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Grafting of Acrylic Acid on to Plantago psyllium Mucilage

Deepak kumar[1], Sanjeev kumar[2]
[1-]Dept.Of Chemistry, Amani Group Of Institutions.
[2-] Lecturer, Government Inter College, Amroha.

Abstract: *Psyllium (Psy) mucilage, a food grade polysaccharide is reported as a substrate for the graft copolymerization of acrylic acid (AA). Psyllium mucilage was extracted from psyllium husk. Polymerization was initiated by ceric ion in aqueous medium under* N_2 *atmosphere. The progress of the reaction was monitored gravimetrically. The effect of different reaction parameter, such as monomer concentration, level of ceric ammonium nitrate /*HNO_3 *(CAN) initiator, reaction time temperature, on the percentage grafting PG was studied. Grafting of polyacrylic acid (PAA) onto Psy was confirmed by Fourier – transform infrared spectroscopy.*

I. Introduction

In many polymers fundamental units are not all the same but are two or more similar molecules, such substance are called copolymer. **Mishra at al (2006).**

nA + mB → — (A—B—A—B—A—B—A)n+m

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. **kaith at al (2011).**

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.

—A—A—A —A—A—A—-A—
I I I I I I I
B B B B B B B
I I I I I I I
B B B B B B B

A graft copolymer is a macromolecular chain with one or more species of block connected to the main chain as side chain(s). Thus, it can be described as having the general structure, where the main polymer backbone, commonly referred to as the trunk polymer, has branches of another polymeric chain emanating from different points along its length. This fascinating technique may be considered as an approach to achieve novel polysaccharide-based materials with improved properties including all the expected usefulness of these biomaterials. **Maithi at al (2012).**

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. 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. **Ikhuoria at al (2010).** Graft copolymerization is an effective method to incorporate useful properties to the main polymer backbone, and these are useful in many applications in diverse field. 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. **Banyal at al (2011).** All the graft copolymer exhibits good stability in the acidic medium, while all of these readily degraded in the alkaline medium. Radical graft copolymerization have been successful in term of obtaining a grafted derivative, however grafted product characterization being inherently difficult in its own right, is further complicated by homopolymer formation. **Pati at al (2011).**

Ceric Ion Initiation :-

Cerium is member of group IIIA of periodic table .it is tetravalent atom . cerium has two common oxidation states 3^+(Cerrous CeIII) and4^+ (ceric, ceIV) The oxidation potential for the reaction.

$Ce^{+4} \quad +e^- \quad \rightarrow \quad Ce^{+3}$

In most of the homogenous oxidation of substrate by Ce^{+4},the formation of intermediate complex has been found to be an important prerequisite.

The mechanism of ceric ion reaction involves , the formation of chelate complex ,that decomposes to generate free radical sites on polysaccharide backbone .These active free radical sites in presence of acrylic acid monomer generate graft copolymer. The number of free radical sites so generated should be proportional to the concentration ceric ions. in other words , the length of the grafted chains at a fixed monomer concentration should be largest in case of low ceric ion concentration vice-versa. **sigh at al (2011).**

Typical ceric ion intitiation is performed under acidic aqueous condition. Acid concentration is believed to effect the rate of polymerization initiated by the ceric ion, but the relationship depends on the type of acid used. For instance, the following equilibrium, show in the following equation is observed in aqueous perchlorate acid solutions, where the ceric ion concentration is dependent upon the acid concentration.

$$Ce^4 + H_2O \leftrightharpoons CeOH + H^+$$

Generally aqueous ceric ion initiations are performed under acidic conditions to promote higher concentration of Ce(IV). **Shanmugapriya at al (2011).**

II. Experimental

Materials

Description of Mucilage
Description of Chemicals Used
Techniques and Equipments Used
Description of mucilage

Fig.-1 P.psyllium plant .

Fig.-2 Psyllium husk.

