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Indian Journal of Advances in Chemical Science

Indian Journal of Advances in Chemical Science 1 (2012) 28-32

Synthesis and Characterisation of Guar Gum-g-Poly(Acrylamidoglycolic acid) by Redox Initiator

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ABSTRACT

Graft copolymer of acrylamidoglycolic acid with guar gum was synthesized and its reaction conditions were optimized for better yield using potassium persulphate as initiators. The effect initiator, guar gum, and monomer along with reaction time and temperature were studied by determining the grafting parameters: % grafting ratio, % efficiency. The graft copolymer was characterized by Fourier transform infrared spectroscopy and thermal analysis. It was observed that the maximum yield occurred at which time of 2h at temperature 60°C.

Key words: guargum, graft copolymer, polysaccharide, acrylamidoglycolic acid, FTIR, thermal analysis.

1. INTRODUCTION

Modification of natural polymers by grafting has drawn much attention in recent years [1]. Guargum is a seed gum obtained from the seeds of cyamopsis tetragonalobus, it is leguminase plant, which is native to north western parts of India. Guargum is high molecular weight carbohydrate polymer, has the characteristic of being rigid and non-ionic [1,2]. It consists of $(1\rightarrow 4)$ - β -D-manno-pyranosyl units with α -D-galacto-pyranosyl units attached by $1 \rightarrow 6$ linkages. It forms colloidal dispersions with water at room temperature and imparts extraordinary viscosity, because of this property, native guargum as well as its derivatives are commercially impart and find use in such diverse applications like oil well drilling, paper and textile sizing, as a binding agent for explosives, and is widely used in food industry [3]. Guargum crosslinked with borax was investigated for water retention applications [4]. Although guargum has wide industrial applications, from some draw it suffers backs like biodegradability [5], which limits its uses considerably. These drawbacks can be improved through the grafting of vinyl monomer, which imparts new properties to the polymeric backbone.

Acrylamidoglycolic acid (AGA) refers to a class of acrylamides containing -OH, -COOH and -CONHfunctional groups that shows excellent hydrophilic as well as responsitivity in biological fluids [6]. In this present work we report synthesis and characterisation of Guar gum grafted poly (acrylamidoglycolic acid).

2. EXPERIMENTAL

2.1 Materials

Guargum (GG) was purchased from Merk Limited, Mumbai. Acrylamidoglycolic acid (AGA) was purchased from Alfa Acer (Japan). Potassium persulphate (KPS) was purchased from s.d. fine chem limited Mumbai, and were all used without further purification. Double-distilled water was used in all experiments.

2.2 Graft copolymerisation

Graft copolymer of GG and AGA was synthesised by free radical polymerization. 0.25 g of GG was dispersed in 30 ml (1.66 mole) of AGA dissolved in a 250 ml round-bottom flask. Then 0.0015-0.0091 mole of AGA dissolved in 10ml (0.55 mole) of water, added to GG solution and the mixture was stirred overnight. A quantity of redox initiator $(K_2S_2O_8)$ equivalent to 0.0002-0.0016 mole was dissolved in 10 ml of water and added to the above solution. Polymerization was carried out at 40-70 °C under continuous nitrogen atmosphere for 60-240 mins in a thermostatic water bath under constant stirring. After complete polymerization, the product was cooled by running under tap water and poured into excess of acetone to induce precipitation. The graft (GG-g-AGA) solid polymer was washed several times with methanol:water (80:20 v/v) mixture [7] to remove the

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homopolymers formed in the grafting reaction and vacuum dried at 40 $^{\circ}$ C to a constant weight. The percentage of grafting (%G), grafting efficiency (%GE) and present conversion (%C) were calculated [7-9] by using

%Grafting (%G) = $\frac{W_1 - W_0}{W_0} \times 100$ %Grafting efficiency (%GE) = $\frac{W_1 - W_0}{W_2} \times 100$ %Conversion (%C) = $\frac{W_1}{W_2} 100$

where W_0 , W_1 and W_2 denote the weight of GG, graft copolymer and monomer respectively.

