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Synthesis and characterization of graft copolymers of methacrylic acid onto gelatinized potato starch using chromic acid initiator in presence of air

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ABSTRACT

The graft copolymerization of methacrylic acid onto gelatinized potato starch has been carried out at 70^0 C using chromic acid as initiator. The different reaction parameters such as effect of temperature, initiator and monomer concentrations were optimized to determine the maximum percentage grafting. The maximum grafting efficiency of 87.5% was optimized at reaction temperature (60^0C), monomer concentration (0.81molL^{-1}) and initiator concentration (0.02 mmol.L^{-1}). The grafted samples were evaluated for other physico-chemical properties such as swelling behavior, moisture absorption and chemical resistance. The grafted samples were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) techniques. The additional peaks observed in FTIR spectra of grafted samples confirmed the grafting of monomer onto gelatinized starch. The grafted co-polymers have been successfully used for the removal metal ions and organic dyes from aqueous system. Copyright © 2012 VBRI Press.

Keywords: Potato starch, methacrylic acid, graft copolymerization, chromic acid and characterization.

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Introduction

Starch as one of the most abundant polysaccharides, is produced from renewable natural resources and consists of two macromolecules, amylose and amylopectin comprising of glucose monomers unit joined through α-1, 4 linkages **[2-4]**. Starch has gained more importance in recent years due to its very low cost and biodegradability. Increasing environmental pollution by synthetic polymers has motivated the scientist and industries to utilizing biodegradable naturally occurring polymers such as starch for preparing end use materials **[5]**. The hydrophilicity and brittleness of such materials limit their use in practical and industrial application **[6-7]**. Therefore, the attempts have been made to solve these problems by including biodegradability into polymer in everyday use through slight modification of their structure **[8]**. Graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic polymers without drastically affecting its basic properties **[9]**. Grafting is generally considered as result from the propagation by radical sites generated on the polymer backbone. Graft copolymerization of monomers onto natural polymers was reported by various researchers for the synthesis of polymeric materials **[10-11]**. Chemical modification of starch via vinyl graft co-polymerization is a most effective method for improving starch properties, thereby enlarging the range of its utilization. Alfrey and Bandel were the first to synthesize graft co-polymer in 1951 **[12]**. In the recent years, the grafting of acryl amide **[13]**, methacrylamide **[14]**, acrylonitrile **[15]**, acrylic acid **[16]** on the starch was studied in the presence of initiators. The synthesized starch-g-poly (vinyl alcohol) copolymer was used for food packing, biomedical fields, coating and adhesives, drag reduction, textile industry and preparing biodegradable hydrogels [**17-19**]. The starch based superabsorbent polymers were developed by grafting with vinyl monomer which are used for the removal of metal ions and dyes from water system **[20]**. Various researchers have studied the synthesis, characterization and control drug delivery of the polymer hydrogels **[21]**.

Granular starch has limited solubility in neutral water. Even a physical treatment of aqueous starch dispersion could not result in complete dissolution of granular starch **[22]**. Recently Han et. al. **[23]** have measured the molecular weight of starch by dissolved in strong alkaline solutions. The strong alkali in aqueous medium breaks the intermolecular bonds of starch and form a more homogenous starch solution. The substantial changes in the molecular characteristics of granular starch during the gelatinization and dissolution processes **[22]** have promoted the proposed work.

In present article, grafting of methacrylic acid onto gelatinized potato starch using chromic acid as initiator has been reported. The effect of reaction parameters such as temperature, monomer concentration and initiator concentration were also studied. The starch grafted copolymer was characterized by using spectral techniques such as FTIR, SEM, XRD and TGA. The physico-chemical properties of graft copolymers were also attempted. The grafted sample was utilized for the removal of organic dye and metal ions from water system.

Experimental

Materials

Potato starch was purchased CDH, India and used without any further purification. Methacrylic acids (CDH, 97 % purity), chromic acid (SD fine, 99 % purity) were used as received. Nitric acid, sodium hydroxide and ethyl alcohol of 97 % purity was obtained from RANKEM, India were used.

