Carbohydrate Polymers 191 (2018) 152–160

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Super water absorbing polymeric gel from chitosan, citric acid and urea: Synthesis and mechanism of water absorption

Abathodharanan Narayanan, Ravishankar Kartik, Elanchezhian Sangeetha, Raghavachari Dhamodharan*,[1]

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

ARTICLE INFO

Keywords:
Superabsorbent
Macroporous polymer
Water retention in soil
Chitosan
Hydrothermal synthesis

ABSTRACT

A new superabsorbent with maximum water absorption capacity of ~1250 g/g is prepared by hydrothermal synthesis from sustainable and biodegradable resources such as chitosan, citric acid and urea (denoted as 'CHCAUR'). CHCAUR is characterized extensively by various analytical techniques such as PXRD, SSNMR, FTIR, and TGA. Pure and saline water absorption study showed that CHCAUR could be a better adsorbent compared to the super absorbent polymer (SAP) used in commercial diaper material. The mechanism of water absorption is shown to arise out of a combination of electrostatic attraction of water to the ionic crosslinks and the presence of macropores as well as undulated surface due to the formation of nanofibrous bundles. When applied to soil CHCAUR was found to decrease water evaporation rate significantly.

1. Introduction

Super absorbing polymers (SAPs) absorb and retain very large quantity of liquid up to several hundred times their own weight (Omidian, Rocca, & Park, 2005) and when the liquid being absorbed is water they find application in fields such as agriculture, personal hygiene, etc. There are two main classes of SAPs: synthetic (petrochemical based) and natural (biopolymers). The SAPs used in commercial applications are manufactured from non-renewable petrochemical resources and especially from acrylic acid and acrylamide based monomers (Krul et al., 2000). Every year, several million metric tons of synthetic SAP materials are produced and used for different applications. The World's consumption of SAP is many orders of magnitude more for personal hygiene and health care than any other application ("Super Absorbent Polymer (SAP) Market: Global Industry Analysis and Opportunity Assessment 2015 – 2020," n.d.). Hydrogels, a special form of SAPs, exhibit water absorption capacity in the vicinity of 100%, swell in water and retain a significant fraction of water (> 20%) within their structure without dissolving (Buchholz & Graham, 1998). The flexibility of hydrogels is comparable to natural tissue due to the flexible macromolecular component and water content and therefore is gaining importance as scaffolds in tissue engineering.

The disposal of SAPs after use in landfill causes pollution in the environment as they do not biodegrade within reasonable period in nature (Zohuriaan-Mehr et al., 2008) and hence there continues to be interest in developing SAPs that are part synthetic and part natural. In this context, the synthesis of SAP material through graft copolymerization of synthetic monomers with biopolymers such as cellulose, chitosan, starch, alginates and their derivatives as one of the ingredients has been reported. These materials by design are not fully biodegradable, since the grafts such as poly(acrylate) or poly(acrylamide) or poly(acrylic acid) are not biodegradable (Liu et al., 2017; Liu, Miao, Wang, & Yin, 2009; Omidian, Rocca, & Park, 2006; Ye, Tang, Hong, & Hui, 2016). Among the biopolymers, the preparation of graft copolymers of chitosan with acrylic acid, acrylates, acrylonitrile and acrylamides acquired significance in applications demanding high water uptake capacity (Fernández-Gutiérrez et al., 2016; Huacai, Wan, & Dengke, 2006; Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004; Zhang, Wang, & Wang, 2007). Water absorption capacity in the range 150–650 g/g has been reported. It was shown that chitosan-starch citrate crosslinked polymer exhibited high water uptake in water as well as saline medium (Salam, Pawlak, Venditti, & El-Tahlawy, 2010).

The most important challenge in the area of biodegradable SAPs is to synthesize or fabricate fully biodegradable polymer based super-absorbing materials that would rapidly and reversibly absorb water with good mechanical strength. For this purpose biopolymers such as starch, cellulose and cellulose derivatives, chitosan, and marine polysaccharides would be most ideal. Among the biopolymers, chitosan is more promising for application in super water absorbency in view of

---

* Corresponding author.
E-mail address: damo@iitm.ac.in (R. Dhamodharan).

