Carbohydrate Polymers 101 (2014) 231–239

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Photopolymerisation and characterization of maleylatedcellulose-g-poly(acrylic acid) superabsorbent polymer

Amatjan Sawut[a], Mamatjan Yimit[a], Wanfu Sun[b], Ismayil Nurulla[a,*]

[a] Key Laboratory of Oil and Gas Fine Chemicals, Educational Ministry of China, School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China
[b] Physics & Chemical Testing Center, Xinjiang University, Urumqi 830046, China

ARTICLE INFO

Article history:
Received 7 July 2013
Received in revised form
10 September 2013
Accepted 16 September 2013

Keywords:
Maleylated cotton stalk cellulose
Superabsorbent
Ultraviolet photopolymerisation
Acrylic acid

ABSTRACT

A novel biodegradable superabsorbent polymer has been prepared from maleylated cotton stalk cellulose (MCSC) crosslinker and acrylic acid (AA) by ultraviolet (UV) photopolymerization in aqueous solution at room temperature, and irgacure 651 as a photoinitiator. The resulting superabsorbent was characterized by FT-IR, ^{1}H NMR, SEM and TGA. The effects of preparation conditions such as degree of substitution (DS), amount of maleylated cotton stalk cellulose, exposed time, photoinitiator amount and monomer concentration on the water absorbency and the monomer conversion in graft were evaluated. The swelling kinetics, salt-resistance, water retention capacity and biodegradability of the MCSC-g-PAA superabsorbent were investigated. It was found that, the obtained superabsorbent have good swelling degree that greatly affected by its composition and preparation conditions. Owing to its considerable good water retention capacity, being economical and environment-friendly, it might be useful for its application in agriculture field.

1. Introduction

Superabsorbent polymers (SAPs) are lightly crosslinked hydrophilic functional polymers with three-dimensional network structures, which have the ability to absorb large quantities of water, ranging from hundreds to thousands of times of their mass in a relatively short time and retain water even under pressure (Liu, Wang, & Wang, 2007). The hydrophilic groups and domains in their structure play the key role in having the superabsorbent properties. These excellent characteristics allow the application of SAPs as functional materials in the field of hygiene (Kamat & Malkani, 2003), drug delivery (Pourjavadi, Barzegar, & Zeidabadi, 2007), water treatment (Dalaran, Emik, Güçlü, İyim, & Özgümüş, 2011), concrete (Song, Wei, & He, 2009), food additive (Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010), agriculture and horticulture (Tian et al., 2012; Xie, Liu, Ni, & Wang, 2012). However, SAPs are mainly petroleum-based synthetic polymers with high production cost and poor biodegradability, widespread use of those polymers may lead to environmental pollution (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002; Marc, Mele, Palmisano, Pulito, & Sannino, 2006).

Cotton is one of the most abundant crops in the northwestern China. The increase in cotton planting has permitted production of a huge amount of cotton stalks. These big quantities of stalks become an environmental problem, because of loosing their importance as fuel and ending with bad quality results in paper making industries (El-Hendawy, Alexander, Andrews, & Forrest, 2008). Currently, cotton stalks are mostly burned on the ground since they are harboring diseases that could affect future cotton crops (Reddy & Yang, 2009). However, cotton stalks which mainly contain cellulose are abundant, cheap, biodegradable and annually renewable sources, and some attempts have been made to study on the potentials of utilizing cotton stalks (Nahil & Williams, 2012; Reddy & Yang, 2009; Shi, Sharma-Shivappa, Chinn, & Howell, 2009; Silverstein, Chen, Sharma-Shivappa, Boyette, & Osborne, 2007). The mass utilization of this agricultural waste and converting them into a value-added product can provide an environmentally sound method of disposal. Moreover, the development of biodegradable/bio-based superabsorbent materials from renewable sources is nowadays being viewed as a strategic research area (Chang & Zhang, 2011; Sannino, Demitri, & Madaghiele, 2009).