Botanical Name - Plantago ovata
Family - Plantaginaceae
Sanskrit Name - Sat Isabgol
Common name - Isabgol
Part used - Husk

$\rightleftarrows$

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%) **Fischer at al 2009**. Psyllium mucilage ananionic natural polysaccharide consisting of pentosan and uronic acid obtained from the seeds plantago psyllium. **Dholakia at al (2011).**

Description of Other Chemicals Used:-

Monomer Used: Acrylic Acid
Solvents: Acetone, Isopropyl Alcohol and Nitric acid.
Inhibitor: Hydroquinone
Other Requisites: Apart from the above-mentioned materials nitrogen gas was used for maintaining the inert atmosphere during synthesis of copolymer.

Acrylic Acid

It was purchased from Aldrich Chemical Co. (USA) and used without further purification.

Acetone

It was obtained S.D.Fine Chem Ltd., and was used as received.

Ethanol (EtOH)

It was obtained from S.D.Fine Chem Ltd., and was used as received.
Isopropyl Alcohol (IPA)
The analytical reagent grade of IPA (Ranbaxy) was used as received**.**

Nitric Acid

Commercial concentrated nitric acid (Analar, grade, BDH, India) used as received, for dissolving the indicator Ceric Ammonium Nitrate (CAN).

Hydroquinone

Hydroquinone (BDH) was used to quench or terminate the grafting reaction.

Ceric Ammonium Nitrate (CAN)

CAN (Merck Chemical Co. extra pure) was used as received without further purification.

Nitrogen Gas

Nitrogen gas was used for maintaining the inert atmosphere during synthesis of copolymers. Compressed Nitrogen Cylinders were purchased. This gas may contain traces of oxygen, which is removed by passing it through Fieser's solution. **(Vogel, 1989)** Fieser's solution consists of an alkaline solution of sodium dithionite to which sodium anthraquinone-2-sulphonate is added.

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Grafting Parameters

The %grafting was calculated by the equation

$$\% \text{ grafting} = \frac{W_0 \text{ x}100}{W}$$

The %efficiency was calculated by the equation

$$\% \text{ grafting efficiency} = \frac{W_0 \text{ x}100}{W_0+W_1}$$

Where
W_0 = weight of Grafted polymer.
W = weight of polysaccharide.
W_1 = weight of homopolymer.

III. Results and Discussion

This chapter describes the results of synthesis of Acrylic Acid -grafted copolymers of psyllium mucilage. Psy-g-AA was synthesized by grafting Acrylic Acid AA onto purified Psyllium mucilage by radical polymerization method in aqueous system using ceric ion/nitric acid redox initiator **(Singh et al., 2000; Mishra et al., 2002; Mishra & Bajpai, 2005; Deshmukh et al., 1987; 1986;).** The most important feature of the ceric ion initiated polymerization technique is that the oxidation proceeds via single electron transfer with the formation of free radicals on reducing agent. In this system the free radical is produced on the mucilage (substrate backbone), which in the presence of acrylic acid, initiates polymerization to produce a graft copolymer. The number of free radical sites so generated should be proportional to the concentration of ceric ions. In other words, the length of the grafted chains at a fixed monomer concentration should be largest in case of low ceric ion concentration and vice versa. This method of grafting yields substantially pure graft copolymer, since the free radicals produced exclusively on the backbone. To obtain a better reproducibility in the results, the reaction was carried out under a constant light source because the oxidative capability of the Ce (IV) ions increases considerably under light **(Vazquez et al., 1992).** The reaction parameters and the percent grafting and efficiency are given in the table