Copolymerization of gelatinized potato starch

In typical synthesis, 1g potato starch was dissolved in 100 ml of 0.1 N NaOH, stirred for 60 minutes at 70 ^{0}C before grafting reaction was carried out. After cooling to the reaction temperature of 50 ^{0}C, the definite amount of initiator (chromic acid) was added to the reactor and allowed to react with starch for 10 minutes. Thereafter, definite amount of monomer (methacrylic acid) were added into the reactor with continuously stirring at a particular temperature for a definite time period. After cooling, the reaction mixture was poured into 25 ml of ethanol to precipitate the graft copolymer and kept for 24 hours at room temperature. The precipitates were filtered and dried at 60 ^{0}C in a hot air oven. Different reaction parameters such as monomer concentration, initiator concentration and effect of temperature were optimized to obtain the maximum graft yield. Graft copolymers were extracted by washing thoroughly with methanol and distilled water to remove the attached homopolymer. The graft copolymer was dried at 50 ^{0}C till constant weight was obtained. The percent grafting yield and grafting efficiency were calculated as follows:

$$\text{Grafting yield} = \frac{W_3 - W_1}{W_1} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

where, W_1 is initial weight of the sample, W_2 is the weight of the grafted sample before the extraction of homopolymer and W_3 is the weight of the grafted sample after extraction of homopolymer.

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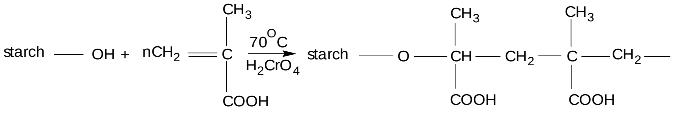

Methacrylic acid Starch-g-poly(MAA)

Scheme 1. Methacrylic acid grafting onto potato starch

Measurements and characterization

Fourier transform infrared (FTIR) spectra of raw and grafted polymer were recorded by Perkin Elmer FTIR spectrophotometer using KBr pellets. FTIR spectra of the sample were analyzed in the range of 450-5000 cm^{-1} with a resolution of 2 cm^{-1}.

X-ray studies were carried out on Brucker D8 Advanced X-ray diffractometer, using Nickel-filtered Cu Kα radiation (λ=0.15406 nm) and scanned from 2 to 60^{0}C at a scan speed of 2^0/min. Finely powdered samples was placed in central cavity of sample holder made up of Polymethacrylic acid (PMAA) for X-ray diffraction studies.

TGA measurements were made on Perkin Elmer Pyris Diamond thermal analyzer in air. All the samples were subjected to a constant heating rate of 10 ^{0}C/min. Thermal studies were performed over a temperature range of 25 ^{0}C to 1000 ^{0}C in the air with flow rate of 200 ml/min.

The surface morphologies of the starch and graft copolymers were studied with the help of scanning electron microscopy (SEM). SEM analysis was made on Leo scanning electron spectroscopy machine 435 VP. The image resolution was set at 500X and at 50X. Before focusing electron beam on the samples, the samples were gold-sputtered in order to make them conducting.

Swelling studies

Swelling studies of raw and grafted samples were carried out in water, carbon tetrachloride and n-butanol. For this purpose, 40 mg of sample was kept in 20 ml of solvent for 24 hours at room temperature. After filtration the surface water from the swollen sample were removed by softly pressing them between the folds of filter paper. It was followed by measuring the increased weight. An increase in weight was noted. Percent swelling (P_s) was calculated as follows:

$$P_s = \frac{W_f - W_i}{W_i} \times 100$$

where, W_f is the weight of the swollen sample and W_i is the weight of dry sample.

Moisture absorption behavior

A sample of known weight was placed in the humidity chamber maintained at a definite humidity level for 2 hours. The sample was then taken out and final weight was noted immediately. Percent moisture absorbance was calculated as follows:

$$\%\ \text{Mass}_{abs} = \frac{W_f - W_i}{W_i} \times 100$$

where, W_i is the initial weight of the sample and W_f is the final weight of the sample.