Recently, several researches on the preparation of cellulose based SAPs have been reported, the highest water absorbencies of the obtained superabsorbent hydrogels were 417 g/g (Liu, Miao, Wang, & Yin, 2009), 620 g/g (Wang & Wang, 2010), 680 g/g (Bao, Ma, & Li, 2011), and 875 g/g (Wu, Zhang, Liu, & Yao, 2012), respectively. However, the major drawbacks of these methods are (a) the presence of a considerable amount of ungrafted cellulose in the hydrogel due to the lack of reactive groups of the cellulose chains, (b) using costly divinyl crosslinker such

* Corresponding author. Tel.: +86 991 8583575; fax: +86 991 8583575.
E-mail addresses: ismayilnu@sohu.com, ismayilnu@126.com (I. Nurulla).

0144-8617/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.carbpol.2013.09.054

as N,N-methylenebisacrylamide (MBA) which can crosslink vinyl monomers but the conventional crosslinker may not improve the grafting extent of cellulose, and (c) commonly used thermal polymerization which causes energy consumption and pollution of environment. Preparing SAPs from modified cotton stalk cellulose with acrylate via UV photopolymerization method could be attractive alternatives to overcome some of the above-mentioned drawbacks. The main reasons are as follows: Modifying cellulose through the use of maleic anhydride (De Melo, da Silva Filho, Santana, & Airoldi, 2009; Zhou, Jin, Hu, Zhang, & Ma, 2012) produces degradable ester bonds, reactive carbon–carbon double bond and hydrophilic carboxylic acid end groups. Therefore, the modified cotton stalk cellulose has the better hydrophilicity and is easier to graft monomer than cellulose. The raw materials and reagents are abundant and cheap. Furthermore, compared with time-consuming thermally induced polymerization, UV photopolymerization has many advantages such as solvent free, time-saving, low energy consumption, high efficiency and less pollution (Wan, Wang, Yuan, & He, 2006; Weiqing, Xiaogong, Yanqing, Yuli, & Aijie, 2006).

In this study, cotton stalk cellulose (CSC) was separated from cotton stalks by alkali pretreatment method, and reacted with maleic anhydride at different feed ratio synthesizing MCSC. Preparation of maleylatedcellulose-g-poly(acrylic acid) (MCSC-g-PAA) superabsorbent polymer by photopolymerization with MCSC and AA was investigated. We predict that the maleate groups on the cellulose backbone in cotton stalks lead to the crosslinking of polymer chains during photopolymerization process. The effects of various factors on the water absorbency of the synthesized superabsorbent and monomer conversion in graft were investigated. The structure and properties of the superabsorbent materials were evaluated.

2. Experimental

2.1. Materials

Cotton stalks were obtained from the waste residue after 2009/2010 harvesting season in cotton farms of Korla, Xinjiang Uygur Autonomous Region. The stalks were air dried, milled and passed through a 100-mesh screen prior to further experiments. The composition of the cotton stalks in terms of cellulose, hemicellulose, lignin and ash content were determined according to standard biomass analytical methods (Sluiter et al., 2008), the cotton stalks predominantly contains cellulose (41.2 ± 0.6%), hemicellulose (23.8 ± 0.7%), acid insoluble lignin (19.6 ± 0.5%), acid soluble lignin (2.2 ± 0.5%) and ash (1.6 ± 0.3%). Acrylic acid (AA, 99.5%, Damao Chemical Industry, Tianjing, China) was distilled under reduced pressure before use. Maleic anhydride (MA, analytical grade, Chemical Reagent Subsidiary Industry, Shanghai, China) was used as received. The sodium hydroxide (98.0%, Baishi Chemical Industry limited company, Tianjin, China) was used as neutralistic reagent. The photoinitiator (PI): Irgacure 651(2,2-dimethoxy-2-phenylacetophenone) was supplied from Ciba-Geigy Co (New Jersey). Other All reagents used in the experiment were all of analytical grade and all solutions were prepared by using distilled water.

