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Research Article

A Microwave- irradiated Novel Superabsorbent Polymer Hydrogel (Guar gum-g- PAA): Synthesis, characterization and property studies

Abstract

The main aim of the present study was to synthesize Guar gum grafted poly acrylic acid (Gg-g-PAA) superabsorbent polymer (SAP) hydrogel via free radical emulsifier-free emulsion graft polymerization technique using microwave irradiation. The so prepared superabsorbent polymer hydrogel was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM). The properties like swelling ability and biodegradability were also studied which has a profound influence in agriculture, biomedicine, pharmaceuticals, etc. The SAP may potentially be used for the fast release of medicine in high pH environment. It also may have found its application and sustainability in the removal of heavy metal ions from the waste water through adsorption leading to water remediation.

Introduction

Superabsorbent polymer hydrogels are the organic materials with cross linked three dimensional networks possessing high swelling ability in aqueous media due to the presence of ionic functional groups. SAPs can be used in many medical applications such as drug delivery system, healing products, treatment of edema, etc [1,2]. Beyond this hygienic use, the SAPs have found very wide applications in other sectors i.e. in agriculture, pharmaceuticals, separation technology, textiles, water swelling rubbers and constructions [3-5]. Guar gum is a hydrophilic, non-ionic natural polymer which swells in cold water. It has a vast application in various industries like food, cosmetics beverages, paper, pharmaceuticals drilling and mining due to its non-toxic nature, cost effective emulsifying and water thickening stabilizing agents [6-8]. During graft copolymerization the cross linked structure of polyacrylic acid copolymer is affected by monomer concentration and the pH which causes swelling behavior due to hydrogen bridge and covalent bond formation [9]. Therefore, it has been widely used in controlling the delivery of the drugs to the intestine or for gastric retention application.

In this work, we have tried to synthesize a superabsorbent polymer hydrogel by grafting of AA onto the backbone of guar gum via microwave assisted emulsifier-free emulsion process [10,11]. The use of microwave irradiation throughout the

research work increases the rate of polymerization rapidly and improve the quality of the products which results less energy consumption [12,13].

Materials and Methods

Materials

Guar gum (Gg), ammonium persulphate (APS), methylene bis acrylamide (MBA), sodium bicarbonate (NaHCO₃), sodium chloride, calcium chloride, aluminium chloride, hydrochloric acid and Lutrol F[®]127 were purchased from Himedia, Mumbai, India Ltd. Acrylic acid (AA) (molar mass 72.06g/mol; density 1.051 g/cc; solubility in water 1.75g/100ml at 0°C) is 99% purity was purchased from LACHEMA, Germany, and was used as such without purification.

Preparation of hexamine cobalt (III)Chloride [Co(NH₃)₆] Cl₃

It was prepared by the method available in the literature [14]. About 240g (1mole) of cobalt (III) chloride 6-hydrate and 160g (1mole) of ammonium chloride were added to 200ml of water. The mixture was shaken until most of the salts had dissolved. Then 4g of activated decolorized charcoal and 500ml of concentrated ammonia were added. Air was bubbled vigorously through the mixture for about 4h until the red solution becomes yellowish brown. The air inlet tube

was of fairly large bore (10mm) to prevent clogging with the precipitated hexamine cobalt (III) salt. The crystals and carbon were filtered on a Buchner funnel and then added to a solution of 15 to 30ml of concentrated HCl, and 1500ml of water sufficient acid was used to give the entire mixture an acidic reaction. The mixture was heated on a hot plate to get complete solution and was filtered hot. The hexamine cobalt (III) chloride was precipitated by adding 400ml of concentrated HCl and slowly cooled to 0°C. The precipitate was filtered and washed with first 60% and then 95% alcohol and dried at 80–100°C.

