



## Graft Copolymerization Methacrylamide onto Pectin in Homogeneous Solution

MOHAMMAD SADEGHI\*, SOUDEH SAFARI, HADIS SHAHSAVARI, HOSSEIN SADEGHI and FATEMEH SOLEIMANI

Department of Chemistry, Science Faculty, Arak Branch, Islamic Azad University, Arak, Iran

\*Corresponding author: E-mail: m-sadeghi@iau-arak.ac.ir

(Received: 13 July 2012;

Accepted: 18 February 2013)

AJC-13025

In the present paper, attention is paid to chemically modified polysaccharide, pectin, by graft copolymerization of methacrylamide (MAAm) in an aqueous medium using ammonium persulfate as an initiator under argon atmosphere and determination of grafting parameters produced copolymer. The structure of pure pectin and grafted with monomer was characterized by FTIR, SEM spectroscopies and TGA analysis. The thermal properties of pure pectin and grafted with monomer were evaluated with a simultaneous thermal analysis system. The results showed that the thermal stability of grafted polymethacrylamide samples was remarkably improved.

**Key Words:** Pectin, Acrylamide, Grafting parameters, Modify structure, TGA analysis.

### INTRODUCTION

Pectin is a naturally occurring biopolymer that is finding increasing applications in the pharmaceutical and biotechnology industry. It has been used successfully for many years in the food and beverage industry as a thickening agent, a gelling agent and a colloidal stabilizer. Pectin also has several unique properties that have enabled it to be used as a matrix for the entrapment and/or delivery of a variety of drugs, proteins and cells. However, it may need to be further modified for some special applications<sup>1-3</sup>.

Among the diverse approaches that are possible for modifying polysaccharides, grafting of synthetic polymer is a convenient method to add new properties to a polysaccharide with minimum loss of the initial properties of the substrate<sup>2</sup>. Graft copolymerization of vinyl monomers onto polysaccharides using free radical initiation has attracted the interest of many scientists. Up to now, considerable works have been devoted to the grafting of vinyl monomers onto the substrates, specially cellulose<sup>3</sup>. Of the monomers grafted, acrylonitrile (AN) has been the most frequently used one, mainly due to its highest grafting efficiency Athawale and other<sup>2,4</sup> improving the thermal resistance of the graft copolymer<sup>5</sup> and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents<sup>2,5</sup>.

The literature survey, reveals that few of the modifications deal with chemical grafting of a pre-modified polysaccharide such as pectin. Ammonium persulfate-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate<sup>5,6</sup>, acrylonitrile/methyl methacrylate

mixture<sup>7</sup> and 4-vinylpyridine<sup>8,9</sup> onto pectin has been reported. However, to the best of our knowledge, no report has been published on the optimization of acrylamide (AAm) graft polymerization onto pectin using ammonium persulfate-saccharide initiating system. As a part of our research program on polysaccharide modification, herewith we report the optimized ammonium persulfate-induced synthesis of pectin-g-polymethacrylamide under an inert atmosphere.

### EXPERIMENTAL

Pectin (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Methacrylamide (MAAm, Merck) was used after recrystallization. Ammonium persulfate (APS, Merck) was used as received. All other chemicals were of analytical grade.

**Synthesis of copolymer:** A facial one step preparative method was used for synthesis of Pec-polyacrylamide copolymer. Pectin (0.50-1.5 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. After complete dissolution of pectin to form a homogeneous solution, a definite amount of ammonium persulfate solution (0.15 g in 5 mL H<sub>2</sub>O) was added to pectin solution and was allowed to stir for 10 min. After adding ammonium persulfate, certain amounts of monomer (MAAm 1.50 g in 5 mL H<sub>2</sub>O) was added to the pectin solution. After 90 min, the reaction product was allowed to cool to ambient temperature. The produced material was poured to excess non solvent ethanol (200 mL) and kept for 3 h to remove water.

Then ethanol was decanted and the product scissored to small pieces. Finally, the filtered copolymer is dried in oven at 60 °C for 10 h.

