

Preparation, Swelling and Water-retention Properties of Crosslinked Superabsorbent Hydrogels Based on Guar Gum

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Abstract. Utilization of natural polymer as matrix for preparing hydrogels can improve the performance of the materials and render them environmentally friendly. In this work, the guar gum-g-poly(sodium acrylate) (GG-g-PNaA) superabsorbent hydrogels were prepared by the solution graft copolymerization of natural guar gum (GG) with partially neutralized acrylic acid (NaA) using ammonium persulfate (APS) as initiator and *N,N'*-methylenebisacrylamide (MBA) as crosslinker. FTIR spectra confirmed that NaA had been grafted on GG chains. The effects of reaction variables including the concentration of APS and MBA, the weight ratio of acrylic acid (AA) to GG and the neutralization degree of AA on water absorption were investigated. The superabsorbent hydrogel prepared under optimal condition gives the best absorption of 1107 g·g⁻¹ in distilled water and 88 g·g⁻¹ in 0.9 wt% NaCl solution. Effects of external pH on the swelling properties of hydrogels were investigated, and the practical water retention properties of the hydrogels were also evaluated. Results indicated that the hydrogels exhibited excellent pH-stability in a wide pH range from 4 to 11, and the water-retention capabilities of sand soils were also greatly improved after utilizing the superabsorbent hydrogels. This superabsorbent hydrogels could be used as potential eco-friendly water-saving materials for agricultural or ecological application.

1 Introduction

Superabsorbent can absorb and retain huge volumes of aqueous fluids even under some pressure compared with traditional absorbents (i.e. cotton, sponge, colloid silica etc.), so it found extensive application in various fields including hygienic products, agriculture and horticulture, wastewater treatment and drug-delivery system^[1], etc. Currently, most of the superabsorbent used in practice is mainly petroleum-based synthetic polymers with high production cost and poor environmentally friendly characteristics, and thus the study and development of natural polymer-based superabsorbents has become subject of great interest due to their commercial and environmental advantages^[2]. Presently, many natural polysaccharides such as starch^[3], cellulose^[4], chitosan^[5] and alginate^[6] etc. and their derivatives have been adopted to prepare new type of superabsorbents.

Guar gum (GG) derived from the seeds of guar plant "*Cyanopsis tetragonolobus*" family Leguminosae is a natural nonionic branched polymer with β -D-mannopyranosyl units linked (1-4) with single membered α -D-galactopyranosyl units occurring as side branches (Scheme 1). GG and their derivatives have been used in many fields e.g. thickening agent, ion exchange resin and dispersing agent. However, little research is focused on the applications of GG in superabsorbent field so far. On the basis of above background, in this work, the nove guar gum-g-poly(sodium acrylate) (GG-g-PNaA) superabsorbent hydrogels were synthesized by solution polymerization and characterized by Fourier transform infrared spectra (FTIR) and thermogravimetric analysis (TGA). The effects of reaction conditions on water absorption were studied, and the effects of external pH

value on the swelling properties as well as the water-retention properties of hydrogels in sand soil were also evaluated systematically.

2 Experimental

Materials. Guar gum (GG, food grade, number average molecular weight 220,000) was from Wuhan Tianyuan Biology Co., China. Acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, China) and *N,N'*-methylenebisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corp., China) were used as purchased. The sandy soil used for water-retention testing was taken from the Tenggeli Desert (Inner Mongolia, China). All other reagents were analytical grade and all solutions were prepared with distilled water.