2.3. Characterization

Fourier transforms infrared spectroscopy (FTIR) spectroscopy was used to confirm the presence of functional groups of GG-g-AGA copolymer. Infrared spectra were recorded by KBr pellet method in the region 4000-500 cm⁻¹ using a Perkin Elmer instrument, model SPECTRUM 2, Singapore. Differential scanning calorimetric (DSC) curves were recorded on a TA instruments (Model: STA, Q_{600} USA). The sample was weighed between 10 to 12 mg. The samples were heated from 30 to 600 °C at a heating rate of 10° C/min in nitrogen atmosphere (flow rate 100 mL/min).

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

Grafting of AGA on GG was confirmed by FTIR studies. FTIR spectra of (a) GG, (b) GG-g-AGA and (c) AGA are represented in figure 1. FTIR spectrum of GG exhibits the characteristic absorption band at 3383 cm⁻¹ and 2925 cm⁻¹ due to O-H stretching vibrations of the polymer associated with C-H stretching vibrations. Additional information from the characteristic absorption bands of GG appears at 1401 cm⁻¹ and 1025 cm⁻¹ due to C-H bending and O-H bending vibrations. In the FTIR spectrum of AGA, was observed the characteristic absorption bands at 2631 cm⁻¹, 1731 cm⁻¹, and 1651 cm⁻¹ are regarding to O-H stretching vibration of carboxylic acid group, C=O stretching vibrations of carboxylic acid group and C=O stretching vibrations of amide group. Additional characteristic absorption bands of AGA appears at 1607 cm⁻¹ and 1534 cm⁻¹ due to C=C stretching vibrations and N-H bending vibrations. The appearance of a new characteristic absorption band at 1734 cm⁻¹ in the FTIR spectrum of GG-g-AGA is due to carbonyl stretching vibration frequency of ester indicate the formation of graft copolymer, the possible schematic representation of GG-g-AGA is shown in scheme I.

3.2. Differential scanning calorimetric analysis (DSC)

DSC technique is used to study the thermal property of pristine and graft copolymers. DSC thermograms of GG (a) and GG-g-AGA (b) are shown in the figure 2. The graft copolymer shows endothermic transitions at 178 °C, 324 °C, which attribute water retention involving -OH group of GG, -COOH group and -OH group of AGA of graft copolymer. GG normally undergoes exothermic transitions at 348 °C, 437 °C, 518 °C. In case of graft copolymer, exothermic transition at 500 °C in the DSC thermogram of graft the copolymer may be due to imide decomposition of cyclized imide groups of PAGA. At high temperatures, acrylamides generally form imides via cyclization [14]. These results support the grafting of AGA onto GG.



Figure 1. FTIR Spectroscopy (a) GG (b) GG-g-AGA and (c) AGA.



Figure 2. DSC thermograms of GG and GG-g-AGA.

3.3. Thermo gravimetric analysis (TGA)

TGA of pristine GG and GG-g-AGA is presented in figure 3. Higher thermal resistance of AGA-g-GG is clearly evident from the spectrum. GG loses 8% weight at 100°C, is the result of desorption of water. GG-g-AGA polymer began to degrade at 150 °C, weight loss of graft polymer about 8% at 150 °C, results of desorption of water. The rate of weight loss of GG increased with increasing temperature, attaining its maxim sum at 300 °C and decreasing thereafter, a broad endothermic peak obtained at 320 °C, 60% of graft polymer degraded at 365 °C. By heating up to 600 °C, graft copolymer only loses 92% weight, whereas GG loses almost all its weight, no appreciable weight loss until 100 °C. Thermal degradation of GG was completed in two steps, 180 °C to 365 °C and 390 °C to 504 °C. There were two T max values, one is at 302 °C and a second one is at 437 °C. The weight of about 60%, 18% occurred in the first and second steps of degradation process. Thermal degradation of graft polymer was completed in three steps, one is at 150°C to 300°C, second one is at 320 °C to 410 °C, and third one is at 420 °C to 500 °C. There are three T max values, 200 °C, 350 °C, and 550 °C. The weights of about 30%, 20% and 27% occurred in the first, second and third steps of degradation.



Figure 3. TGA curves of GG and GG-g-AGA.