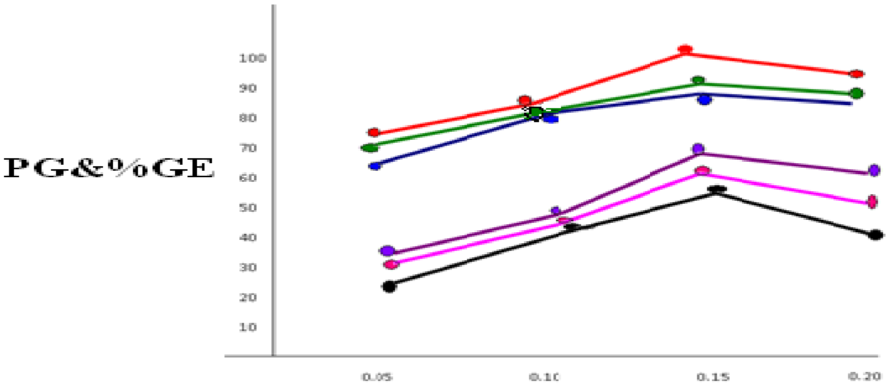
Influence of Reaction Parameters:-

Effect of Initiator (CAN) Concentration

The effect of initiator concentration (CAN) on percentage of grafting is shown in figure 5.1. On increasing the concentration of initiator i.e., CAN from 0.5 X 10^{-3} moles to 1.5 X 10^{-3} moles, PG increased due to increase in the free radicals on polysaccharide chain. With further increase in CAN concentration, up to 2.0 X10^{-3} moles, PG decreased. The falling of PG at higher CAN concentration is a well-known phenomenon and ascribed to the increasing participation of the ceric ion in the termination of the growing grafted chains (**Hashem et. al., 2005).**

Table : Details of graft reaction

Sample No.	Moles of Acrylic Acid (AA)	Moles of Ce IV×10^3	Percentage Grafting (%)	Grafting efficiency (%)	Time (hours)	Temp. (°C)
1	0.009	0.05	25.8	60.8	2	30
2	0.018	0.05	37.2	74.4	2	30
3	0.027	0.05	31.1	66.2	2	30
4	0.009	0.10	43.6	74.5	2	30
5	0.018	0.10	47.2	83.2	2	30
6	0.027	0.10	40.1	78	2	30
7	0.009	0.15	40.4	80.2	2	30
8	0.018	0.15	55.2	95.2	2	30
9	0.027	0.15	50.2	84.4	2	30
10	0.009	0.20	35.1	72.80	2	30
11	0.018	0.20	50.2	90.0	2	30
12	0.027	0.20	45.6	80.9	2	30
13	0.018	0.15	47	87.1	1	30
14	0.018	0.15	56.8	96.8	6	30
15	0.018	0.15	52	92.1	24	30
16	0.018	0.15	48.8	89.8	1	50
17	0.018	0.15	56.2	96.0	1	40
18	0.018	0.15	30.2	70.2	1	20



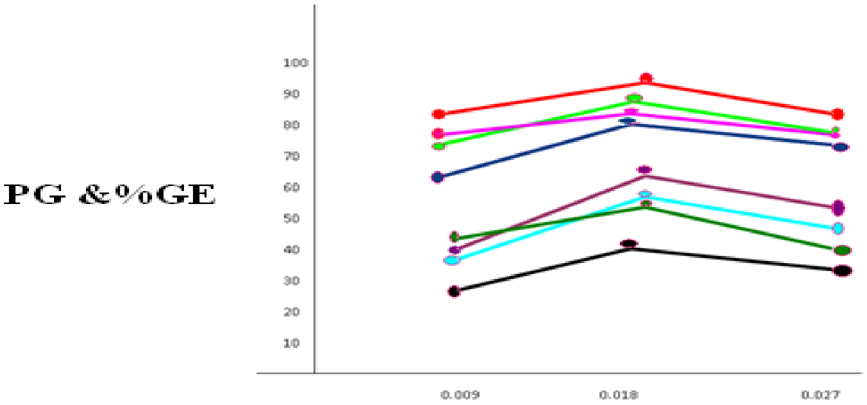
CAN concentration (moles /L x10^{-3})

Fig 5.1 Effect of CAN concentration on PG &GE.