[1] This work constitutes a part of patent application No. 2505/CHE/2015.

https://doi.org/10.1016/j.carbpol.2018.03.028
Received 25 October 2017; Received in revised form 13 February 2018; Accepted 12 March 2018

several important properties such as biodegradability (Salam et al., 2010; Vårum, Myhr, Hjerde, & Smidsrød, 1997), biocompatibility (Hirano and Noishik., 1985) and bioactivity (Domard, Domard, & Lyon, 2002). Chitosan is reported to be haemostatic (Malette, Quigley, Gaines, Johnson, & Rainer, 1983), fungi- and bacteria- static (Strand, Vandvik, Vårum, & Østgaard, 2001). It is also known to support cell proliferation and tissue regeneration (Boucard et al., 2007; Montembault et al., 2006). The preparation of a multi-membrane structured material based on chitosan and sodium alginate without an external crosslinker was reported (Ladet, David, & Domard, 2008). The presence of an amino group and a primary as well as secondary hydroxyl groups per repeat unit of chitosan makes it a hydrophilic polymer (Hamed, Özogul, & Regenstein, 2016; Martínez, Blanco, Davidenko, & Cameron, 2015; Zohuriaan and Kabiri, 2008). An interesting recent example demonstrates that a mixture of polysachcharide (comprising of carrageenan and calcium alginate) functions as a fast swelling composite absorbent for saline water with high mechanical strength. (Ye et al., 2016). The preparation of superabsorbing materials from polysaccharides and proteins (Ichikawa & Nakajima, 1996) as well as shellfish waste (Dutkiewicz, 2002; Ichikawa & Nakajima, 1996) have been reviewed.

The use of chitosan or chitosan based materials as SAP demands that the physicochemical properties of chitosan be studied to take advantage of the delicate balance between the hydrophobic (-NHCOCH3) and hydrophilic (−OH and −NH2) groups (Schatz, Viton, Delair, Pichot, & Domard, 2003; Sorlier, Denuzire, Viton, Domard, & Denuzie, 2001) and optimize the physical microstructure (Spagnol et al., 2012; Vunain, Mishra, & Mamba, 2016; Zhang, Zeng, & Cheng, 2016). Porous films and three dimensional scaffolds of chitosan were prepared by freeze drying its solution in aqueous acetic acid. This resulted in pore size and pore thickness larger than several hundreds of micrometers (Anitha et al., 2014; Esquerdo, Cadaval, Dotto, & Pinto, 2014; Kim et al., 2011; Madihally & Matthew, 1999). Such films and scaffolds exhibited relatively less and slow water uptake due to low specific surface area that in turn results in less exposure of water to hydrophilic groups present in the backbone.

The method of direct crosslinking of polysaccharides and more specially cellulose derivatives with divinyl sulphone/epichlorohydrin/glyoxal/$POCl_3$/citric acid is well known (Demitri et al., 2008; Sannino et al., 2003). An interesting recent development in this area is the synthesis of SAP using citric acid as one of the monomers (Kim, Koo, Kim, Hwang, & Im, 2017). An important recent development as far as using chitosan as a superabsorbent, is the successful preparation of nanoporous chitosan films from dioxane, DMSO and aqueous acetic acid, a ternary solvent system, which is noteworthy in many aspects (Wang, Lou, Zhao, & Song, 2016).

Recently, we reported on the synthesis ad characterization of a SAP based on chitosan, EDTA, and urea (CHEDUR). The maximum water absorption capacity of this material was 500 g/g (Narayanan & Dhamodharan, 2015). The high water absorption of CHEDUR was proposed to result from the presence of macro pores in the predominantly chitosan matrix as well as due to the presence of oligomers of EDTA and urea that were present in smaller quantity and possibly functioned as crosslinks between the chitosan molecules. This study left us with few unanswered questions such as: can natural multifunctional acids replace EDTA? the precise mechanism of high water uptake, the mechanical properties of the gels (whether they can be tuned), biodegradability of the product, exploring specific applications. In this work, the synthetic methodology adopted for the preparation of a SAP using chitosan, urea and citric acid is reported (CHCAUR). The structure of CHCAUR is elucidated by extensive analytical tools, its water absorption capacity and water retention in soil are also presented in this paper.