**Instrumental analysis:** Fourier transform infrared (FTIR) spectroscopy absorption spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature. Thermogravimetric analyses (TGA) were performed on a Universal V4.1D TA Instruments (SDT Q600) with 8-10 mg samples on a platinum pan under nitrogen atmosphere. Experiments were performed at a heating rate of 20 °C/min until 600 °C. The surface morphology of the copolymer was examined using scanning electron microscopy (SEM). After Soxhlet extraction with methanol for 24 h and drying in an oven, the graft copolymer powder was coated with a thin layer of gold and imaged in a SEM instrument (Leo, 1455 VP).

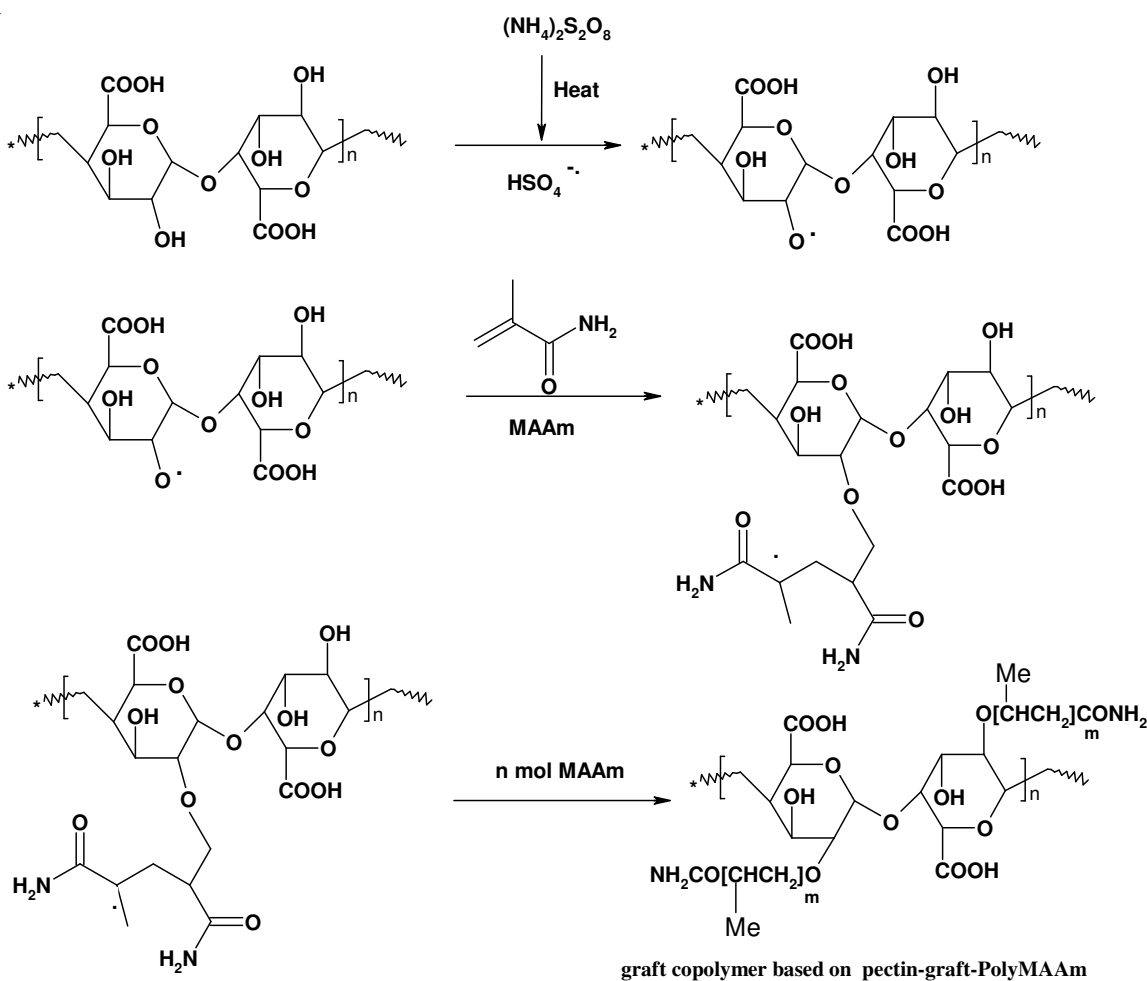
## RESULTS AND DISCUSSION

**Synthesis and characterization:** Methacrylamide monomer was grafted onto pectin in a homogenous medium using ammonium persulfate as a radical initiator and under an inert atmosphere. The mechanism of copolymerization of polymethacrylamide onto pectin in the presence of initiator is shown in **Scheme-I**. At the first step, the thermally dissociating initiator, *i.e.*, ammonium persulfate, is decomposed under

heating to produce sulfate anion-radical. Then, the anion-radical abstracts hydrogen from one of the functional group in side chains (*i.e.*, OH) of the substrate to form corresponding radical (alkoxide radicals). Then, these macroalkoxides initiate crosslinking reaction between some adjacent polymethacrylamide pendant chains. These macroradicals initiate grafting of MAAm onto pectin backbones leading to a graft copolymer<sup>6,7</sup>.