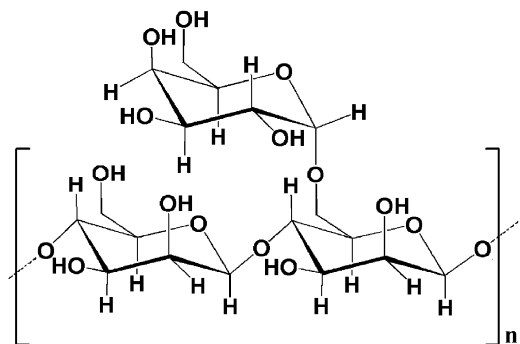
Preparation of GG-g-PNaA Hydrogels. GG (1.04 g) was dispersed in 36 mL of 0.067 mol/L NaOH solution (pH 12.5) in a 250 mL four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a nitrogen line. The dispersion was heated to 60 °C for 1 h to form colloidal slurry. Then 8 mL of aqueous solution of APS (21.6 mg) was added to the flask and stirred for 10 min. 7.2 g of AA was neutralized using 8.5 mL 8.0 mol/L NaOH solution and then 4.4 mg of crosslinker MBA was charged into the neutralized AA solution under magnetic stirring. After cooled to 40 °C, the mixture solution was added and temperature slowly rose to 70 °C and kept for 3 h to complete polymerization. The dried gel product was ground and passed through 40-80 mesh sieve (180 ~ 380 μm).

Measurements of Water Absorption and Swelling Kinetics. The sample (0.05 g) was immersed in excessive distilled water or various pH solution (adjusted with standard 1 mol/L HCl or NaOH aqueous solutions) at room temperature for 4 h to reach swelling equilibrium. Then the swollen samples were filtered using a 100-mesh sieve, and then drained on the sieve for 10 min until no free water remained. The water absorption of the hydrogels (Q_{eq} , $g \cdot g^{-1}$) was derived from the mass change before and after swelling.

Swelling kinetics of the superabsorbent hydrogels was measured as follows: dry samples (0.05 g) were contacted with 200 mL solution at a certain time intervals. The water absorption of the samples was measured according to above method. All samples were carried out three times repeatedly and the averages are reported in this paper.

Measurement of the Water-retention Properties in Sandy Soil. A sample of GG-g-PNaA with various crosslinking degrees (0, 0.2, 0.5, 1.0, or 2.0 g) was well mixed with 200 g of dry sandy soil and kept in ventilated paper cups. Then, 100 mL of tap water was slowly added to these cups and weighed (w_1). The cups were maintained at 25°C (relative air humidity = 28%) and were weighed at a certain interval (w_i). The water retention ratio [w (%)] of sandy soil was calculated with Equation $w\% = 1 - (w_1 - w_i)/100$ (Eq. 1).

Characterization. The Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet NEXUS FTIR spectrometer in 4000–400 cm^{-1} region using KBr pellets.



Scheme 1 Chemical structure of natural guar gum

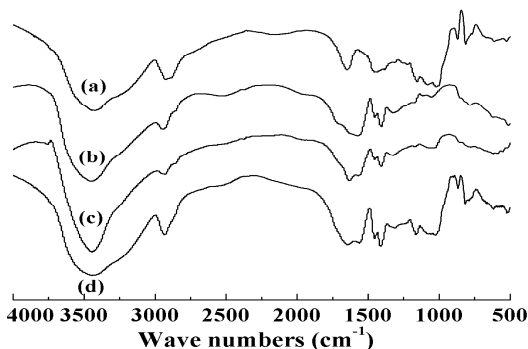


Fig. 1 FTIR spectra of (a) GG, (b) PNaA, (c) GG-g-PNaA and (d) physical mixture of GG and PNaA ($m/m=1:6$)

3 Results and Discussion

FTIR Spectra Analyses

It can be noticed from Fig. 1 that, (i) the absorption bands of GG at 1642 cm^{-1} (H-O-H bending) and at 1439 cm^{-1} (C-OH bending vibration) disappeared after reaction and the new bands at 1627 cm^{-1} (C=O stretching of -COOH groups), 1559 cm^{-1} (asymmetric stretching of -COO⁻ groups) and 1450 and 1405 cm^{-1} (symmetric stretching of -COO⁻ groups) appeared in the spectrum of GG-g-PNaA, which were close to the characteristic absorption of PNaA; (ii) the bands at 1013 cm^{-1} (C-O stretching), 1077 cm^{-1} (C-OH stretching) and 1153 cm^{-1} (C-O-C stretching) for GG were also observed in the spectrum of GG-g-PNaA with weakened intensity, but these bands appeared in the spectrum of the physical mixture of GG and PNaA with considerable intensity. This information gives direct evidence that the PNaA chains have grafted onto GG macromolecular chains, and the -COOH and -COO⁻ groups coexist in the grafting copolymer.