Chemical resistancy

Chemical resistance was studied as a function of percent weight loss by immersing the known weight of grafted sample in 1N HCl and 1N NaOH for 72 hours. It was followed by drying the sample at 50 ^{0}C till constant weight was obtained. The final weight of the sample was noted and percent weight loss was calculated as follow:

$$\text{Weight loss} = \frac{W_i - W_f}{W_i} \times 100$$

where, W_i is the initial weight of the sample and W_f is the final weight of the sample.

Removal of metal ions

The graft copolymer was used for removal of magnesium, nickel and zinc from water system. Adsorption of metal ion was carried out by shaking 0.04 g of the grafted sample in glass bottle containing 25 ml of metal salts for 30 minutes at room temperature. The solutions were filtered and the residual metal ion concentration in the filtrate was estimated. The percentage adsorption was calculated as follow:

$$\%\ \text{Adsorption} = \frac{C_o - C_e}{C_o}$$

Dye adsorption behavior:

Batch adsorption experiments were carried out to study the dye adsorption capacity of the grafted sample. In this experiment, fixed amount of sample was placed in a 250 ml glass stoppered Erlenmeyer flasks and dye solution of different concentration was added. Then the mixtures were agitated in a thermoshaker at a constant temperature and speed for a given time. The suspension was centrifuged at 3000 rpm for 15 min and filtered. The equilibrium concentrations of dye in the solution were measured at 663 nm using UV-visible spectrophotometer.

$$\text{Dye adsorption } (q_e) = \frac{C_o - C_e}{W}\ V$$

where q_e is amount of dye adsorbed, C_0 and C_e are the initial and equilibrium concentration of dye (mg L^{-1}), V is volume of solution (L) and W is the weight (g) of grafted sample taken

Results and discussion

Graft copolymerization of methacrylic acid onto gelatinized potato starch was carried using chromic acid initiator. The –OH group present on the backbone polymer acts as the active sites for the graft copolymerization of poy(MAA) onto the potato starch.

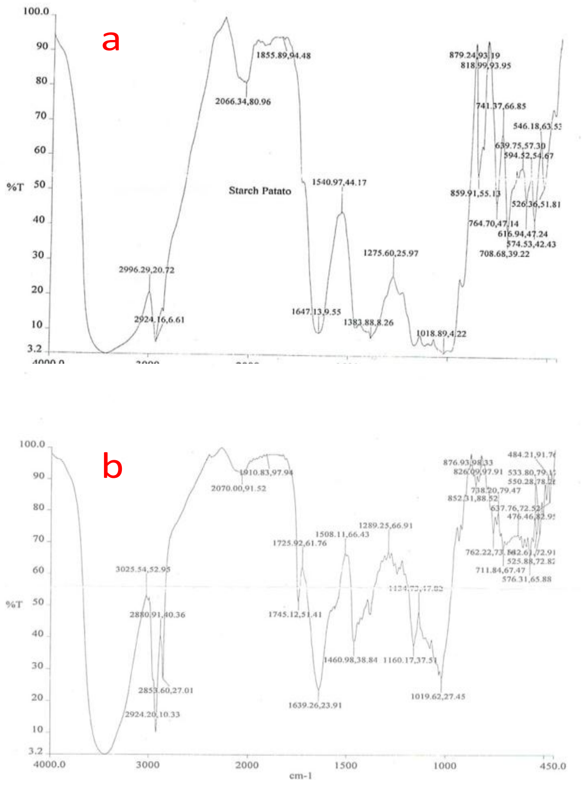

Fig. 1. (a) FTIR spectra of potato starch, **(b)** FTIR spectra of starch- g-poly(MAA).

FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to identify the structure of unknown composition or its chemical group and intensity of the absorption spectra associated with molecular composition [**24**]. The FTIR spectra of potato starch and starch-g-poly(MAA) samples were shown in **Fig. 1a** and **b.** The FTIR spectra of the grafted sample (**Fig. 1b**) indicate the appearance of absorption bands at 1745 cm^{-1} and 1460 cm^{-1} which were not observed in the spectrum of potato starch (**Fig.1a**). These absorption peaks was due to –COOH stretching vibrations and $–CH_3$ stretching in grafted sample. The absorption peak at 2924 cm^{-1} was due to –OH vibrations. Absorption band at 1020 cm^{-1} inferred the C-O stretching.

