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Original Research Article

Development of an antibacterial superabsorbent hydrogel based on tara gum grafted with polyacrylic acid

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An antimicrobial superabsorbent was prepared by grafting polyacrylic acid on tara gum and adding chitosan quaternary ammonium salt (2-N-Hydroxypropyl-3-trimethylammonium chloride chitosan, HTCC). The effect of the amount of HTCC on swelling ratio of the product was investigated. The product was characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The results showed that polyacrylic acid was successfully grafted on tara gum and a three-dimensional network structure was formed. The maximum swelling ratio in distilled water and 0.9 wt % NaCl solution reached 650 g/g and 65 g/g, respectively. The addition of HTCC increased the antibacterial property of superabsorbent against Staphylococcus aureus and Escherichia coli. The prepared antimicrobial superabsorbent will broaden the application field of tara gum and chitosan quaternary ammonium salt. This study provides a new path to prepare functional superabsorbent hydrogel.

Key words: Tara gum, chitosan quaternary ammonium salt, superabsorbent hydrogels, antibacterial properties

INTRODUCTION

Superabsorbent polymer (SAP) is a polymer material with a three-dimensional network structure as its internal structure, which can absorb water in large amount and swell and keep water from flowing out due to hydrophilic groups (Dragan and Apopei, 2011). Currently, SAP has been a vital member of the new functional polymer materials. For example Malik et al. (2003) prepared acrylic acid-acrylamide (P (AA/AM)) superabsorbents with acrylamide and acrylic acid as monomers by solution polymerization Pourjavadi et al. (2007) used carboxymethyl cellulose and acrylonitrile with cerium ammonium nitrate as an initiator to prepare a graft copolymer in an argon atmosphere. However, these types of superabsorbent polymers are not readily degradable and tend to contaminate the environment after disposal.

Therefore, there are many environmentally friendly materials such as guar gum, xanthan gum, sodium alginate are used for synthesis of superabsorbent polymer due to good degradability and nontoxic properties (Cano et al., 2015; Murakami et al., 2010) and Kumar et al. (2009) used xanthan gum and polyacrylamide to synthesis a kind of water-absorbing material with cerium as an initiator in a microwave-assisted environment. Yadav et al. (2011) used carboxyl methyl guar to graft copolymerize. Alla et al. (2012) used tara gum and acrylic acid to synthesis superabsorbent polymer by graft polymerization with γ-ray irradiation. Yoshimura et al. (2006) used cotton fiber and succinic anhydride as raw materials to prepare a superabsorbent polymer which has a high water absorption and a good degradability that it can be substantially degraded completely under natural conditions in 25 days. However, most of the superabsorbent resin prepared from natural polymers do not have antibacterial properties. Sahiner et al. (2015) used tannic acid to prepare a hydropghel polymer with antibacterial, antiviral, anticancer, anti-inflammatory and antioxidant properties.

Tara gum (TG) is a galactomannan consisted of a linear main chain of (1-4)-b-D-mannopyranose units linked with branched chains of (1-6)-a-D-galactopyranose. TG is an cheap polysaccharide from the seed endosperm of

Caesalpinia spinosa, a tree native to Peru that is widely refined in many countries (Pizato et al., 2013). Tara gum is often used as stabilizers, thickeners and gelling agents in the food industry in everyday life (Picout et al., 2002). Quaternary chitosan (HTCC) is a quaternary ammonium salt product prepared by chitosan (Kean et al., 2005) which can be dissolved in water under acidic, neutral and alkaline conditions. Besides, it has good biocompatibility, flocculation and cell adhesion Murata et al. (1997). It is often used in antibacterial wound material due to its antibacterial properties, as well as biodegradability (Li et al., 2011).

In this study, tara gum, the natural polysaccharides is grafted with acrylic and chitosan quaternary ammonium salt was blended to prepare a superabsorbent material. This method made the water-absorbing materials had antibacterial properties and biodegradability, which broaden the application of superabsorbent.