Effect of APS Concentration on Water Absorption

As shown in Fig. 2, the water absorption of the superabsorbent hydrogel increases with increasing APS concentration and then decreases with a further increase of the APS concentration. As described previously [7], the molecular weight in free-radical polymerization will decrease with increasing initiator concentration. With the decrease of molecular weight, the relative amount of polymer chain ends increases. Due to that the polymer chain ends do not contribute to the water absorption [8], the increase of initiator concentration leads to the decrease of water absorption. However, the free radicals on the macromolecular chains of GG can not be adequately formed when APS concentration is lower than 0.525 mmol/L which restricts the process of chain transfer reaction and affects the growth of grafting polymer chains. As a result, below the optimal value, increasing the content of APS will certainly enhance the water absorption of the hydrogel.

Effect of MBA Concentration on Water Absorption

As shown in Fig. 3, the water absorption sharply decreases with increasing the crosslinker concentration from 0.467 to 2.335 mmol/L . According to Flory's theory [9], a high crosslinker concentration will induce the generation of more crosslink points and the increase of crosslinking density. As a result, the network voids for holding water is minimized and the water absorption is decreased. However, the insufficient crosslinker concentration makes the 3-D hydrophilic network fail to form and results in the increase of soluble portion concentration. The relationship between equilibrium water absorption and crosslinker concentration follows the following power law $Q_{eq}=kC_{MBA}^{(-n)}$ (Eq. 2) [10]. C_{MBA} is the concentration of crosslinker MBA; k and n are power law constants for an individual superabsorbent, which can be obtained from the curve fitted with Eq. 2. For superabsorbent hydrogel GG-g-PNaA, the effect of crosslinker concentration on water absorption follows the relations $Q_{eq}=18.30C_{MBA}^{(-0.5413)}$ in distilled water and $Q_{eq}=14.45C_{MBA}^{(-0.2374)}$ in 0.9 wt\% NaCl solution.

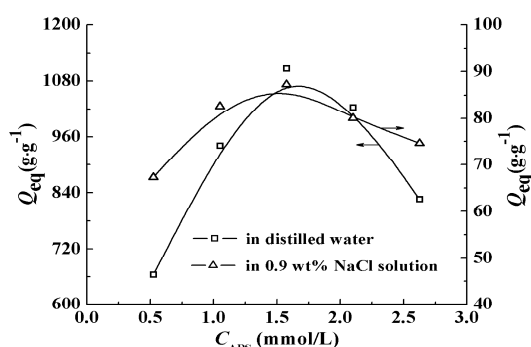


Fig. 2 Effect of APS concentration on the water absorption

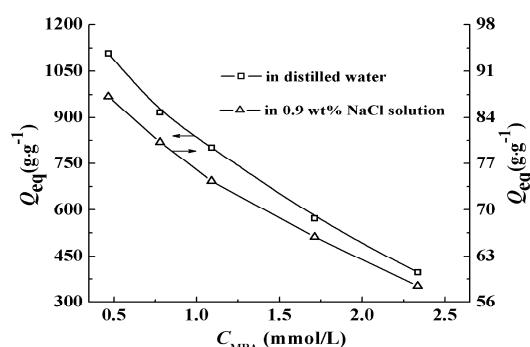


Fig. 3 Effect of MBA concentration on the water absorption

Effect of Weight Ratio of AA to GG on Water Absorption

Due to the definite concentration of APS in reactants, the numbers of free-radicals generated by the decomposition of APS is unvaried. Under this condition, the concentration of monomers decides the reaction rate and grafting efficiency. With increase weight ratio of AA to GG, the numbers of monomers that can react at grafting sites also correspondingly increase, which is very favorable to the enhancement of grafting efficiency and water absorption. However, when this ratio exceeds the optimum value, the water absorption decreases (Fig. 4). This can be ascribed to the increase in crosslinking density resulting from the higher monomer concentration, which directly leads to a decrease of water absorption.

