (C) which is a $\text{-C}\equiv\text{N-}$ peak, an immediate from the hydrolysis to carboxylic group. Most of the other peaks are related to the polymer backbone (starch).

Conclusion

The results from this study show that the level of grafting is affected by the concentrations of the initiator and the monomer. Study of the IR spectra provides a strong evidence of grafting. The grafted copolymer could be used as flocculants.

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