MATERIALS AND METHODS

MATERIALS

N-N' methylene-bis-acrylamide (MBA, analytical regent (AR)) was purchased from Regent Chemicals Co., Ltd. (Tianjin,Chnia). HTCC (>91% degree of substitution, AR) with an average molecular weight of 50,000 was purchased from Tianhua Bio-Assistants Co., Ltd. (Shandong, China). Sodium hydroxide (AR) was purchased from Guangfu Technology Development Co., Ltd. (Tianjin, China). Potassium persulfate (AR) was provided by Sitong Chemical Plant (Tianjin, China). Acrylic acid (AAc, AR) was provided by Tianli Chemical Reagent Co., Ltd. (Tianjin, China), purified by activated carbon before use. Tara gum (TG) was obtained from Dymatic Fine Chemical Co., Ltd. (Guangzhou, China). Staphylococcus aureus and Escherichia coli were purchased from Haibo Co., Ltd. (Shandong, China).

Preparation of TG/AAc hydrogels

2 mol/L of NaOH solution, purified AAc, MBA and HTCC were mixed together to make a solution by agitation in an ice bath. A certain amount of TG was added into 4-neck round bottom flask with some distilled water. After fully dissolved, it was placed in the water bath at 60 °C, and the solution was stirred under nitrogen atmosphere. The initiator (potassium persulfate, 2 g/100 ml) was added into the bottle after a period of time. Then, the mixed solution (2 mol/L of NaOH solution, purified AAc, MBA and HTCC) was added into it. The product can be obtained after a period of time.

The whole process was under nitrogen atmosphere. The product was dried in drying oven at 60 °C after an immersion cleaning by ethyl alcohol. Finally, the product was crushed into a certain size of granularity for characterization.

Measurement of Swelling

A certain quality of superabsorbent polymer with 80 to 120 mesh was put into the 200-mesh nylon sieve pouch. The pouch was then immersed into a certain quality of distilled water. After a certain time, the pouch with superabsorbent polymer was taken out from water and standed for 30 min in the air to filter out the excess water through natural filtration by gravity. After that, the weight of the swollen resin was measured. The swelling ratio was calculated by the equation as follows:

$$Q = (m_1-m_2-m_3) / m_3 \quad (1)$$

where Q is swelling ratio (g/g), m_1 is the weight of the swollen resin (g), m_2 is the weight of the nylon sieve pouch (g), and m_3 is the weight of the dry resin (g) (Feng et al., 2010)

Characterizations

FTIR spectra were recorded on a MAGNA 560 ESP spectrometer (Nicolet Co., USA) in the range of 400 cm^{-1} to 4000 cm^{-1}. The thermal stability of superabsorbent samples were measured using a Q500 thermalgravimetric analyzer (TGA) (Waters, Shanghai, China) with a temperature range of 20 °C to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Morphology examination of the superabsorbent polymer was carried on a scanning electron microscope (SEM) (Quanta 200, Philips-FEI Co., AMS, Netherlands).

Measurement of Antibacterial Property

The samples of supersbsorbent polymer were compressed before the bacteriostatic experiment. The size of the inhibition zone surrounding the samples on the medium was the criterion for judging whether the antibacterial properties was good or not. The strains used in the experiment are Staphylococcus aureus and Escherichia coli.

RESULTS

Swelling Analysis

The swelling properties of superabsorbent resin synthesized with different amounts of HTCC were measured in distilled water and 0.9 wt % NaCl at room temperature. With the amount of HTCC increasing, the water absorbency increased at first and then decreased as shown in Figure 1. There was a peak when the addition of HTCC is 50%.The trend of absorption of distilled water and 0.9 wt % NaCl were the same. The main reason is that the HTCC is a cationic product with intermolecular hydrogen bonds and good water solubility. After the addition of resin, it formed osmotic pressure with the outside world solution which was conducive to absorption of moisture. However, when the added amount is excessive, the increasing Na^+ concentration resulted in the ion shielding effect which

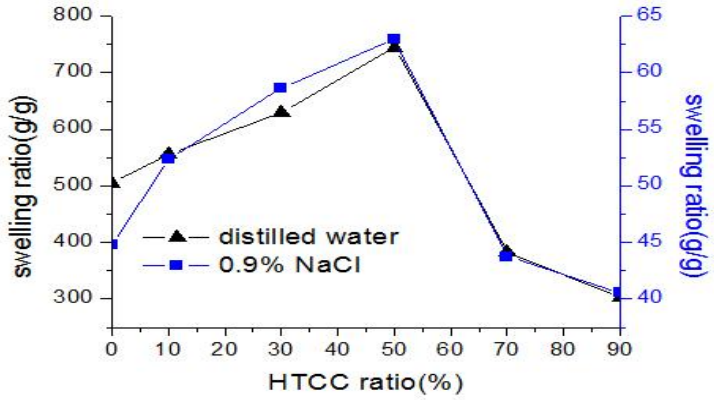


Figure 1: The effect of the amount of HTCC on swelling ratio of SAP

hindered the diffusion of water molecules into the high absorbent resin network structure, reducing the amount of water absorption (Zhan et al., 2004)