Effect of Neutralization Degree of AA on Water Absorption

It can be noticed from Fig. 5 that the water absorption tends to increase with the increase of the neutralization degree of AA, to reach an optimum value and then decrease. This is attributed to the facts that (i) the cooperative absorbing effect between $-\text{COOH}$ and $-\text{COO}^-$ groups in gel network is superior to either group^[11]; (ii) the neutralization of AA with NaOH solution can increase the amounts of $-\text{COO}^-$ located in gel network and enhance the osmotic pressure between gel network and swelling medium as well as rubbery elasticity among graft chains; (iii) the decrease of $-\text{COOH}$ groups resulting from the neutralization of AA breaks the hydrogen bonding network between $-\text{COOH}$ groups, and thus the effective crosslinking density of hydrogel is lower. However, the further increases in the neutralization degree of AA result in the introduction of more sodium ions, which reduces the electrostatic repulsion by screening the negative charges of $-\text{COO}^-$ groups and then decreases the water absorption.

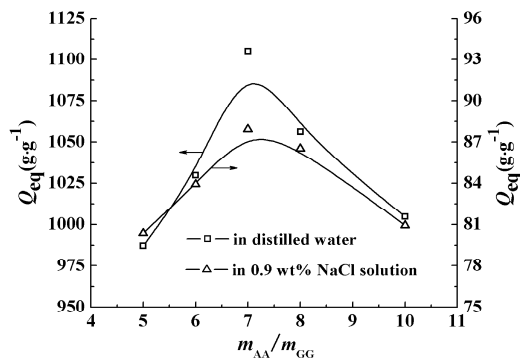


Fig. 4 Effect of mass ratio of AA to GG on the water absorption

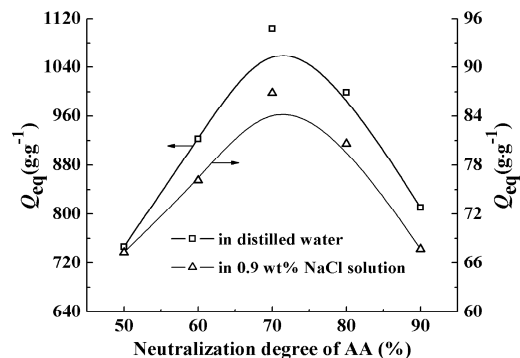


Fig. 5 Effect of neutralization degree of AA on the water absorption

Effects of External pH on Water Absorption

As shown in Fig. 6, the water absorption of GG-g-PNaA superabsorbent hydrogels with various crosslinking degrees sharply increases at the pH range from 2 to 4 and decreases at the pH range from 10 to 13, but almost keeps constant at pH 4–10. As an anionic-type superabsorbent, GG-g-PNaA hydrogel contains numerous dissociable hydrophilic $-\text{COOH}$ and $-\text{COO}^-$ groups which can ionize at high pH but unionize at low pH. When the pH of external solution increasing from 2 to 4, the ionized degree of $-\text{COOH}(\text{Na})$ groups also increases. As a result, the osmotic swelling pressure between gel network and external solution as well as the electrostatic repulsion among $-\text{COO}^-$ groups on graft chains increases, and thus the gel networks can adequately expand and hold more water. However, when the $\text{pH} > 10$, the increased ionic strength of the swelling medium causes the rapid decreases of ion osmotic pressure and ultimately reduces the equilibrium swelling capacity. It is worthy to point out that the hydrogel can keep high water absorption that is close to the equilibrium swelling capacity in distilled water at a wide range of pH from 4 to 10, which is caused by the buffer action of $-\text{COOH}$ and $-\text{COO}^-$ groups^[12] and is very advantageous for the application of superabsorbent in agriculture and ecological project.