3.4. Graft copolymerization

Graft copolymerization was carried out by free radical initiated process in homogeneous solution. Several reports have been published in literature [10,11] on graft copolymerization mechanism. The probable reaction mechanism of present study is given in scheme1. Graft copolymerization of AGA onto GG was achieved by dissolving the GG in monomer solution, then added initiator at the required temperature.

KPS is used as a redox initiator to produce radicals on the polymer backbone [12], grafting reaction is facilitated due to the generation of free radical site by abstracting hydrogen atom from the -OH group of the polymer (GG). Free radicals formed could then react with the double bond of the vinyl monomer, resulting in a covalent between the monomer and GG to propagate the chain. Termination of the graft copolymer may be due to the combination of the two macro radicals.

3.5. Effect of temperature

Temperature plays a vital role in determining the extent of grafting. In general, grafting yield increases with increase in temperature until a limited value is reached. By the increasing of temperature, it may lead to various effects on grafting, they are: (i) swelling of GG to larger extent, (ii) increase in solubility of the monomer



Figure 4. Effect of temperature on %G (♦) and %GE (■).





(iii) increase in monomer diffusion to the grafting sites, (iv) easy decomposition of the initiating redox system (v) enhancement of rate of initiation and propagation and (vi) increase in the rate of termination. The factors (i) to (v) could increase grafting, while factor (vi) may have the reverse effect on grafting. Effect of temperature on graft copolymerisation of AGA onto GG was investigated at five different temperatures ranging from 40 to 70 °C, keeping other conditions constant, and the results are presented in figure 4. Maximum %G and %GE are attained at the temperature of 60 °C. Raising the temperature up to 70 °C causes %G and %GE to decrease rapidly due to the chain-transfer and termination reactions, which are known to be favoured at higher temperatures in free radical polymerization.

3.6. Effect of monomer concentration

Initiation of graft copolymerization by free radical mechanism involves the formation of free radicals; free radicals can react with the monomer to initiate graft copolymerization. The efficiency of graft copolymerization depends upon the concentration of monomer present in the mixture solution. Larger



Figure 5. Effect of AGA on %G (♦) and %GE (■).

the concentration of monomer more favoured will be the reaction between free radicals and the monomer that triggers the grafting process. Increasing the amount of monomer in the feed leads to an increase in % grafting and % grafting efficiency and % conversion increases. The %G, %GE increases with increasing monomer concentration from 0.00153 mol to 0.091mol of AGA (figure 5). The %G, %GE reached their maximum values, at the monomer concentration of 0.061 mol. Increasing amount of monomer even further, %G, %GE and %C were decreased due to the formation of higher % of homopolymers in the growing grafted chain. It is expected that, swelling of the base polymer at higher monomer concentrations were not favourable for grafting.

3.7. Effect of initiator concentration

Increasing the concentration of KPS initially leads to an increase in the %G, %GE and %C, but further



Figure 6. Effect of KPS on %G (\blacklozenge) and %GE (\blacksquare).

radicals, since an increase in concentration facilitates more GG macro radicals and more active sites to react with AGA, on further increase in the concentration KPS from 0.0011 mole, the concentration of KPS radicals would increase, which could help the polymerization of AGA thus, resulting in a decrease of %G and %GE. In case of grafting initiated by a chemical initiator, the extent of grafting increases with initiator concentration up to a certain limit, beyond which grafting no longer increases. This could ascribe to the decay of macro radicals [13]. Effect of KPS concentration on grafting was studied in the range of 0.0002-0.0016 moles. The highest %G and %GE were obtained at 0.0011 moles, above the 0.0011 moles KPS concentration, a decrease in grafting was observed (figure 6). This phenomenon may be due to the efficiency of KPS to participate in the termination reaction of growing grafted chains as well as homopolymerization.

3.8. Effect of time



Figure 7. Effect of time on %G (\blacklozenge) and %GE (\blacksquare).