Synthesis of graft copolymer, Gg-g-PAA, hydrogel

Required amount of guar gum was added to various reaction vessels along with 30 ml of deionized water each and stirred at 250 rpm for 10 min. After dissolving Gg, the desired quantities of monomer AA, and the crosslinker MBA, Lutrol F[®]127 (foam stabilizer) were simultaneously added and the reaction mixture was stirred for 15 min. Then the initiator APS and Cobalt (III) chloride complex, NaHCO₃ (foaming agent) was added (Table 1). The solution was stirred at 400–500 rpm while maintaining the temperature in inert atmosphere under microwave irradiation constantly in a RotoSYNTH Microwave synthesizer (Milestone, Italy). The microwave synthesizer automatically reproduces a preset temperature/time profile tuning the emitted microwave power. At present, attaining the constant temperature of 70°C, the microwave oven was automatically operated at power of 40W and the polymerization was continued for 120s–300s. After polymerization, the product was extracted with boiling ethanol, collected by centrifugation and dried in the oven under vacuum at 80°C for 24 h.

Characterization

FT-IR spectra

FTIR spectra were used to analyze composition of the SAP₁₃ that gives the information about grafting and functional groups present in the hydrogel. The spectra of virgin and crosslinked

polymer SAPs were recorded in the range 400–4000 cm⁻¹ on a Perkin Elmer Paragon 500 FTIR spectrophotometer using KBr pellets.

TGA

TGA gives the thermal stability of the SAP₁₃ hydrogel. The TGA data were recorded with a shimadzu DTG-50 thermal analyzer. The samples were heated from room temperature to 600°C at a heating rate of 10°C per min.

SEM

It gives the morphological characteristics of the SAP₁₃. The SEM of gold-coated sample was obtained using JSM - 6390LV scanning electron microscope (Jeol Ltd, Japan).

Measurements of swelling ability of superabsorbent hydrogel (SAP)

Swelling ability of the prepared SAP₁₃ was carried out by tea bag method. About 0.2 g of sample was added to a small nylon bag (50 mm x 90 mm; 200 mesh). Then the bag was completely dipped in de-ionized water at room temperature for 24 h until equilibrium was reached. Then the tea bag was removed from the de-ionized water and excess water was drained for 10 min. The swelling behavior of SAP samples were studied by using different concentration of salt solutions (Na⁺, Ca²⁺, Al³⁺) The weight of swollen sample and dried sample were taken. The equilibrium swelling was calculated using the following equation,

$$ES (g/g) = (W - W_1) / W_1$$

Where W= weight of the swollen sample, W₁ = weight of the dried sample

Biodegradability

Biodegradability of SAP₁₃ was done in activated sludge water which was collected from sewerage water. The activated sludge water and 0.2gm of the sample (SAP₁₃) were placed in a sterilized vessel at room temperature (28±/– 2°C) for 90 days. After the required time period, the samples were washed thoroughly 4/5 times with de-ionized water at 60°C for 24h. Then the samples were weighed to determine the weight loss.

Results and Discussion

FTIR spectra

IR spectrum of Gg in figure 1 (a) showed broad peaks at 3446.15 cm⁻¹ (O-H stretching of carbohydrates), 2900 cm⁻¹ (–CH₂ asymmetric stretching), 1430.77 cm⁻¹ (–CH and –CH₂ in plane bending in carbohydrates), 1023.08cm⁻¹ (–CO stretching region as complex bands resulting from C–O and C–O–C stretching vibrations) and 630.77 cm⁻¹ (pyranose ring) [15,16]. For Gg-g-PAA, SAP₁₃, figure 1 (b) showed the peaks at 1662.64 cm⁻¹ (C = O stretching of COOH group), 2924.09 cm⁻¹ (–CH₂ stretching), 896.50 cm⁻¹ (–CH₂ in plane bending) and 615.29 cm⁻¹ (–OC, –OH defragmentation of COOH). All of these bands are related to AA and hence the FTIR spectra confirm the grafting of AA onto Gg [16].

Table.1: Composition of the feed mixture.