Practical Water-retention Properties

As a water-manageable material, the practical water retention properties are significant to its applications in agriculture and even in the recovery of desolate desert. As shown in Fig. 7, the content of water remaining in sandy soil decreases with the time increasing, but the reduction rate is obviously different for sandy soil with and without the superabsorbent. The sandy soil mixed with the GG-g-PNaA superabsorbent hydrogel ($C_{MBA} = 0.467$ mmol/L) exhibits a slower water-evaporation rate compared with that without the superabsorbent. The sandy soil without the superabsorbent loses all of the absorbed water in 13 days, whereas the water-retention period of the sandy soil dosed with the various amounts of superabsorbent hydrogel can be prolonged to 30 days. When 2 wt % of superabsorbent hydrogel is utilized, 8 % of the initial absorbed water can still remain after 30 days. As described previously, the use of GG-g-PNaA in sandy soil obviously improves its water-holding capability. Therefore, the superabsorbent can be used as an effective water-saving material for agriculture and ecological recovery.

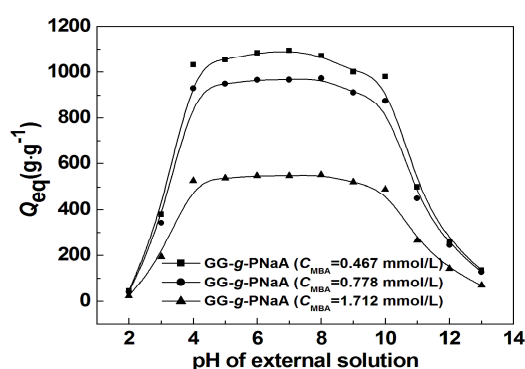


Fig. 6 Effect of external pH values on the water absorption

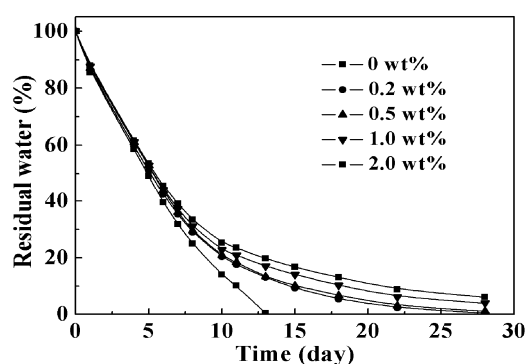


Fig. 7 Practical water-retention properties of the hydrogel in sandy soil at different dosages

4 Conclusion

Novel GG-g-PNaA superabsorbent hydrogels were synthesized by grafting NaA onto natural GG in aqueous solution. The hydrogel acquires the best absorption of $1107 \text{ g}\cdot\text{g}^{-1}$ in distilled water and $88 \text{ g}\cdot\text{g}^{-1}$ in 0.9 wt% NaCl solution under the optimal synthesis conditions: APS concentration, 1.576 mmol/L; MBA concentration, 0.467 mmol/L; weight ratio of AA to GG, 7; neutralization degree of AA, 70%; reaction temperature, 70 °C; reaction time, 3 h. The graft copolymerization reaction occurs between GG and NaA. The hydrogel can keep high water absorption at a wide pH range from 4 to 10, which is favorable to its potential application in agriculture or ecological project. The utilization of the hydrogel remarkably enhances the water-holding capability of sandy soil. The superabsorbent hydrogels based on renewable and biodegradable natural GG exhibited could improve swelling capability and swelling rate, which can be used as promising water-manageable materials for various applications.

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