2. Materials and methods

2.1. Materials

Raw chitosan (Mn = 48700 Da; 80% deacetylated as determined by FTIR; (Muzzarelli, Tanfani, & Scarpini, 1980)) was purchased from M/s. Matsyafed, Kochi. Citric acid (GR grade), 25% v/v ammonia solution (GR grade), urea (GR grade), and methanol (GR grade) were purchased from M/s. Vijaya Scientific Company, Chennai and used without further purification. Water absorbing material from “Huggies” [Kimbery-Clark Lever Ltd.] commercial baby diaper was used.

2.2. Synthetic methodology for the preparation of CHCAUR and control reactions

The new material was prepared by reacting hydrothermally chitosan with citric acid and urea in the weight ratio of 1:2:2 and denoted as CHCAUR. The reaction was performed in a cylindrical stainless steel reactor of volume 900 mL that was closed permanently at the bottom. The required quantity of powdered chitosan, citric acid and urea were added to the reactor through the top. Then the desired amount of water (66 mL/g of chitosan) was added and the mixture was stirred well for 10 min at room temperature. During this process the solution turned very thick forming a highly viscous mass. The pH was found to be between 5 and 6. It was then sealed securely with a circular SS flange and a Viton ‘O’ ring that was placed in between the lid at the top and bottom part of the reactor and tightened. The reactor was then placed in a programmable hot air oven and heated. For all the preparations, the same heating program was used: heating from 35 °C to 100 °C at 5 °C per min followed by isothermal heating at 100 °C for 650 min. After this duration, the reactor was allowed to cool to room temperature under ambient conditions. The product obtained was a gel (pH = 7 to 7.5 irrespective of the composition of the gel) and this was rinsed with basic methanol solution (pH 8). This step was repeated several times to remove the unreacted substances and other byproducts that could be present in the gel, as confirmed by analytical methods such as PXRD, SSNMR and FTIR. The gel thus obtained was dried in a hot air oven maintained at 50 °C overnight to remove the residual solvent. The product was powdered well using agate mortar and packed in airtight bottle for further studies. The water to chitosan ratio was varied between 200 mL/g to 50 mL/g to prepare gels of different water absorption capacity. The batch size varied between 3–10 g of chitosan. The preparations at the 10 g scale were carried out thirty times and were found to be reproducible as assessed by PXRD, SSNMR and FTIR.

Three control reactions were performed to understand the formation of CHCAUR. The first one was the reaction between chitosan and citric acid and the product obtained was denoted as CHCA. The second was the reaction between chitosan and urea and the product obtained is denoted as CHUR. The third control reaction was performed between citric acid and urea and the product was denoted as CAUR. For all these control reactions the reaction composition and conditions were similar to that used in the preparation of CHCAUR and mentioned above.

3. Characterization

Gel permeation chromatography of chitosan was performed using Waters GPC (two ultra-hydrogel 250 SS columns 30 cm × 7.8 mm; 0.1 N sodium nitrate in 20 mL glacial acetic acid and 1000 mL water as the mobile phase, 0.8 mL/min flow rate) equipped with a RI detector. Narrow molecular weight PEG standards were used for calibration. Powder x-ray diffraction pattern was recorded using Bruker D8 Advance diffractometer equipped with Cu anode (Cu Kα source of the wavelength of 1.5406 Å) between 5–60° (2&z.Theta;). Differential scanning calorimetry was performed using TA Instruments Q200 MDSC. The thermal decomposition of all the materials was studied using TA Instruments Q500 Hi-Res TGA. Around 5 mg of sample was taken in a Pt