Thermogravimetric analysis

Thermogravimetric analysis of the potato starch and grafted starch (**Fig. 2a, b)** revealed that grafted starch is more thermally stable than raw starch. The initial weight loss has been observed from 100 ^{0}C -200 ^{0}C with 12.19 % and 8.13 % for potato starch and grafted starch, respectively. The primary decomposition reaction was observed due to dehydration upto 200 ^{0}C.The total weight loss was 63.92 % upto 580 ^{0}C for starch-g-poly(MAA) sample as compared to 66.07 % weight loss for potato starch upto 500 ^{0}C.

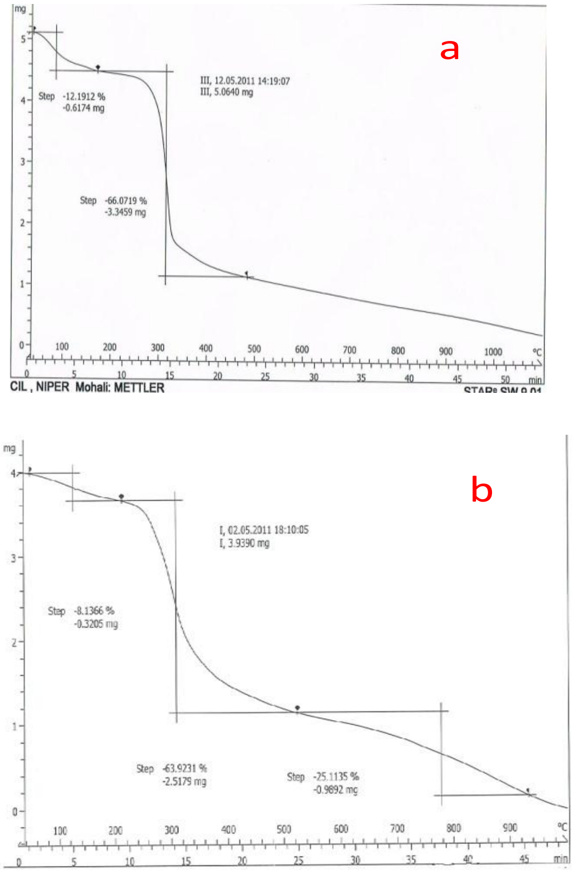

Fig. 2. (a) TGA of pure potato starch and (b) starch-g-poly(MAA).

Morphological studies

The surface morphologies of the starch and the graft copolymer were viewed by scanning electron microscopy. The starch granules (**Fig. 3a)** have an irregular oval shape and varied particle sizes with smooth surface while the starch graft copolymer **(Fig. 3b)** have a different surface morphology. The SEM photographs of grafted sample have course surface rather than smooth surface. These morphological changes were due to grafting of MAA onto starch.

XRD study

X-ray diffraction pattern of grafted sample was shown in **Fig. 4**. It has been evident that the starch-g-poly(MAA) sample shows halos typical for amorphous polymer. It is observed from the previous study that crystallinity was lost on grafting [**16**].This was the case with XRD pattern observed for the grafted sample.

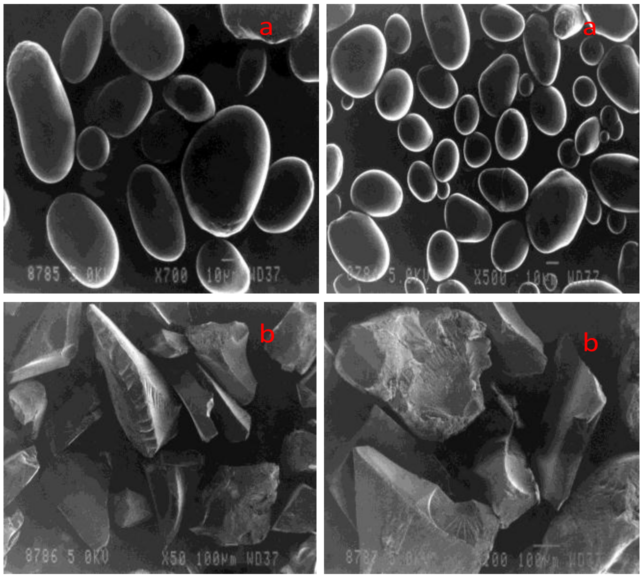

Fig. 3. (a) SEM of pure starch and (b) starch-g- poly(MAA).