For identification of the produced copolymer, infrared spectroscopy was used. Fig. 1 shows the IR spectroscopy of pectin-g-polymethacrylamide copolymer. The graft copolymer product comprises a pure pectin backbone with side chains that carry carboxamide functional groups that are evidenced by peaks at 1678 cm<sup>-1</sup>. In fact, In the spectrum of the copolymer (Fig. 1b), new peaks are appeared at 3206 and 1660 cm<sup>-1</sup> that may be attributed to amide NH stretching, asymmetric and symmetric amide NH bending, respectively<sup>10</sup>.

**Thermogravimetric analysis:** TGA curves for pure pectin and pectin-g-poly(methacrylamide) copolymer are shown in Fig. 2. The grafted pectin has shown improvement in thermal stability as clear from TGA curve. The initial decomposition temperature of the pectin on grafting was increased from 155-411 °C with maximum decomposition rate at 519 °C, in comparison to original decomposition temperature of 321 °C of pectin. These observations have clearly indicated that grafting of pectin-g-poly(methacrylamide) copolymer has improved the thermal stability of pectin<sup>11</sup>.



**Scheme-I:** A brief proposed mechanism for APS-induced grafting of polymethacrylamide onto pectin

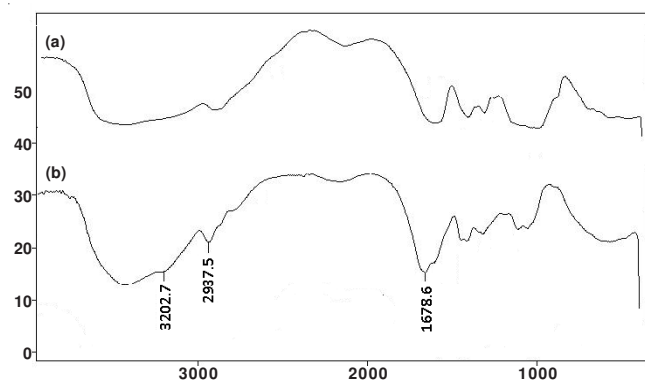


Fig. 1. FTIR spectra of (a) pure pectin and (b) pectin-g-poly(methacrylamide) copolymer

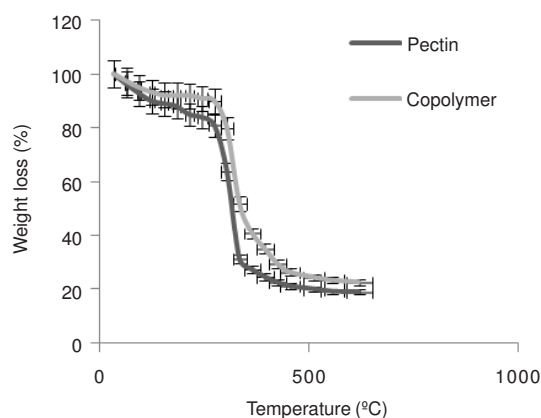


Fig. 2. TGA thermograms of (A) pure pectin and (B) pectin-g-poly(methacrylamide) copolymer. Heating rate 20 °C/min, under N<sub>2</sub>