(.) PG & (.) **GE with the concentration 0.018 mole/ L**

(●) PG & (●) **GE with the concentration 0.018 mole/ L**

(●) PG & (●) **GE with the concentration 0.027 mole/ L**



(A A) concentration moles/L

Fig 5.2: Effect of monomer concentration on PG & GE

(●) PG &(●) GE with the concentration .05x10^{-3} mole/ L

(●) PG &(●) GE with the concentration .05x10^{-3} mole/ L

(●) PG &(●) GE with the concentration 0.15x10^{-3} mole/ L

(●) PG & (●) GE with the concentration 0.20x10^{-3} mole/ L

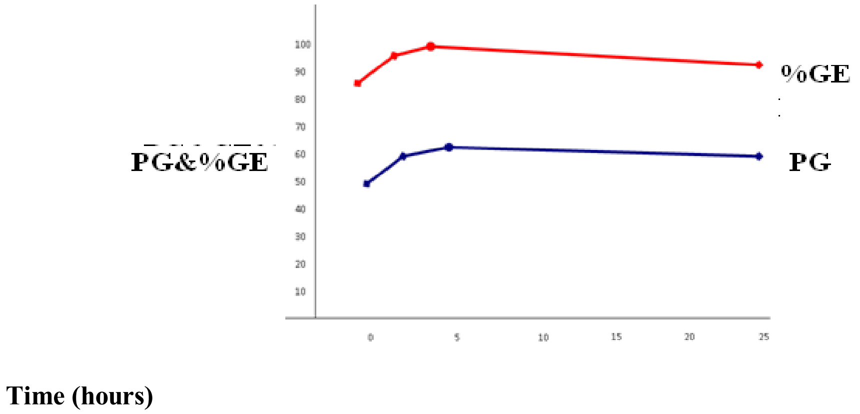


Fig 5.3- Effect of time on PG & %GE

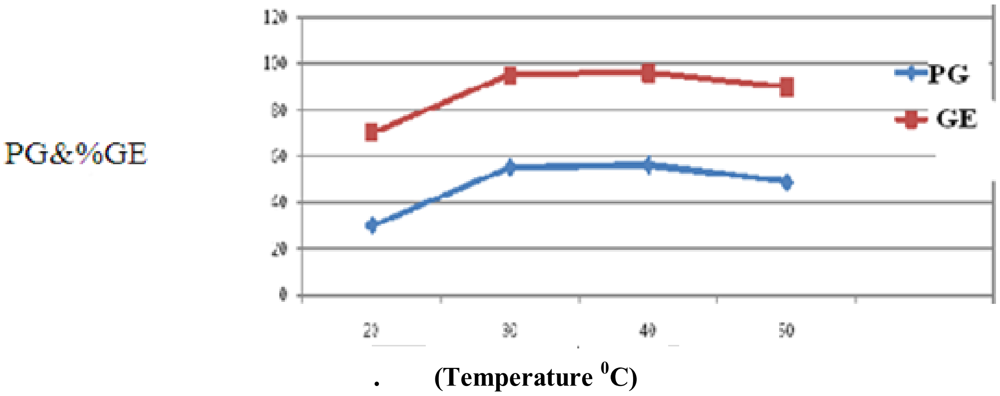


Fig 5.3:Effect of Temperature

Effect of Monomer Concentration

The effect of monomer concentration on percentage grafting (PG) is shown in figure 5.1. The best PG was obtained for 0.018 moles of AA. The increase of PG till .018 moles was expected with increase in AA concentration due to the availability of AA monomer with respect to polysaccharide macroradicals, leading to larger possibility of grafting. When more than .018 moles of AA was taken in the reaction medium the formation of homopolymers i.e. PAA hinderd the rates of penetration of monomer molecules to the polysaccharide free radicals, resulting in decrease in PG **(Fares, 2003).**

Effect of Time

The effect of time on %GE is shown in figure 5.3. The PG and %GE increased with increasing grafting time **(Yao and Tang 1992)** up to 6H. But a slight decrease in PG and %GE was observed after 24H .this decline or constancy of grafting after 6H is a clear remark on the depletion of monomer from the solution **(fares , 2003).**

Effect of Reaction Temperature

Reaction temperature is an important reaction condition in the graft copolymerization. The effect of temperature on percentage grafting and grafting efficiency is shown in figure 5.4. PG and %GE both increased on varying the reaction temperature from 20 to 30° C and started decreasing on further increase in temperature upto 50^{0}C. The decreased PG observed with increase in temperature at 50^{0}C might be attributed to faster rate of termination and more homopolymerization at higher temperature **(Shukla et. al., 2003).**

Characterization of Graft Copolymers by IR:-

The FTIR spectra of pure Psy and Psy-g-PAA (PG=56.8%) are shown in Fig 5.5 and 5.6 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 -CH_3 at 2923 cm-1. In the grafted sample of Psy-g-PAA, the characteristic absorption at 1722 cm-1 of C=O [Fig.5.6] 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.