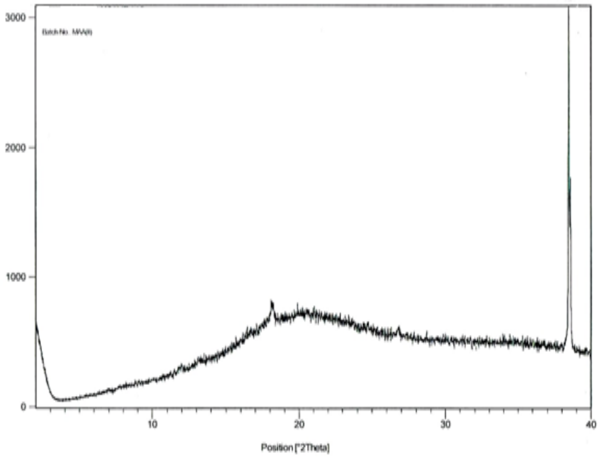

Fig. 4. XRD of starch-g-poly(MAA).

Optimization of grafting parameters

The different reaction parameters such as effect of temperature, initiator and monomer concentrations were optimized to obtain the maximum percent grafting.

Reaction temperature

Table 1 shows the variation of grafting yield and grafting efficiency at different temperature. It is observed that temperature has a considerable effect on the grafting reaction. The grafting yield increases with increase in temperature and maximum was found at 60 ^{0}C. However, further increase in temperature (above 60 ^{0}C) resulted in decrease in grafting yield. This may be due to predominance of homo-polymerization over copolymerization at high temperature **[25].**

Table 1 Optimization of reaction temperature

Sr. No.	Grafting Temp.(^{0}C)	Grafting Yield(%)	Percent Efficiency
1.	35	1	20.00
2.	50	4	50.00
3.	60	9	69.23
4.	70	3	42.85
5.	90	2	33.30

Monomer concentration

Table 2 shows the variation of grafting yield with monomer concentration. It is evident that grafting yield increases with increase in monomer concentration upto 0.81 molL^{-1} and then decease with increase in monomer concentration. This is due to reason that with increase in monomer concentration beyond optimum level results in increased cross linking, which prevent the accessibility of more solvent into the polymer. Further, the viscosity of the reaction medium increases with increase in monomer concentration, restrict the movement of free radicals and monomer molecules **[10]**.

Table 2 Optimization of monomer concentration

Sr. No.	Monomer Conc.(molL^{-1})	Grafting Yield(%)	Percent Efficiency
1.	0.23	5	62.5
2.	0.46	9	69.23
3.	0.58	14	77.7
4.	0.81	28	87.5
5.	1.05	2	25

Concentration of initiator

The effect the initiator concentration on the percent graft yield at various monomer concentrations was investigated to obtain the optimum value. **Table 3** shows the variation of grafting yield with initiator concentration. It has been observed that the grafting yield and grafting efficiency were increased with increase in the initiator concentration upto 0.03mmolL^{-1}. However, further increase in concentration of the initiator resulted in decrease of percent grafting. It is due to fact that the high concentration results in more homopolymer formation, which compete with grafting reaction for available monomer [**26**].

Swelling behavior

The swelling studies of raw and starch-g-poly(MAA) samples were performed on in different solvents (**Tables 4** and **5)**. It has been observed that the maximum swelling was observed in water for both raw (75%) and grafted samples (250%). The high swelling behavior of grafted sample may be due to porosity of particles originated after grafting of MAA onto potato starch. The swelling trend of raw and grafted samples was observed in the order of water > n-butanol > CCl_4.

