Synthesis, Characterization and Swelling Behaviour of Guar Gum-g-poly (Methyl Methacrylate) Superabsorbent Nanocomposite

Kartika Rathore1* and Sangeeta Loonker1

1Applied and Environmental Chemistry Laboratory, Department of Chemistry, Jai Narain Vyas University, Jodhpur – 342011, Rajasthan, India.

ABSTRACT

In this work, polymer nanocomposite was synthesized based on guar gum (GG) and methyl methacrylate (MMA) by free radical graft copolymerization reaction using boric acid as a cross linking agent and hydrogen peroxide as an initiator in complete aqueous solution to make it environmental friendly. The composite was synthesized to be used as superabsorbent for the purpose of water absorption. Fourier transform infrared (FTIR) analysis was carried out to confirm grafting of methyl methacrylate onto guar gum. The morphological study of composite was carried out by scanning electron microscopy (SEM). Thermal gravimetric analysis (TGA) confirms the stability of nanocomposite. The composite was characterized by X-ray diffraction (XRD) to study its crystalline nature. The water absorption capacity of superabsorbent was measured in distilled water by free swelling method as a function of percentage swelling and found to be 3000%. The effect of reaction parameters such as guar gum concentration, monomer concentration, initiator concentration, cross-linker concentration and temperature was investigated. The percentage swelling of superabsorbent composite was studied at various pH values between 2.0 and 13.0. The swelling behaviour of composite was also examined in saline solutions. Result shows that swelling
capacity is decreased by increasing the ionic strength of swelling medium. This behavior is because of charge screening effect for monovalent cations as well as ionic crosslinking for multivalent cations.

Keywords: Percentage swelling; copolymerization; grafting; SEM; TGA; saline; charge screening.

1. INTRODUCTION

Superabsorbent polymers are moderately cross-linked hydrophilic network materials that can absorb and retain large quantities of aqueous fluids while preserving their shapes [1]. Because of the unique characteristics they are extensively applied in various fields such as agriculture and horticulture [2,3], hygienic products as disposable diapers and feminine napkins [4], wastewater treatment [5,6,7], bio-medical area as antibacterial materials [8] and drug delivery [9,10]. However the traditional superabsorbents are mainly based on fully organic petroleum based polymers with relatively higher production cost and poor environmental friendly properties [11]. Thus new types of cost-efficient and eco-friendly superabsorbents derived from naturally available raw materials have long been desired.

The modification of natural polymers is a promising method for the preparation of new materials. Graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve these materials. Superabsorbing resins were first developed with a view to utilize in agricultural materials and are typed by the hydrolysed corn starch-g-poly (acrylonitrile), H-SPAN [12]. Presently, natural macromolecules such as starch [13,14], cellulose [15], chitosan [16,17], gelatin [18], alginate [19] etc and their derivatives have been used as polymer matrix for preparing superabsorbents and the resulting materials also exhibited ameliorative properties.

GG is a hydrophilic, nonionic polysaccharide extracted from the endospermic seed of the plant Cyamopsis tetragonalobus. It consists of a linear backbone of - (1-4)-linked D-mannose units and is solubilised by the presence of randomly attached-(1-6) - linked galactose units as side chains. GG and its derivatives form valuable ingredients for foods, cosmetics and pharmaceuticals [20]. GG has better reactivity and can be facilely modified by grafting vinyl monomers onto its backbone to derive new materials with improved structure and performance [21]. The main functions of guar gum are as viscosifier, thickener, emulsifier, binding agent, stabilizer, gelling agent, natural fibre and flocculant [22]. In this paper, we have tried to synthesize and characterize new superabsorbent nanocomposite based on guar gum and methyl methacrylate in complete aqueous solution. The structure of guar gum is shown in Fig. 1.

![Fig. 1. Structure of guar gum](image)
2. EXPERIMENTAL

2.1 Materials

Guar gum (GG, Shri Ram Gum Industries Basni, Jodhpur), Methyl methacrylate (MMA stabilised for synthesis, Merck), Boric acid (H₃BO₃, Qualigens Fine Chemicals), Acetone (Fischer Scientific, Qualigens), Hydrogen peroxide (H₂O₂, Emplura 30% w/v) and Ethanol (C₂H₅OH, Emsure) All of these are used without further purification.

