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Ceric ion initiated graft copolymerization of Insoluble potato starch with acrylic acid

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Abstract

The graft copolymers of insoluble granular potato starch with acrylic acid (AA) were synthesized using ceric ammonium nitrate (CAN) for initiation. The effect of concentration of initiator, concentration of monomer, polymerization time, reaction temperature, material-to-liquor ratio and presence of alcohol in the reaction medium were studied and optimum conditions are defined. The formation of graft copolymers was confirmed using the method of gravimetric estimation. The grafting parameters calculated are reported.

Keywords: potato starch, acrylic acid, ceric ammonium nitrate, graft copolymerization.

Introduction

Starch is probably the most abundant and low cost natural polymer having range of commercial applications. It finds use in variety of fields like in textile and paper industry as sizing agent and thickener (Bayazeed, 1989) ^[3], in superabsorbents (Teli, 2012) ^[9], in adhesives (Wang, 2012) ^[10], as soil stabilizers in agriculture, as an agent to remove metal ions and organic dyes from aqueous systems (Pathania, 2012) ^[7] and as biodegradable thermoplastics in plastics industry (Fang, 2002) ^[4]. Graft copolymerization is widely accepted method of introducing new and desirable properties into starch without drastically affecting its basic properties.

Since the discovery of ceric ammonium nitrate (CAN) as an initiator (Mino, 1958) ^[6], it has been used by many researchers for initiating graft copolymerization onto natural as well as synthetic polymers. The beauty of initiation with CAN lies in minimizing homopolymerization of monomer to be grafted and facilitating grafting by producing free radicals directly onto backbone polymer.

Many vinyl monomers have been grafted onto starch using this method in the past (Athawale, 1997) ^[2] (Sharma, 2003) ^[8] including grafting of acrylic acid onto potato starch using ammonium per sulfate as an initiator (Lele, 2015) ^[5]. In the present work, attempt has been made to synthesize graft copolymers of insoluble potato starch with acrylic acid using CAN as an initiator.

2. Experimental

2.1 Materials

Pure insoluble granular potato starch, L R grade (s. d. Fine Chemicals, India) was dried at 110 °C for about 10 h to remove absorbed moisture/water as it has been experimentally found to be an optimum time for drying to constant weight for starch. Ceric ammonium nitrate (CAN) [(AR), s. d. Fine Chemicals, India.] being hygroscopic in nature was dried in air oven 110°C for about 6 h. Dried starch as well as CAN were stored over anhydrous CaCl₂ in a desiccators. CAN was used in the form of 1.0 mol/L solution prepared in molar nitric acid. Acrylic acid (AA) [(LR) s. d. Fine Chemicals, India.] was freed from inhibitor, dried on anhydrous CaCl₂ and stored in refrigerator. It was brought to room temperature before use.

2.2 Graft Copolymerization (Athawale, 1998) ^[1]

The polymerization reactions were carried out in a two necked round bottomed flask kept in a constant temperature water bath 2 g of granular potato starch was treated with 70 ml of

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distilled water to prepare uniform starch slurry. The predetermined quantity of CAN was added to this slurry and a contact time of 10 minutes was allowed to facilitate free radical formation on the starch backbone. This was followed by the addition of a known amount of monomer and later the total volume of the reaction mixture was made to 100 mL with distilled water. All these operations were carried out with constant stirring and under nitrogen atmosphere. The details of the experimental conditions are listed in the footnote to each table.

Control reactions were carried out with 2 g of starch under identical conditions expect the addition of monomer.

After the desired reaction time, the graft copolymer formed in the reaction mixture was separated from the homopolymer by filtering through Whatman filter paper no. 41. The homopolymer of AA (PAA) is highly soluble in water which was the medium of the reaction. Even then the residue was washed repeatedly with warm water, to ensure the complete removal of PAA.

2.3 Grafting Parameters

The percentage grafting efficiency (%GE), percentage grafting (%G) and %Add-on were calculated as follows:

$$\%GE = 100 (W_2 - W_1) / W_3$$

$$\%G = 100 (W_2 - W_1) / W_1$$

$$\%Add-on = 100 (W_2 - W_1) / W_2$$

Where W_1 , W_2 and W_3 are the weights of pure starch, graft copolymer and monomer charged respectively.