FTIR Analysis

The FT-IR spectra of TG and HTCC-TG/AAc are shown in Figure 2 (a). In the spectrum of TG, a strong peak at 3310 cm^{-1} is a characteristic peak of -OH. It can be observed that there are strong peaks at about 870 cm^{-1}, 1020 cm^{-1} and 1150 cm^{-1} which due to the stretching vibrations of C-O-C from glycosidic bonds and stretching vibrations of O-H bending from the pyranosidic structures of TG (Silva et al., 2012). The band in the region 3000 cm^{-1}-2800 cm^{-1} is due to C-H stretching (Antoniou et al., 2014). Peaks at 1630 cm^{-1} and 1380 cm^{-1} come from the bending vibration absorption of -OH. In the spectrum of HTCC-TG/AAc, the absorption peak at 3333 cm^{-1} of -OH is significantly weakened, which indicates the occurrence of graft polymerization. The absorption peak of -OH at 1041 cm^{-1} is weakened as well.

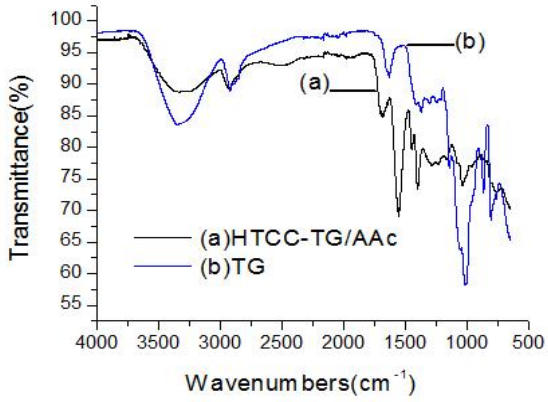
Moreover, the disappearance of the characteristic peaks at 1630 cm^{-1}, 1380 cm^{-1} and 862 cm^{-1} represents -OH is involved in this graft polymerization. The absorption peak at 1451 cm^{-1} is attributed to $-CH_3$ of quaternary ammonium group. The stretching vibration peaks appeared at 1688 cm^{-1}, 1557 cm^{-1} and 1403 cm^{-1} were the C=O of carboxylic acid group. That indicates the acrylic acid has been grafted onto Tara gum skeleton. From the above, it can be shown that copolymerization reaction occurs among acrylic acid, crosslinking agent and tara gum. HTCC existed in the superabsorbent resin as shown in Figure 2 (b).

Morphological Analysis

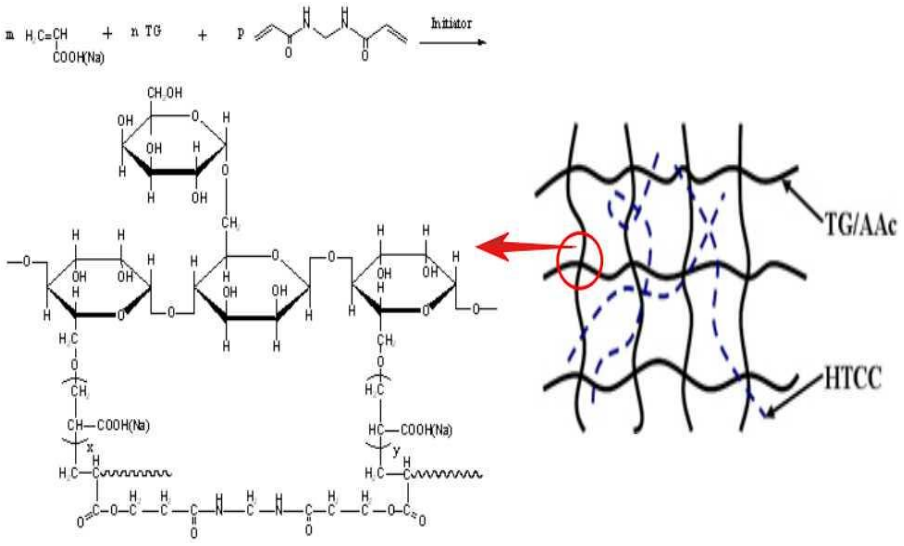
The superabsorbent polymer was placed in distilled water to swell thoroughly and then was freeze-dried. Figure 3 showed that the superabsorbent resin had a three-dimensional network. There are many pores connected with each other in the interior of the SAP which is attributed to the graft copolymerization of TG and sodium acrylate. This internal structure may enhance the infiltration of water into its interior. The original closed network structure fully extend after immersed into water which lead to the volume expanded and the space increased. The structure can accommodate many water molecules and form a barrier to block water molecules overflowing.