2.2 Synthesis of Guar gum-g-PMMA Superabsorbent Nanocomposites

Guar gum (GG) 1.6 % (w/v) was added in 50 mL of distilled water in a round-bottomed flask equipped with stirrer and thermostated water bath. The above solution was stirred for one hour. The monomer MMA (6% v/v) was added in above guar gum slurry and mixture was stirred for half an hour. Then required volume of initiator hydrogen peroxide (1mL/10mL) was added to generate radicals. Further 1% aqueous solution of cross-linker (prepared by heating 0.1 g boric acid in 10 mL distilled water) was added in the mixture. The reaction mixture was continuously stirred and heated to 60ºC for about 3 hours. After that it was precipitated using excess of acetone and kept overnight. Then it was washed several times with mixture of distilled water and ethanol (60:40) to remove homopolymer and unreacted mass. The grafted product was dried in oven at 80ºC. Finally, the dried resulting product was pulverized into powder.

2.3 Absorbency or Swelling Measurement

Absorbency of superabsorbent composite is measured by the free swelling method and calculated in terms of percentage swelling. A 0.1 g of dry sample was immersed in distilled water at room temperature for 24 h to reach swelling equilibrium. The swollen gel was taken out, dried between folds of filter paper (blotting) and weighed. After weighing the swollen samples, the equilibrium water absorbency of the superabsorbent was calculated using Eq. (1)

\[
\text{% Swelling} = \frac{W_2 - W_1}{W_1} \times 100
\]

% Swelling is the equilibrium water absorbency of sample which are the averages of three measurements. \(W_1\) and \(W_2\) are the weight of the dry sample and water swollen sample respectively.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization

The superabsorbent nanocomposite was synthesized by graft copolymerization of methyl methacrylate onto guar gum in presence of a cross-linking agent boric acid and hydrogen peroxide was used as an initiator. The peroxide is decomposed under heating and produced hydroxide radicals that abstract hydrogen from -OH groups of the guar gum backbone. This peroxide-saccharide redox system thus results in active centers capable of initiating radical polymerization of MMA to give a graft copolymer. Since a cross-linking agent, boric acid is present in the system, the copolymer has a crosslinked structure. The composite was characterized by FTIR to confirm grafting of MMA onto guar gum.

Fig. 2. (a) Dry composite (b) Swollen composite
Scheme 1. General mechanism for hydrogen peroxide initiated graft copolymerization of MMA onto guar gum in presence of boric acid

3.2 SEM Analysis

Scanning electron microscopy was used for analyzing surface morphology of prepared composite. Fig. 3 shows SEM micrographs of guar gum and prepared superabsorbent composite at different magnification obtained by Zeiss instrument. SEM observations reveals that prepared superabsorbent composite has an uneven and coarse surface. It is clear from figure that composite has more rougher and porous structure as compared to guar gum. These observations are in good agreement with our water absorbency observations.
Fig. 3. SEM micrographs of (a) Guar gum (Mag = 51 X) (b) Guar gum (Mag = 500 X) (c) GG grafted PMMA composite (Mag = 51X) (d) GG grafted PMMA composite (Mag = 3.8 KX) (e) GG grafted PMMA composite (Mag = 10 KX)
3.3 FTIR Analysis

To study the functional groups and bonds characteristic of prepared superabsorbent, FTIR was carried out on sample made by pelleting with KBr. FTIR spectra was collected in Agilent Cray 600 series spectrophotometer in the range 4000-400 cm⁻¹. The FTIR spectrum for native guar gum showed broad band in a region of 3324 cm⁻¹ attributed to stretching vibration of O–H bond that exhibited the presence of large number of free hydroxyl groups in the guar backbone. The finger printing region of guar gum consists of characteristic peaks from 862 to 1145 cm⁻¹ designated to the C–O bond stretch. The bands at 1636 cm⁻¹ and 1376 cm⁻¹ are due to bending vibration of OH and CH₂ respectively. The sharp band at 2926 cm⁻¹ was due to CH₂ group stretching [23]. The spectra of guar gum grafted PMMA composite exhibited a broad peak at 3453.8 cm⁻¹ which indicates stretching vibration of the OH group, a smaller peak at 2925 cm⁻¹ is attributed to C–H stretching vibrations. The absorption band at 1720 cm⁻¹ is due to C=O stretching vibrations. There is a distinct absorption band from 1250 cm⁻¹ to 1152 cm⁻¹ which can be attributed to C–O–C stretching vibrations. The band at 1426 cm⁻¹ can be attributed to bending vibration of C–H bonds of -CH₃ group. The peak at 1025.7 cm⁻¹ is due to coupling of C–O stretching and O–H ‘in plane’ bending vibrations. The presence of the characteristic peaks clearly proves that PMMA has been successfully grafted onto the guar gum.