Sample code	Guar gum (g)	APS (g)	Co(III) complex	AA (ml)	ES (g/g)
			(ml)		
SAP ₁	0.25	0.1	0.1	2	85.3
SAP ₂	0.5	0.1	0.1	2	92.5
SAP ₃	0.75	0.1	0.1	2	81.2
SAP ₄	0.5	0.1	0.1	2	73.1
SAP ₅	0.5	0.1	0.1	2	67.5
SAP ₆	0.5	0.1	0.2	2	77.2
SAP ₇	0.5	0.2	0.3	2	83.4
SAP ₈	0.5	0.3	0.2	2	89.5
SAP ₉	0.5	0.2	0.2	2	108.3
SAP ₁₀	0.5	0.2	0.2	2	90.5
SAP ₁₁	0.5	0.2	0.2	2	81.2
SAP ₁₂	0.5	0.2	0.2	2	72.5
SAP ₁₃	0.5	0.2	0.2	4	121.2
SAP ₁₄	0.5	0.2	0.2	6	109.3
SAP ₁₅	0.5	0.2	0.2	7.5	98.5

TGA

The TGA technique was used for the thermal characterization property studies of the obtained graft copolymers as shown in figure 2, a two-step characteristic thermogram showed in figure 2 (a) Gg, whereas the major weight loss (73%) took place in the second step within the temperature range of 170–328°C, for a maximum decomposition the temperature was found to be 313 °C. There are three decomposition stages in the thermogram of PAA figure 2(b) as showed. The first decomposition stage in the range 49.2 – 101.5 °C was attributed to the loss of bound water. The second one in the interval of 214.8–302.9 °C was due to the dehydration and decarboxylation of the polymer which leads to the formation of inter- and intra-molecular anhydride. 364.1–468.8 °C, the third decomposition range was a result of the degradation of the residual polymer. The thermal stability of the grafted Gg-g-PAA figure 2 (c) was improved as it is obvious from the TGA curve. In the TGA curve of Gg about 49.8 % weight loss took place in the temperature range of 244–380.2 °C, while it was 36.9 % in grafted copolymer (Gg-g-PAA). (Moreover, the high char yield, up to 28.1 wt%, at 600 °C observed in thermogram indicated that the graft copolymers had significantly higher thermal stability than that of the Gg (Char yield = 26.7%), which was caused by the strong bonding between the grafting polymer chains and Gg matrices in the graft copolymer [17]. These studies indicate the thermal stability of the so formed Gg-g-PAA(SAP₁₃).

SEM

SEM shown in figure 3, depicts much high magnification of SAP₁₃ hydrogel structure in which we can see the surface morphology. The figure verifies that the graft copolymers prepared in this work have a macroporous structure. The surface of SAP₁₃ hydrogel was rough and the approximate diameter of the pores was found to be in between 40–100 μm. The uneven surface may be due to a quite high viscosity of the gel and the solvent evaporation process. It was supposed that these pores were the regions of water permeation and interaction sites of external stimuli with the incorporated drug

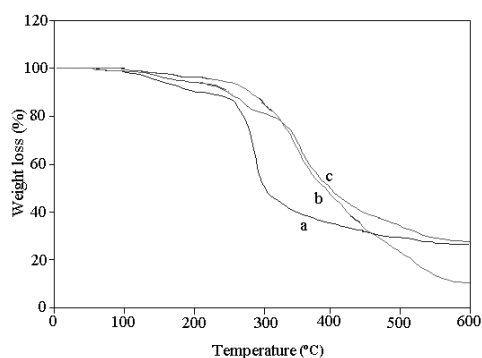


Figure 2: TGA of (a) Gg, (b) PAA, (c) Gg-g-PAA (SAP₁₃).

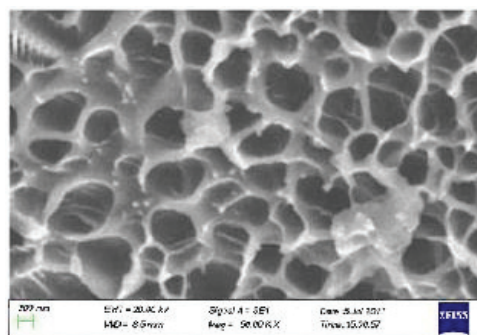


Figure 3: SEM image of the macroporous (SAP₁₃) hydrogel (NaCl solution).