**Scanning electron microscopy:** One of the most important properties that must be considered is graft copolymer microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Fig. 3 shows an SEM micrograph of the graft copolymer obtained from the fracture surface. The graft copolymer has a heterogeneous structure. It is supposed that these heterogeneous surface are the regions of grafted monomers and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

**Characteristic and determination of important-grafting parameters:** The percentage of conversion (PC %), graft yield (Gr %) and graft efficiency (GE %) were evaluated with the following weight-basis expressions as reported by Fanta<sup>12</sup>:

From the increased weight, the percentage of conversion (PC %) can be estimated as the following equation:

$$PC (\%) = 100 \frac{(W_2 - W_0)}{W_1} \quad (1)$$

where  $W_0$ ,  $W_1$  and  $W_2$  designate the weight of pure pectin substrate, MAAm monomer in feed and total weight product (copolymer and homopolymer) respectively. In this study, the value of  $W_1$  was fixed at 0.75 g. The rough products were extracted by dimethyl formamide solution in a centrifugating apparatus at least 48 h for the complete removal of the homopolymer. The graft yield (G %) and graft efficiency (GE %) are estimated as follows<sup>13</sup>:

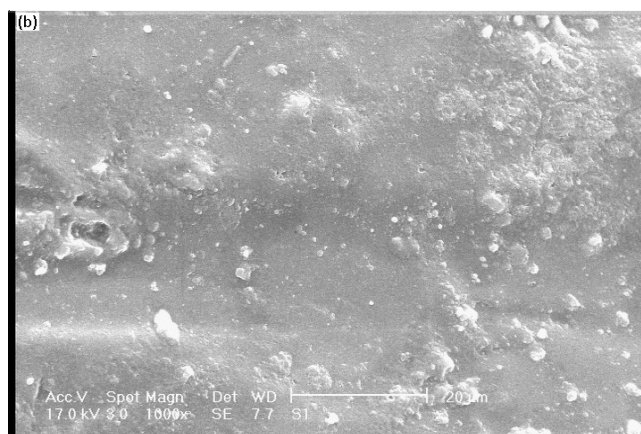
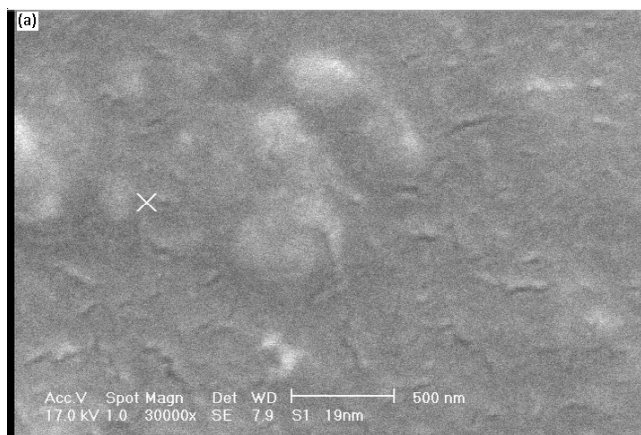


Fig. 3. SEM photograph of the pure pectin (a) and pectin-g-PMAAm copolymer (b)

$$Gr (\%) = 100 \frac{(W_3 - W_0)}{W_0} \quad (2)$$

$$GE (\%) = 100 \frac{(W_3 - W_0)}{(W_2 - W_0)} \quad (3)$$

or

$$GE (\%) = \frac{100(W_3 - W_0)}{(W_4 + W_3 - W_0)}$$

$$Hp (\%) = \frac{W_4}{(W_3 + W_4)} \quad (4)$$

$$Add - on (\%) = \frac{(W_e - W_0)}{W_3} \quad (5)$$

where  $W_3$  and  $W_4$  are the dried weight of grafted pectin after extraction and polyacrylamide homopolymer. Dimethyl formamide is a good solvent for polymethacrylamide as well as a precipitant for pure pectin or grafted pectin, so the polymethacrylamide homopolymer could be easily separated from the rough products. However, it seemed to be difficult to further separate the unreacted pectin from the products and the right separation methods are still in progress in my research. In view of the modification intention, the unreacted pectin is not very necessary to be separated from the products, so the blends of unreacted pectin and the graft copolymer pectin-g-poly(methacrylamide) were actually obtained in this research and their compositions were unknown. In several studies on