2.4 Gravimetric estimation

The graft copolymerization reaction was monitored gravimetrically. The weight of pure starch (W_1), weight of graft copolymer (W_2) and weight of the monomer charged into the reaction (W_3) were noted. The difference in weight between graft copolymer and the quantity of pure starch initially added into the reaction mixture ($W_2 - W_1$) gave the weight of the synthetic polymer grafted onto starch.

3. Results and Discussion

Graft copolymerization facilitates synthesis of tailor made polymer by introducing desired properties into the base polymer. Starch is a renewable, low cost, biodegradable biopolymer. In the present study, attempts have been made to graft acrylic acid (AA) onto pure insoluble potato starch.

3.1 Physical appearance

All the graft copolymers synthesized in the present study were more or less white in color. At higher concentration of CAN, the color of the graft copolymers turned to almost yellow due to presence of unreacted CAN.

3.2 Evidence for grafting by Gravimetric estimation

The graft copolymerization reactions were monitored gravimetrically. The homopolymer AA (PAA) is highly water-soluble, which was the medium of the reaction, and hence was easily filtered off. In spite of the extraction of the homopolymers, there was a remarkable gain in the weight of residue in case of each polymerization reaction, over that of the control reaction. This weight gain testified the existence of grafting of monomers onto starch and formed the basis for the determination of %GE and %G. It was further observed that there was always a loss of 0.13. g of starch per 2 g of starch in Control reactions. Hence this was taken as a correction factor and was added to the amount of actual residue obtained in graft copolymerization reactions.

3.3 Effect of initiator concentration: A glance at Table 1 makes it clear that the grafting parameters show wide changes with initiator concentration.

At very low concentration of CAN, the %GE, %G as well as % Add-on show negligible values. However when the CAN concentration reaches a certain value of 0.003 mol/L, the extent of grafting sharply increases. Any increase in the concentration of initiator thereafter results only in fall in values of grafting parameters.

Table 1: Effect of initiator concentration on the grafting of acrylic acid onto potato starch

[CAN]/mol.L ⁻¹	%GE	%G	%Add-on
0.0005	0.15	0.15	0.15
0.001	0.42	0.42	0.41
0.002	2.30	2.30	2.24
0.003	19.15	19.15	16.07
0.004	11.00	11.00	9.91
0.006	9.35	9.35	8.55
0.008	8.25	8.25	7.62

(Reaction conditions: Starch = 2g; [AA] = 0.2775 mol/L; Total volume 100mL; Temperature = 30°C; Polymerization time: 180min; Solvent = D. H₂O)

The initial low values of %G can be attributed to negligible number of grafting sites formed on the starch macromolecules where grafting of monomer can take place, while at particular concentration of 0.003 mol/L, the sites available are just sufficient to give quite high value of %G i.e. 19.15%. At still higher concentration of CAN, the excess CAN is utilized in the initiation of homopolymerization of acrylic acid rather than initiating the graft copolymerization.

3.4 Effect of monomer concentration: It can be noted (Table 2) that, the %G increases with monomer concentration upto certain concentration and at higher concentration of AA it falls off.

The rise in %G in the initial stages can be rationalized on the basis of increasing availability of monomers in the vicinity of starch macroradicals. At 0.5551 mol/L concentration of AA, all the grafting parameters reach an optimum value. The increase in concentration of AA thereafter favours formation of homopolymers of AA (PAA). This is evident from the rise in viscosity of the reaction medium, at concentrations of AA more than 0.5551 mol/L. PAA is highly soluble in water which is the medium of the reaction.

Table 2: Effect of monomer concentration on the grafting of acrylic acid onto potato starch

[AA]/mol.L ⁻¹	%GE	%G	%Add-on
0.1387	20.18	10.09	9.16
0.2775	19.15	19.15	16.07
0.4163	19.07	28.60	22.24
0.5551	24.4	48.8	32.80
0.694	15.62	39.06	28.09
0.8326	11.30	33.90	25.32
1.110	11.16	44.66	30.87

(Reaction conditions: Starch = 2g; [CAN] = 0.003 mol/L; Total volume: 100mL; Temperature = 30°C; Polymerization time: 180min; Solvent = D. H₂O)

3.5 Effect of polymerization time: Table 3 shows that there is a steady increase in the grafting parameter values with

polymerization time. However, in the first 30 minutes the reaction hardly begins. Hence it can be said that, some induction period is involved in the grafting of AA on to potato starch during which grafting reaction does not take place. Further the %GE, %G and %Add-on values show a gradual increase with polymerization time of upto 150 min. During 150 to 180 min, there is a steep rise in grafting parameter values. Hence 180 min. is taken as the optimum time of polymerization.