Thermal Stability

Tara gum had two stages of weight loss shown in Figure 4. The first stage ranged from 30 °C to 201 °C and the weight loss is about 8%. The second stage stared at 201 °C and continued up to 467 °C where the polysaccharide begins to decompose and the weight loss is 70%. The first phase of the superabsorbent polymer without the HTCC ranged from 29 °C to 178 °C and the weight loss is about 11%, which the mass loss is due to the presence of water and residual organic solvent in resin. The second stage was at 178 °C-361 °C because the small molecule such as the linear oligomers in resin begins to decompose at this time and the weight loss is about 20% (Chi et al., 2016). The third phase ranged from 361 °C to 561 °C when the polymeric network structure began to decompose and the weight loss is about 28%. But, the SAP with HTCC has three stages (Table 1). The first stage ranged from 31 °C to 170 °C when the moisture and residual solvent reduced and the weight loss is about 6%. From 170 °C to 340 °C is the second stage. At this stage, other small molecules such as the oligomer in resin and HTCC begin to break down and the weight loss is about 25%. The third mass loss was at 340 °C to 532 °C and molecules formed by polymerization begins to decompose at this time with a 34% weight loss. Compared to tara gum, the thermal stability of superabsorbent polymer improved obviously, which was related to the stable properties of three-dimensional network of polymeric macromolecules. But the addition of HTCC has little effect on the thermal stability.

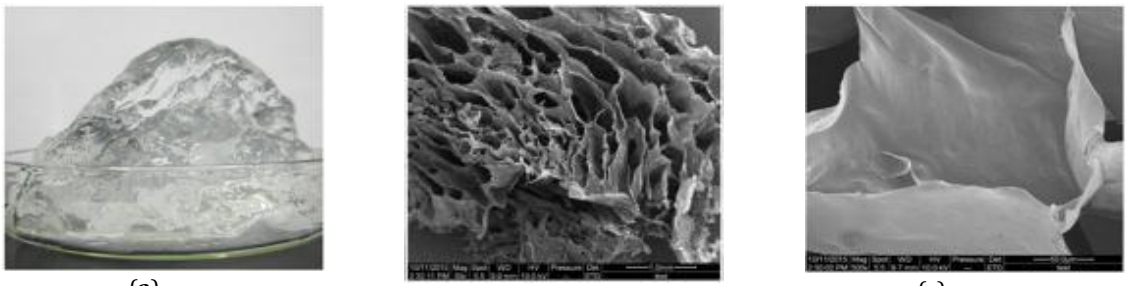


(a)



(b)

Figure 2: FT-IR spectra of TG and HTCC-TG/AAc (a) and the schemetic diagram of HTCC-TG/AAc polymer network (b)



(a) (b) (c)

Figure 3: The photo of swelled(a) and SEM micrographs(b and c) of the superabsorbent polymer

Antimicrobial Activity

The bacteria used in the experiment is *Staphylococcus aureus* and *Escherichia coli*. Superabsorbent resin was crushed into tablets which were then placed in nutrient agar inoculated with bacteria and cultured for 12 h. The culture temperature is 37 °C. Figure 5 shows that the superabsorbent polymer has a certain inhibitory effect due

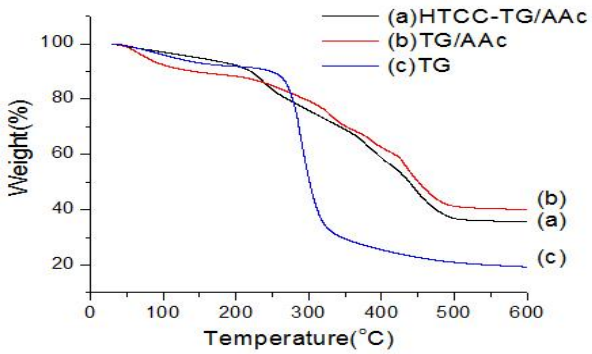


Figure 4: TGA curves of TG, TG/AAc and HTCC-TG/AAc.