the grafting modification of polymer, the unreacted substrate polymer and graft copolymer were also not separated from the products<sup>9,14</sup>. If the unreacted pectin could be separated from the products, the graft copolymer pectin-g-polymethacrylamide with higher grafting yield (%) could be obtained, but the values of percentage of conversion (%) and grafting efficiency (%) would not be affected.

**Gravimetric analysis:** The graft copolymerization reaction was monitored gravimetrically. Increase in the mass of pectin, after extraction of homopolymer, was taken as evidence for grafting. This weight gain in pectin forms the basis for the determination of the grafting parameters.

### Conclusion

A novel copolymer, Pec-g-polymethacrylamide, was synthesized in an aqueous solution by graft copolymerization of methacrylamide monomer onto pectin backbone using ammonium persulfate as an initiator in water solution. The structural characterizations by FTIR spectra have indicated the presence of polymethacrylamide units in the products. The study of FTIR spectra and thermogravimetric analysis provide that the graft copolymerization takes place. The hydrophobically modified pectin exhibited higher thermal stability in comparison with non-modified pectin. The PMAAm-grafted pectin may be a candidate for manufacture of molded plastics, ion exchange resins and plastic films and in cosmetics.

### REFERENCES

1. T. Heinze and T. Liebert, *Prog. Polym. Sci.*, **26**, 1689 (2001).
2. V.D. Athawale and S.C. Rathi, *React. Funct. Polym.*, **34**, 11 (1997).
3. (a) N.K. Sandle, O.P.S. Verma and I.K. Varma, *Thermochim. Acta*, **115**, 189 (1987); (b) V.D. Athawale and S.C. Rathi, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C39**, 445 (1999).
4. A. Hebeish and J.T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer: Berlin (1981).
5. (a) F.E. Okieimen and D.E. Ogbeifun, *Eur. Polym. J.*, **32**, 311 (1996); (b) F.E. Okieimen, *Angew. Makromol. Chem.*, **260**, 5 (1998); (c) F.E. Okieimen and D.E. Ogbeifun, *J. Appl. Polym. Sci.*, **59**, 981 (1996).
6. S.R. Deshmukh, K. Sudhakar and R.P. Singh, *J. Appl. Polym. Sci.*, **43**, 1091 (1991).
7. (a) F.E. Okieimen, *J. Appl. Polym. Sci.*, **89**, 913 (2003); (b) M.L. Leza, I. Casinos and G.M. Guzman, *Eur. Polym. J.*, **25**, 1193 (1989).
8. (a) M.L. Leza, I. Casinos and G.M. Guzman, *Br. Polym. J.*, **23**, 341 (1990); (b) J. Zhang, L.-M. Zhang and Z.-M. Li, *J. Appl. Polym. Sci.*, **78**, 537 (2000).
9. L.-M. Zhang, *Macromol. Mater. Eng.*, **280/281**, 66 (2000).
10. V.D. Athawale and V. Lele, *Starch/Starke*, **52**, 205 (2000).
11. M.J. Zohuriaan, A. Pourjavadi and M. Sadeghi, *Iran. Polym. J.*, **14**, 131 (2005).
12. G.F. Fanta, W.M. Doane, In ed.: O.B. Wurzburg, *Grafted Starches, In Modified Starches: Properties and Uses*; CRC Press: Boca Raton (Florida), pp. 149-178 (1986).
13. L.-M. Zhang and Y.-B. Tan, *Macromol. Mater. Eng.*, **280/281**, 59 (2000).
14. M.M. Ibrahim, E.M. Flefel and W.K. El-Zawawy, *J. Appl. Polym. Sci.*, **84**, 2629 (2002).