3.4 XRD Analysis

X-ray diffraction (XRD) is a powerful nondestructive technique for characterizing crystalline materials. X-ray diffraction (XRD) pattern was obtained with Philips X'pert pyro system Cu Kα radiation (λ=1.54 angstrom and theta = 0-80°) at room temperature. Crude guar gum was largely amorphous and two peaks were observed at the scattering angle (2θ) at 17.5° and 20.4° [24]. The grafted composite showed two peaks at scattering angle (2θ) at 30° and 50.9°. This shows the development of crystallinity in superabsorbent composite. The average crystallite size was calculated using Scherrer equation and found to be 36.7 nm.

3.5 TGA Analysis

Thermal gravimetric analysis of composite was carried out using TGA Q 500 to study its thermal stability. Fig. 6 shows the TGA curves of guar gum, GG-g-PMMA composite and PMMA. TGA of guar gum shows weight loss in two stages. The onset of thermal degradation occurs at 250°C with weight loss of 15% which is due to presence of moisture in sample. The second stage is degradation stage which occurs at 325°C with weight loss of 73%. In TGA curve of composite, thermal degradation occurs at 261°C with a weight loss of 14% which is the result of desorption of water. The composite shows 71% weight loss at 335°C. There is about 84% weight loss at 550°C. At 881°C composite loses 87% of its weight. TGA curve of PMMA shows weight loss of 20% at 337°C. PMMA shows 100% weight loss at 425°C. This shows the better thermal stability of grafted composite.

3.6 Effect of Reaction Parameters

3.6.1 Effect of monomer concentration

The influence of monomer (methyl methacrylate) concentration has been studied by synthesizing series of composites with varied volume of methyl methacrylate. The effect of monomer concentration on water absorbency is shown in Fig. 7. It is clear from the figure that initially water absorbency increases by increasing monomer concentration and reaches maximum at 6 % (v/v) and thereafter it reduces. Co-polymerization between MMA and guar gum increases the percentage swelling thereafter it decreases due to formation of homopolymer of MMA.

3.6.2 Effect of initiator concentration

Initiator has greater influence on rate of polymerization as it involves in initiating free radicals. The effect of initiator concentration was studied by varying initiator concentration from 1 to 14% (v/v). Fig. 8 depicts that continuous increase in water absorbency is observed till an optimum volume of 10% v/v which indicates that initiation of free radicals increases the polymerization which in turn increases absorbency and decreases with further increase in content of initiator. At higher levels of initiator concentration, grafting is unfavourable and this behaviour is attributed to the formation of excess number of free radical sites leading to shorter polymer chains. The molecular weight in free radical polymerization will decrease with an increase of initiator concentration. With the decrease of molecular weight, the relative amount of polymer chain ends increases. The polymer chain ends do not contribute to water absorbency [23,25]. Therefore, the increase of initiator content is responsible for decrease in water absorbency.
Fig. 4. FTIR spectra of guar gum grafted PMMA composite

Fig. 5 XRD pattern of guar gum grafted PMMA composite
Fig. 6. TGA curves of (a) Guar gum (b) GG-g- PMMA composite (c) PMMA

Fig. 7. Effect of monomer concentration on swelling capacity of superabsorbent composite
3.6.3 Effect of cross-linker content

Crosslinking density is an extremely important swelling control element. Relatively small changes can play a major role in modifying the properties of superabsorbent polymers. In our study the water absorbency decreases with increase of cross-linker content from 1 to 12% (w/v). When the crosslinker content is more than 1% (w/v), the absorbency of superabsorbent composite decreases because of an increase of soluble content. On the other hand, a higher crosslinker content results in generation of more crosslink points, which in turn causes the formation of an additional network i.e. intense cross linked structure and decreases the space left for water to enter [25]. The results are in conformity with Flory’s network theory [26] and similar observations were previously reported by others [27,28].