Table 1. Thermal stabilities of TG, TG/AAc and HTCC-TG/AAc

Films	T^a(°C)	$T_{MAX1}{}^b$(°C)	$T_{MAX2}{}^b$(°C)	$T_{MAX3}{}^b$(°C)
Tara Gum	271.90	290.17	-	-
TG/AAc	224.61	331.17	385.34	431.37
HTCC-TG/AAc	213.37	237.59	381.31	443.52

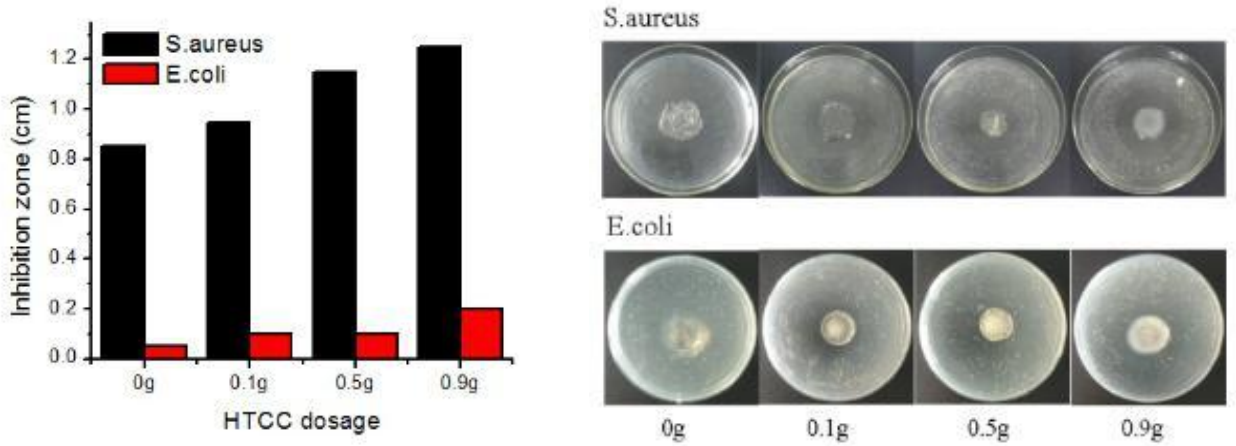


Figure 5: The histogram(a) and the photograph(b) of antibacterial activities of the SAP against *S. aureus* and E.coli

to the close network structure. With the amount of bacteriostatic HTCC increasing, the antibacterial properties for *Staphylococcus aureus* of superabsorbent polymer increased because the inhibition zone was gradually increased. For Escherichia coli, there is no significant inhibition zone but the density of colonies is small around the sample. So, the synthetic superabsorbent have a certain inhibitory effect on Escherichia coli as well.

Conclusions

In this study, superabsorbent polymer was synthesized by tara gum grafted with polyacrylic acid and blended with 2-N-Hydroxypropyl-3-trimethylammonium chloride chitosan. The superabsorbent polymer has an amorphous structure with a three-dimensional network as its internal structure and there is a lot of room to accommodate the liquid molecules. The maximum swelling ratio in distilled water and 0.9 wt % NaCl solution reached 650 g/g and 65 g/g, respectively. The polymer has a porous structure as well. This resin has a good thermal stability and is difficult to decompose which could be safely used up to 200 °C. What's more, the addition of 2-N-Hydroxypropyl-3-trimethylammonium chloride chitosan increases the antibacterial properties of the superabsorbent polymer.

There are obvious inhibitory effect against *staphylococcus aureus* and certain inhibitory effect against colon bacillus.

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Author Contributions: Bingjie Li performed the experiment; Jie Shen analyzed the data and wrote the paper.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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