Table 3. Optimization of initiator concentration

Sr. No.	Initiator Conc. (mmolL^{-1})	Grafting Yield(%)	Percent Efficiency
1.	0.01	2	40
2.	0.02	9	69.23
3.	0.03	26	86.66
4.	0.04	4	44.4
5.	0.05	3	37.5

Table 4. Swelling studies of raw sample in different solvents

Solvent	Initial Weight (mg)	Final Weight (mg)	% Swelling
Water	40	70	75
n-butanol	40	60	50
CCl_4	40	50	25

Table 5. Swelling studies of starch-g-poly(MAA) in different solvents

Solvent	Initial Weight (mg)	Final Weight (mg)	% Swelling
Water	40	140	250
n-butanol	40	70	75
CCl_4	40	60	50

Moisture absorbance

It has been observed that the moisture absorbance decreased in the study on raw starch-g-poly(MAA) sample (**Table 6)**. This behavior of the grafted sample can be explained on the basis that by grafting the active sites responsible for the moisture absorbance was blocked by MAA. Therefore, the affinity of grafted starch toward –OH group of water decreases which results in decrease of hydrophilic character.

Table 6. Moisture absorbance studies of raw and starch-g-poly(MAA)

	Initial Weight (mg)	Final Weight (mg)	%M_{abs}
Raw Sample	70	105	50
Grafted Sample	70	100	42.85

Chemical resistance

The chemical resistance of raw and grafted sample was investigated in 1N HCl and 1N NaOH (**Table 7**). It has been found that both the samples were sensitive and unstable in 1N NaOH. Moreover, the grafted sample was found more resistant in I N HCl. This may be due to blocking of the active site on the polymer backbone by polymerization.

Table 7. Chemical stability of raw and grafted samples in HCl and NaOH

	% Wt. Loss (1N HCl)	% Wt. Loss (1N NaOH)
Raw Sample	87.5	Dissolved
Grafted Sample	75	Dissolved

Removal of metal ions

The grafted starch sample removes metal ions by adsorption on COO^- groups of methacrylic and also by sorption in the bulk of grafted hydrogel. Therefore, the structure of a polymeric hydrogel affects the level of polymer interaction with water and the provision of active sites to absorb or coordinate metal ions. It has been observed that Mg ion uptake percentage was higher compared to Zn and Ni metal ions onto the grafted sample **(Table 8).** This may be attributed to the fact that the Mg ion has a lower atomic radius than other metal ions and consequently its adsorption by polymer is high.

Table 8. Metal ions adsorption onto starch-g-poly(MAA).

Sr. No.	Metal Ions	% Adsorption
1.	Zn	9.5
2.	Ni	15.9
3.	Mg	17.5

Dye adsorption

The adsorption methylene blue dye onto grafted starch was shown in Table 9. The carboxylic and hydroxyl group on grafted was responsible for adsorption of dye. It is evident that the adsorption of MB onto grafted sample was rapid at lower concentrations and thereafter it proceeds at a slower rate.

Table 9. Adsorption of dye onto starch-g-MAA at 663 nm

Sr.No.	Dye Conc. (mg/L)	Adsorption of dye (q_e)
1.	50	17.3
2.	100	31.9
3.	150	48.3

This may be due to the fact that an increase in the initial dye concentration leads to an increase in mass gradient between the solution and adsorbent, and thus acts as a driving force for the transfer of dye molecules from the bulk solution to the grafted sample surface **[27].**

Conclusion

The synthesis of starch-g-poly(MAA) was carried out using chromic acid as an initiator. The various reaction parameters such as temperature, monomer and initiator concentration were optimized to obtain the maximum grafting. It was found that grafted sample showed swelling resistance in different solvent. Chemical resistance study revealed the stability of grafted sample in acidic solution. FTIR spectra and SEM micrographs of starch-g-poly(MAA) confirmed the grafting on MAA onto gelatinized potato starch. Thermal stability of grafted sample was found high compared to raw starch.

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