3.6.4 Effect of guar gum content

The effect of GG content on water absorbency of the superabsorbent is shown in Fig. 10. The water absorbency increased with increasing the amount of GG from 0.2 to 1.6 % (w/v). When the amount of GG was low, the homopolymer content increases which cannot contribute to water absorbency. The homopolymer content decreased with the increase of GG content at a fixed cross-linking density [29].
3.6.5 Effect of reaction temperature

Fig. 11 shows that percentage swelling of superabsorbent composite increase as the reaction temperature increases from 30 to 60°C and decreases with further increase in reaction temperature. When the reaction temperature is decreased, the rate of polymerization also decreases, which results in the enhancement of cross-linking efficiency [28]. At the same crosslinker content, the water absorbency decreases with increase of cross-linking efficiency according to Flory's network theory [26]. With the increase of reaction temperature, the polymerization reaction rate increases and the molecular weight decreases, so the water absorbency is also decreased.

3.6.6 Effect of saline concentration on percentage swelling

The effect of NaCl and CaCl$_2$ concentration on percentage swelling was studied. The percentage swelling is less than in distilled water. Different concentration of NaCl and CaCl$_2$ solutions were prepared in order to study effect of ion charge and ion concentration on water absorption [30]. The water absorption decreases with increasing the ionic strength of saline solution as cited in Flory equation [26]. This can be attributed to change in osmotic pressure in the environment. The same reason results in the decrease in swelling as the concentration of salt is increased. At low salt concentration the swelling rate of composite is faster than at higher concentrations. The factors that caused the water absorption in the polymer included the osmotic pressure difference between the interior and exterior of polymer. The increasing osmotic pressure with increase of salt concentration led to decrease in osmotic pressure difference between the interior and exterior of the superabsorbent polymer [31]. In addition multivalent cations (Ca$^{2+}$) can neutralize several charges inside the gel by complex formation with carboxylate groups, leading to increased ionic crosslinking degree and consequently loss of swelling [32]. The effect of cation charge and its concentration on swelling is shown in Fig. 12.
3.6.7 Effect of pH

The percentage swelling of superabsorbent composite was studied at various pH values between 2.0 and 13.0 at room temperature. To prepare pH media, the stock NaOH (pH 13.0) and HCl (pH 2.0) solutions were diluted with distilled water to reach desired basic and acidic pH respectively. Under acidic pH, most of carboxylate groups are protonated, thus the main anion-anion repulsive forces are eliminated and as a result swelling capacity values are considerably lower. The swelling loss in highly basic solutions can be attributed to charge screening effect of excess Na+ in swelling media, which in turn shields the carboxylate anions and prevents effective anion-anion repulsion [33]. In our study the prepared composite showed maximum percentage swelling (2560 %) at pH 9 as shown in Fig. 13.

4. CONCLUSION

Novel superabsorbent nanocomposite was synthesized using guar gum and methyl methacrylate by free radical graft copolymerization reaction in presence of boric acid as a cross-linking agent and hydrogen peroxide as an initiator in complete aqueous solution to make it biodegradable and environmental friendly. The synthesized composite exhibits hydrophilic–hydrophobic interactions. The composite was characterized by SEM, FTIR, TGA and XRD. The effects of initial monomer concentration, reaction temperature, amount of crosslinker, initiator concentration and guar gum concentration on water absorbency were investigated. Under our experimental conditions, prepared superabsorbent composites has water absorbency of 3000% which has composition of 1% (w/v) crosslinker, 6% (v/v) of methylmethacrylate, 1.6% (w/v) of guar gum, 10% (v/v) of initiator and reaction temperature of 60ºC. The effect of salt concentration and pH has also been studied. The prepared superabsorbent composite can be used in various applications like agriculture, horticulture, removal of toxic dyes, oil spill cleaning etc.

COMPETING INTERESTS

Authors have declared that no competing interests exist.
REFERENCES


© 2017 Rathore and Loonker; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/18172