

Studies in the Graft Copolymerization of Acrylic Acid Onto Plantago Psyllium Mucilage

Deepak kumar¹, Deepak kumar verma², Izhar fatma³

¹Asst.Professor, Amani Group Institutions, Amroha

²Asst.Professor, KGK Degree College, Moradabad

³Asst.Professor, Amani Group Institutions, Amroha

Abstract: Graft copolymers of plantago psyllium mucilage (PSY) and acrylic acid (AA) 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 favored by initial increase in the monomer concentration.

I. Introduction

Polysaccharides are naturally occurring polymer, which can be considered as derived from aldoses or ketoses by polymerization with loss of water (Crini, et al. 2004). Natural polymer, mainly polysaccharides, are biodegradable, cheap, fairly shear stable and easily available from reproducible agricultural resources. The biodegradability of natural polymer reduces their shelf life (singh et al 2000). In many polymers fundamental units are not all the same but are two or more similar molecules, such substance are called copolymer. Copolymerization increases the properties and the utility of a system in various application copolymerizations modifies the symmetry of the polymer chain and modulate both intramolecular and intermolecular forces, so property such as glass transition temperature, crystallinity, elasticity permeability and chemical reactivity can be varied within wide limits (Chhatbar, et al. 2009). Graft copolymer, on the other hand, are branch molecules where the main chain is made entirely of one repeat unit, while the branch-chain are made of yet another repeat unit. 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 copolymerization is an effective method to incorporate useful properties to the main polymer backbone, and these are useful in many applications in diverse fields. The natural polymers are vulnerable to degradation by acids, bases or water, which limit their application-spectrum, especially in harsh conditions. These limitations can be improved by graft copolymerization of vinyl monomers onto the polymeric backbones, which improves their chemical resistance, moisture repellency, and solvent resistance and dye uptake. Repellency, solvent resistance and dye uptake. All the graft copolymer exhibits good stability in the acidic medium, while all of these readily degraded in the alkaline medium (Banyal, et al. 2011).

II. Materials and methods

Psyllium (Psy) is a natural plant polysaccharide obtained from plantago ovata and its mucilage is composed of neutral arabinoxylan (arabinose 22.6%, xylose 74.6%). Psyllium mucilage an anionic natural polysaccharide consisting of pentosan and uronic acid obtained from the seeds plantago psyllium. Sodium salt of partially carboxymethylated is one of psyllium derivative and it is improve characteristics of psyllium such as increases swell ability as well as reactivity to monomer and initiator. Sodium salt of partially carboxymethylated (Na-PCMPsy) shows numerous applications in the field of biodegradable, textile, medicinal and hydrogels. Grafting techniques have received considerable attention from scientists all over the world, especially regarding those systems in which a natural polymer is a polysaccharide probably due to its abundant availability and low cost (Dholakia, et al. 2011). Psyllium husk is derived from the seed of the plantago ovate plant. Psyllium is also known as ispaghula and isabgol. The raw material plantago psyllium mucilage was obtained from its husk (the Sidhpur Sat-isabgol factory, Gujrat, India) and it was used after purification. Its purification was carried out by precipitation from aqueous solution with alcohol and it was finally washed with acetone and dried (Mishra, et al.2004).

Synthesis

Graft copolymerization of acrylic acid onto PSY 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 PSY 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) quinol 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 2MNaOH 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

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

$$\text{Gr}\% = \frac{\text{weight of grafted polymer}}{\text{weight of plantago psyllium mucilage}} \times 100$$

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

$$\% \text{conversion} = \frac{\text{weight of grafted polymer}}{\text{weight of monomer}} \times 100$$

Table 1. Grafting parameters at constant initiator concentration.

| Monomer concentration (mol/l) | Wt.psy-g-PAA(g) | Wt. of homopolymer +grafted polymer | % monomer conversion | Gr % grafted ratio |
|-------------------------------|-----------------|-------------------------------------|----------------------|--------------------|
| 1.00 | 10.90 | 1.00 | 11.00 | 9.10 |
| 2.00 | 11.50 | 2.10 | 11.67 | 20.10 |
| 3.00 | 12.87 | 3.50 | 15.00 | 35.70 |
| 4.00 | 12.00 | 2.50 | 7.30 | 24.60 |
| 5.00 | 11.75 | 2.15 | 5.50 | 23.00 |

Table 2. Grafting parameters at constant monomer concentration.

| Ceric ion concentration (mol/l) | Wt.psy-g-PAA(g) | Wt. of homopolymer +grafted polymer | Gr % grafted ratio | % monomer conversion |
|---------------------------------|-----------------|-------------------------------------|--------------------|----------------------|
| 1.00 | 11.50 | 1.10 | 10.60 | 2.30 |
| 2.00 | 12.00 | 2.40 | 24.50 | 5.40 |
| 3.00 | 13.50 | 4.00 | 40.30 | 9.52 |
| 4.00 | 13.00 | 3.50 | 41.50 | 9.20 |
| 5.00 | 11.10 | 1.50 | 17.20 | 3.50 |

III. Result and Discussion

The backbone polymer (PSY) was grafted with acrylic acid monomer. The effects of monomer concentration on the level of conversion and quantities of grafted acrylic acid on PSY 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 there after 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 macro radicals and the nonexistence of homopolymer on acrylic acid (**Nayak and Singh, 2001**). Maximum values of 35.70 and 15.00% 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. Moreover, large amounts of homopolymer deposits may block the way of monomer molecules to the PSY macroradicals resulting in further decrease in percentage monomer conversion and yield. Therefore 3 M was taken as the maximum concentration at which monomer (acrylic acid) can be complexes. 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 012 Int. J. Biotechnol. Mol. Biol. Res.