2.2. Pretreatment of cotton stalk

CSC was separated from cotton stalks by a microwave heating alkali-cooking method. The dissolution process of cellulose was carried out according to the literature (Zhang, Zhang, Deng, & Sun, 2011). At the pretreatment step, the cotton stalk in 12% alkali solution with the ratio of 1:9 was heated under 200 W microwave for 6 min. After filtration, cellulose was bleached with 10% NaClO for 3 h at 35 °C, and extracted for 10 min by 5% HCl at room temperature. Finally, The product was washed with distilled water until neutralized, then dried at 60 °C for 6 h.

2.3. Synthesis of maleylated cotton stalk cellulose

The dried CSC (5.0 g) was dispersed in acetone with constant magnetic stirring, an appropriate amount of maleic anhydride and pyridine (act as catalyst) were added. The CSC was reacted with maleic anhydride at different mass ratio (CSC:Maleic anhydride = 5:1; 5:2; 5:3) under acetone reflux in the reaction flask which immersed in the oil bath at 65 °C for 4 h. The products were precipitated and washed with distilled water, and finally with acetone, respectively. After that, the modified cotton stalk cellulose was dried at 90 °C for 24 h.

The degree of substitution of MCSC was determined by the back titration method (Zhou et al., 2012). This method is based on adding an excess of NaOH solution which reacted with carboxyl group of MCSC in the test solution, the remaining NaOH solution was titrated with HCl solution. According to this, 0.1000 g MCSC was treated with 0.0100 mol L^{-1} NaOH solution (100.00 mL) in round bottom flask at room temperature for 2 h with constant stirring. Then, 25.00 mL supernatant fluid was treated with 0.0100 mol L^{-1} HCl solution after the materials were filtered. The experiment was carried out in parallel three times. The degree of substitution (DS) was calculated as Eq. (1)

$$DS = \frac{1/2(C_{NaOH} \times V_{NaOH} - 4 \times C_{HCl} \times V_{HCl}) \times M_{MA}}{m_{MCSC}} \quad (1)$$

where C_{NaOH} is the concentration of NaOH solution (mol L^{-1}), C_{HCl} is the concentration of HCl solution (mol L^{-1}), V_{NaOH} is the volume of NaOH solution (L), V_{HCl} is the volume of HCl spent in the titration of excessive non-reacted NaOH solution (L), M_{MA} (g mol^{-1}) is the molecular weight of maleic anhydride and m_{MCSC} (g) is the mass of the MCSC in this experiment.

2.4. Synthesis of MCSC-g-PAA superabsorbent polymer

3.6 g of AA and adequate volume of 5 M sodium hydroxide solution (to 75% of neutralization) were introduced into 50 mL double quartz tube equipped with a magnetic stirrer, and the total monomer concentration was adjusted with adequate volume of water. The mixture was stirred and cooled until the room temperature completely, and then appropriate amount of MCSC and PI were fully dispersed in the mixed solution. UV irradiations were performed for a certain period of time in a dark box using unfiltered light of medium pressure mercury lamp (300 W, the main wavelength 365 nm, average intensity of 12.3 mW/cm^2) which was placed in the axial position of double quartz glass cylinder which was cooled by water circulating in order to avoid overheating. The solutions were thoroughly degassed by bubbling oxygen-free nitrogen during the reaction. The temperature was kept always below 25 °C to ensure a minimum contribution of the thermal process. Polymers thus formed and were stirred in 100 mL acetone water mixture (volume ratio of 3:7) to remove the soluble fraction. The polymers were dried at 80 °C for 48 h in vacuum oven and then was milled.

2.5. Characterizations

The FTIR spectra were recorded on BRUKER EQUINOX-55 FTIR spectrometer in 4000–500 cm^{-1} region using KBr pellets.

Liquid state nuclear magnetic resonance (^{1}H NMR) spectroscopy was used to determine the chemical structures of the modified cotton stalk cellulose and the superabsorbent. ^{1}H NMR spectra were