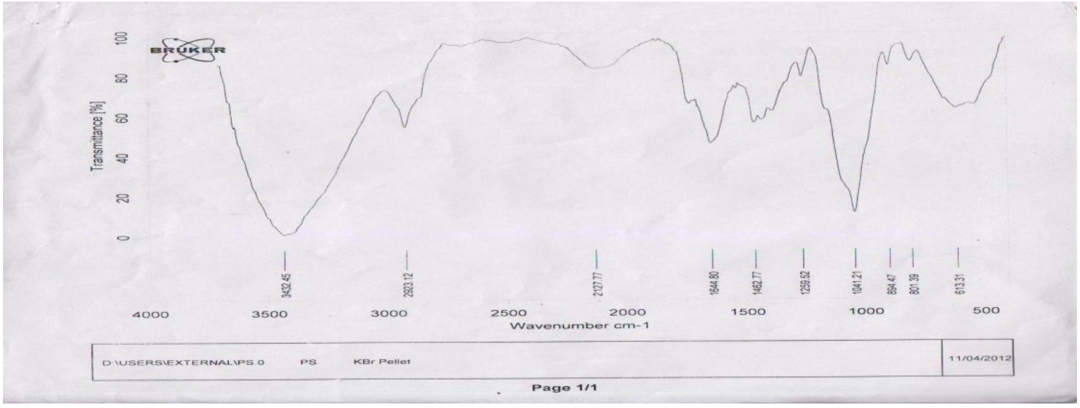


Fig. 3- IR Spectrum of PSYllium mucilage

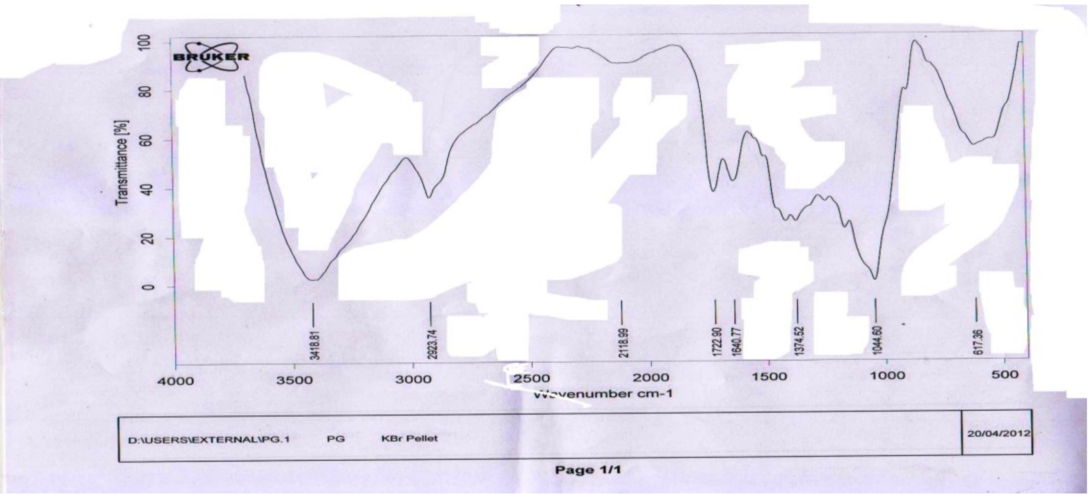


Fig. 4- IR spectrum of Psy-g-PAA

IV. Conclusion

Grafting of Psyllium mucilage to prepare its Acrylic Acid grafted copolymer has been done successfully by using a CAN/HNO_3 redox initiator system. The maximum percent grafting (56.8%) and grafting efficiency (96.8%) was obtained,when Acrylic Acid and CAN concentrations in reaction mixture were 0.018 mol/L and 0.15x10^{-3} moles respectively. The IR spectrum confirmed the grafting of Acrylic Acid onto the mucilage chains.

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