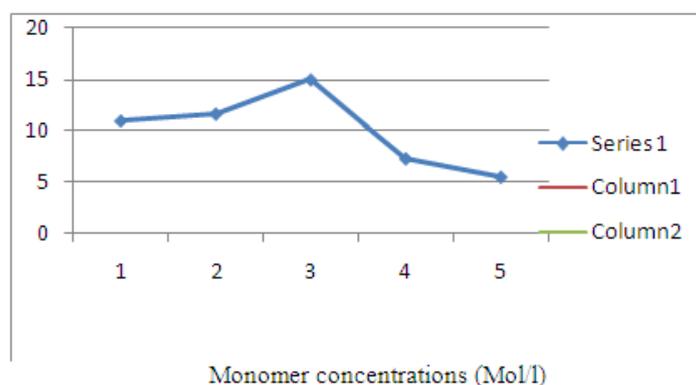


Figure 1. Effect of Monomer concentration on % monomer conversion

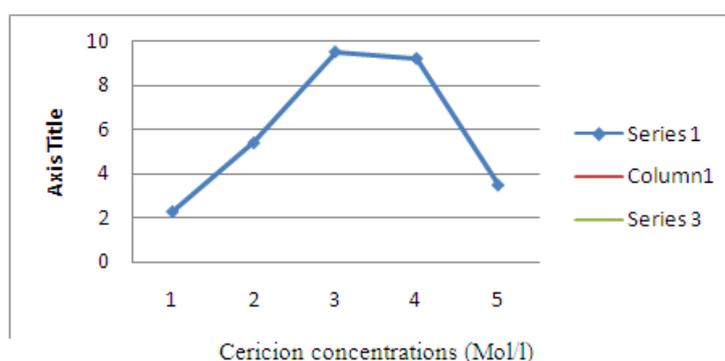


Figure 2. Effect of ceric ion concentration on the % monomer conversion.

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 PSY 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, 2004). The results also showed that the grafting ratio reached the maximum value of 4.00% 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 PSY 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

PSY, 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 PSY was obtained. This shows that the grafted PSY could be used as flocculants.

Characterization of Graft Copolymers by IR:-

The FTIR spectra of pure Psy and Psy-g-PAA are shown in Fig 3 and 4 respectively. The FTIR spectra of purified Psyllium shows characteristic peaks of -OH between 3432 cm⁻¹, -CH stretching between 2923- cm⁻¹, -CO stretching at 1040 and 1644 cm⁻¹ and -CH₃ at 2923 cm⁻¹. In the grafted sample of Psy-g-PAA, the characteristic absorption at 1722 cm⁻¹ of C=O [Fig.4] indicates grafting of PAA with Psy. The O-H stretching frequency in the grafted product is broader 3418 cm⁻¹ as compared to that in spectrum of Psy. This is due to unequal hydrogen bonding in the grafted product again attributing to the fact that grafting has occurred.

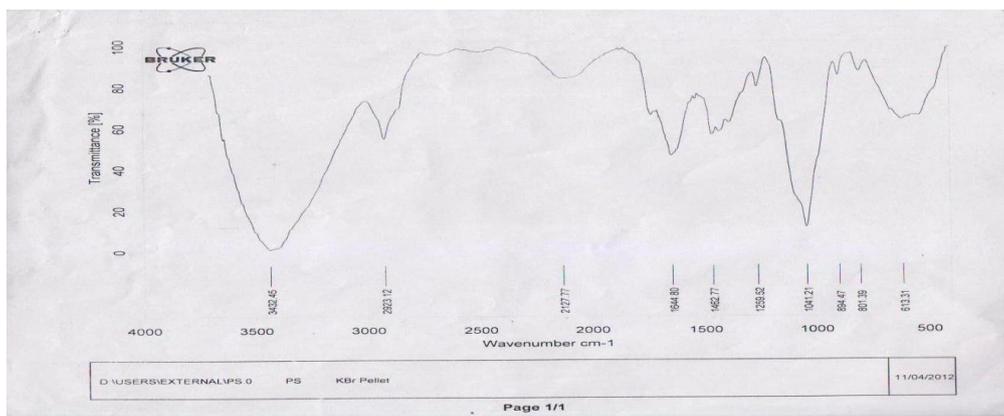


Fig -3 IR Spectrum of Psyllium mu

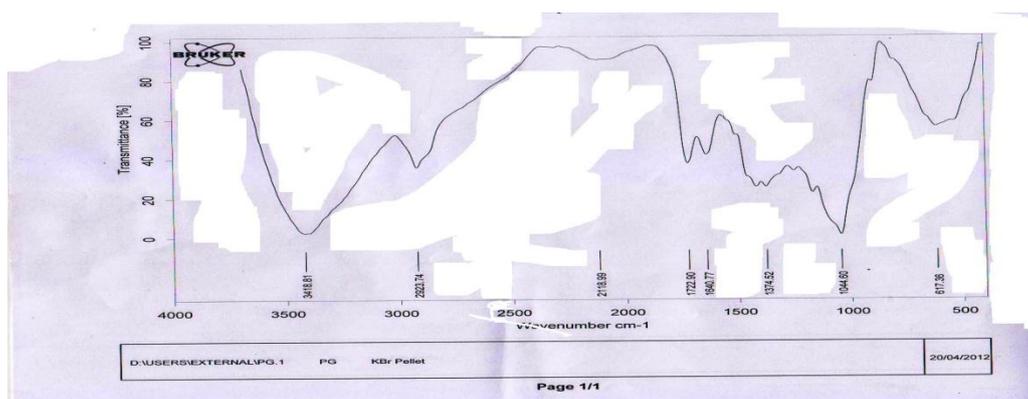


Fig -4- IRspectrum of Psy-g-PAA

IV. 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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