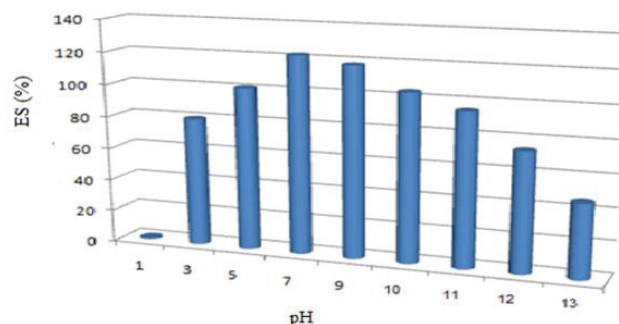


Figure 4: Effect of pH values on equilibrium swelling of (SAP₁₃) at 25 °C

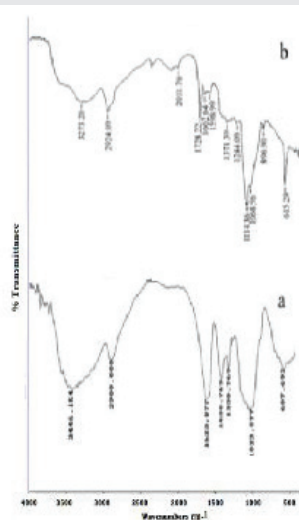


Figure 1: FTIR spectra of (a) Gg, (b) Gg-g-PAA (SAP₁₃).

or hydrophilic groups of the graft copolymers [18]. Therefore, the porous structure is the main reason for the higher swelling rate.

Swelling studies

Effect of pH on swelling behavior: Swelling behavior of SAP₁₃ depends upon the pH values 1.0–13.0, Swelling behaviour of SAP₁₃ at room temperatures with different pH values was shown in figure 4. At pH values 3.0–4.5, the swelling capacity was decreased as maximum number of carboxylate anions undergoing protonation. At pH values 5.0–7.4, the swelling capacity was increased due to ionization of less number of carboxylate groups. At pH >7.4, the swelling was further decreased. In other words, the presence of large number of ionic groups in the polymer chains result in the increased swelling behaviour, because the ionic groups are more strongly solvated than non-ionic groups in the aqueous medium [19].

Effect of type and concentration of salt solutions on swelling behavior: Swelling behaviour of SAP₁₃ also depends upon the type and concentration of salt solution as shown in figure 5. Multivalent cations (Al³⁺, Ca²⁺) decrease the swelling ability than the univalent cation (Na⁺) as the presence of carboxylate groups induce the formation of intermolecular and intramolecular complexes [19,20].

Reswelling ability: Reswelling ability of SAP₁₃ was shown in figure 6. It required 15 min to swell up to maximum (121.3g/g) and 10 min to deswell completely (i.e. 12.5g/g). The deswollen hydrogel was again allowed to undergo further swelling-deswelling cycle [21,22]. The reswelling and deswelling ability of SAP₁₃ depends upon the pH variation. The equilibrium swelling of SAP₁₃ decreases at pH =1.0 and increases at pH =7.4. The deswelling ability at pH =1.0 arises due to protonation of maximum number of COO⁻ groups to yield uncharged -COOH groups. The reswelling ability of SAP₁₃ at pH =7.4 arises due to ionization of carboxylic groups and diffusion of solvents into the outer surface of the hydrogel through the macropores. This reswelling and deswelling ability of SAP₁₃ are able to make controlled drug delivery system [23].

Biodegradation Study

Biodegradability of Guar gum, PAA and Gg-g-PAA (SAP₁₃) were given in figure 7. In 90 days all samples show satisfactory results, but Gg-g-PAA (SAP₁₃) is more degradable as compared to others. It is due to hydrophilic nature of SAP₁₃ or high water content in the SAP₁₃ which facilitates the growth of micro-organisms rapidly and is responsible for enhancing the biodegradation which is leading to weight loss [7,24].