The effect of change in duration of grafting reaction has been studied by varying the time period from 60 to 120 min, and the results are given figure 7. It has been observed that the %G,

%GE and %C increased with increases in time from 60 to 120 min, but beyond this, the grafting parameters and rate of grafting decreased, whereas homopolymers was found to increase. With increasing time, the propagation of grafting chains occurred because of the availability of more active species, which accounted for the higher grafting. With further increases in the interval, mutual annihilation of growing grafted chains occurred, which resulted in the grafted parameters and rate of grafting decreasing but homopolymer formation increasing.

4. CONCLUSION

In the present study, GG was grafted by AGA using KPS as a free radical initiator. Reaction conditions such as temperature, time, initiator content, monomer concentration have shown an influence on %G, %GE, and %C. The maximum %G was possible by using KPS at 60 ^oC, 2 hr of reaction time, 0.0011 mole concentration of KPS and 0.00919 mole AGA. The grafting has been confirmed by FTIR spectroscopy and Thermal studies. The synthesized graft (GG-co-AGA) polymer could be used to develop pH sensitive hydrogels for controlled release and toxic metal ion removal applications.

Acknowledgements

Authors thank the Department of Science and technology (DST), New Delhi, India, (DST No.**SR/FT/CS-047/2009**) for a financial support and Board of Research in Nuclear Sciences (BRNS) for partial financial support for this work (Grant No.: **2010/37C/53BRNS/2538, Dated 23-02-2011).**

5. REFERENCES

- [1].J.K. Seaman., (1980) In Hand book of water soluble Gums and Resins; Mc Graw-Hill: New York.
- [2].H. Keles, M. Celik, M. Sacak L. Aksu, (1999) Graft copolymerization of methyl methacrylate upon gelatin initiated by benzoyl peroxide in aqueous medium, *Journal of Applied Polymer Science*, 74, 1547-1556.

- [3].M. Sacak, M. Celik, (1996) Hydrogen peroxide initiated grafting of acrylamide onto poly (ethylene terephthalate) fibers in benzyl alcohol, *Journal of Applied Polymer Science*, 59, 1191-1194.
- [4].G.J.S. Raid, (1985) in biochemistry of storage carbohydrates, P.M. Day, R.A. Dixon, Eds., Academic Press: London.
- [5].R.L. Wistler, (1973) Industrial gum; Academic press: New York.
- [6].B.L. Rivas, B. Quilodram, E. Quiroz, (2006) Metal ion retention properties of waterinsoluble polymers containing carboxylic acid groups, *Journal of Applied Polymer Science*, 99, 697-705.
- [7].T. Sun; P. Xu; Q. Liu; J. Xue; W. Xie, (2003) Graft copolymerization of methacrylic acid onto carboxymethyl chitosan, *Europian Polymer Journal*, **39**, 189-192.
- [8].K.S.V. Krishna Rao, Ildoo Chung, Chang-Sik Ha, (2008) Synthesis and characterization of poly(acrylamidoglycolic acid) grafted onto chitosan and its polyelectolyte complexes with hydroxyapatite, *Reactive and Functional Polymers.* 68. 943-953.
- [9].S. Vandana, T. Ashutosh, N.T. Devendra, S, Rashmi (2005) Poly(acrylonitrile) grafted *Ipomoea* seed-gums: A renewable reservoir to industrial gums, *Biomacromolecules*, 6, 453.
- [10]. H.F.J. Nauib, (2002) Chemically induced graft copolymerization of itaconic acid onto sisal fibers, *Polymer Research*, 9, 207.
- [11]. T. Yoshida, K. Hattori, Y. Swada, Y. Choi, T. Uryu, (1996) Graft copolymerization of methyl methacrylate onto curdlan, *Journal of Polymer Science Polymer Chemistry*, 34, 3053-3060.
- [12]. K.V. Harish Prashanth. R.N. Tharanathan, (2003) Studies on graft copolymerization of chitosan with synthetic monomers. *Carbohydrate Polymers*, 54, 343-351.
- [13]. S.N. Battacharya, D. Maldas, (1984) Graft copolymerisation onto cellulose, *Progress in Polymer Science*, 10, 171-270.
 - [14]. D. R. Biswal. R.P. Singh, (2004) Charecterisation of carboxymethylcellulose and poly acryl amide graft copolymer, *Carbohydrate Polymers*, **57**, 379-387.

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