The increase in grafting parameters on increasing time of polymerization thereafter is merely due to addition of monomers to the growing grafted chains. The leveling off of the extent of grafting at longer periods of polymerization time can be due to unavailability of monomers.

Table 3: Effect of polymerization of time on the grafting of acrylic acid onto potato starch

Time In Min	%GE	%G	%Add-on
30	0.585	1.17	1.16
60	8.05	16.10	13.87
120	9.72	19.43	16.27
150	13.67	27.33	21.46
180	24.40	48.80	32.80
210	25.23	50.45	33.53
240	26.60	53.20	34.73
300	28.10	56.23	36.00
360	30.63	61.25	37.98

(Reaction conditions: Starch = 2g; [CAN] = 0.003 mol/L; [AA] = 0.5551 mol/L; Total volume: 100mL; Temperature = 30°C; Solvent = D. H₂O)

3.6 Effect of monomer-to-liquor ratio: The monomer to liquor ratio was varied by altering the volume of water added to reaction medium.

Table 4: Effect of monomer to liquor ratio on the grafting of acrylic acid onto potato starch

Monomer-To-Liquor Ratio	Volume Of Water	%GE	%G	%Add-on
1:16:67	100	24.40	48.80	32.80
1:13:3	80	18.13	36.26	26.60
1:10	60	17.25	34.50	25.65
1:6:67	40	13.94	27.87	21.80
1:3:33	20	13.63	27.23	21.40

(Reaction conditions: Starch = 2g; [CAN] = 0.003 mol/L; [AA] = 0.5551 mol/L; Temperature = 30°C; Polymerization time: 180 min Solvent = D. H₂O)

It can be seen that the reduction in the volume of water less than 100mL, results in the decline in extent of grafting.

It can be rationalized on the basis of restricted movement of monomers in the reaction medium at still lower volume of water. The restricted motion does not facilitate the availability of monomers in the vicinity of free radical sites formed on the starch macromolecule.

Nevertheless, the ratio of 1:16:67 was taken as the optimum ratio for the graft copolymerization of AA onto potato starch.

3.7 Effect or reaction temperature: It can be noticed from table 5 that, the rise in reaction temperature has an adverse effect on the extent of graft copolymerization. It can be ascribed to certain morphological changes taking place in the starch making it unfriendly towards the grafting of AA. Hence the room temperature of 30°C was taken as optimum temperature for this reaction.

Table 5: Effect of reaction temperature on the grafting of acrylic acid onto potato starch

Temperature/°C	%GE	%G	%Add-on
30	24.40	48.80	32.80
35	5.41	10.82	9.76
40	4.75	9.50	8.68
45	3.86	7.73	7.18

(Reaction conditions: Starch = 2g; [CAN] = 0.003 mol/L; [AA] = 0.5551 mol/L; Temperature = 100 mL; Polymerization time: 180 min Solvent = D. H₂O)

3.8 Effect of presence of alcohol: Acrylic acid is miscible to some extent with alcohol. Hence it was decided to study the effect of presence of alcohols including methanol. Alcohol and water were added in the ratio of 1:3 maintaining the total volume of the reaction to 100 mL. Addition of any alcohol resulted in a drop in % G. However, the drop was proportional to the chain length of alcohol. In case of presence of 2-Butanol, the product was hazy and oily and hence posed difficulties in its filtration.

Table 6: Effect of presence of solvent on the grafting of acrylic acid onto potato starch

Solvent	%GE	%G	%Add-on
Methanol	7.00	14.00	12.28
Ethanol	6.72	13.44	11.85
Isopropanol	5.04	10.07	9.15

(Reaction conditions: Starch = 2g; [CAN] = 0.003 mol/L; [AA] = 0.5551 mol/L; Total volume: 100 mL; Temperature = 30°C; Polymerization time: 180 min Alcohol: 25 mL.)

4. Conclusion

It is possible to graft acrylic acid onto potato starch using ceric ammonium nitrate as an initiator. The optimum conditions for the grafting are listed below:

For 2 g of insoluble potato starch,

[CAN] = 0.003 mol/L

[AA] = 0.5551 mol/L

Polymerization time = 180 min

Reaction temperature = 30°C

Material to liquor ratio = 1:16:67 (volume of water 100 mL)

In absence of any alcohol in reaction medium.

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