Conclusion

The SAP₁₃ hydrogel (Gg-g-PAA) was synthesized via microwave assisted free radical emulsifier-free emulsion graft polymerization method. Then the so prepared hydrogels were well characterized through FTIR, TGA, SEM and on comparison the SAP₁₃ hydrogel exhibited high sensitivity to pH, so that several swelling changes of the hydrogel were observed in pH variations of a wide range 1–13. The main driving force responsible for such abrupt swelling changes is the ionic repulsion between charged groups incorporated in the hydrogel matrix by an external pH modulation. Furthermore,

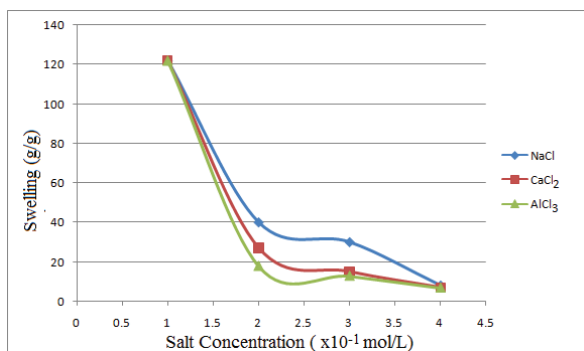


Figure 5: Variation of swelling capacity of SAP₁₃ in saline solutions with various concentrations.

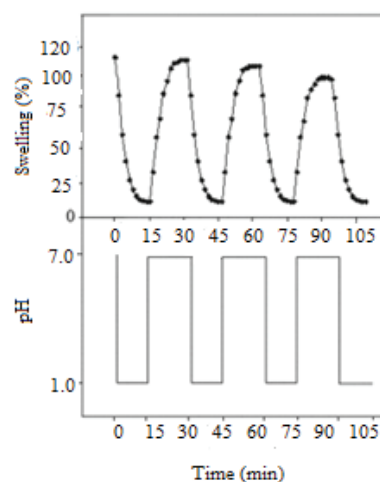


Figure 6: Equilibrium reswelling ability of SAP₁₃ (pH 1.0-pH7.0 at 37°C).

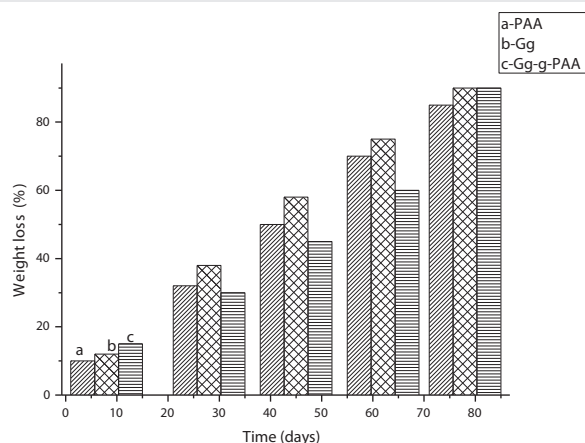


Figure 7: Biodegradation of (a) AA, (b)Gg, (c) Gg-g-PAA(SAP₁₃)

the reversible swelling-deswelling behavior in solutions with acidic and basic pH makes the hydrogel suitable for controlled drug delivery systems. Swelling measurement of the prepared hydrogels in different salt solutions resulted in the appreciable change in swelling capacity. However, swelling loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. Modification of guar gum via graft copolymerization and network formation with acrylic acid improves the property profile and usability of the polymer in various biomedical applications because of its high water absorption capability, good swelling and deswelling ability, biodegradability. This material may be good for the fast release of medicine in high pH environments such as the human intestine. The SAP₁₃ hydrogel may potentially be used in agriculture, biomedicine, pharmaceuticals, controlled delivery of bioactive agents, adsorption of heavy metal ions from waste water leading to water remediation which is in progress in our laboratory.

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