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Urea free synthesis of chitin-based acrylate superabsorbent polymers under homogeneous conditions: Effects of the degree of deacetylation and the molecular weight

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ABSTRACT

In order to understand the chemical structure of chitin-based acrylate superabsorbent polymers (SAP), chitin was dissolved in NaOH aqueous solution via freezing-thawing cyclic treatment without urea, subsequently, a transparent hydrogel was prepared by copolymerizing the alkali-chitin solution and acrylic acid directly. The effects of the degree of deacetylation (DDA) and the molecular weight (Mw) of chitin on the properties of SAP were investigated in detail. With increasing the DDA and Mw, the yield improved while the water absorbency decreased, yet the effect of DDA is insignificant if the Mw is smaller enough. The structures were characterized by FT-IR, XRD, TG, DSC, XPS, solid-state ^{13}C NMR and elemental analyses. The results indicated that the poly(acrylic acid) chains were successfully grafted onto the chitin backbones, and the reaction sites were the $-NH_2$ on the chitosan units. The possible mechanism was further discussed, which was similar to that suggested for chitosan-g-poly(acrylic acid) SAP.

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1. Introduction

China is one of the countries with severe water scarcity in the world, and the spatial and temporal distribution of water resources is extremely uneven. Water shortage in some areas has become one of the key issues restricting economic and social development (Xu, Song, & Zhang, 2016). Particularly in the agricultural fields, water shortage has a significant impact on the growth and production of crops. Effective and rational application of the limited water resources is one of the key measures to increase the production and quality of crops (Zhang, Wu, Liu, & Yao, 2013). Superabsorbent polymer (SAP) is a kind of novel functional polymer, which contains many kinds of hydrophilic groups and with a suitable degree of cross-linking (Chen, Liu, Tan, & Jiang, 2009). Due to their unique properties, SAP has been widely used in the fields of agriculture, forestry, industry, construction, oil exploration, drug-delivery systems, daily chemical industry, personal care and others (Liu, Wang, & Wang, 2007; Liu et al., 2013). In particular, plenty of remarkable results have been achieved for SAPS as a kind of water retaining agent for soil in the field of agriculture and forestry (Hussien, Donia, Atia, El-Sedfy, El-Hamid, & Rashad, 2012).

Due to the inherent drawbacks of synthetic SAPs, such as poor biodegradability, single features, indigent renewability, lacking salt tolerance, and so on, in recent years, the green superabsorbent polymers based on the biodegradable biomass materials have been one of the new research hotspots. Some non-toxic and low-cost natural polymeric materials, including starch (Zhang, Chen, Du, Xue, Chen, & Yang, 2014; Zou et al., 2012), cellulose (Ma, Li & Yan 2015), protein (Li, Liu, Su, Yue, & Gao, 2014), chitosan (Chen, Tang, Liu, & Tan, 2016; Jiang, Hua, & Tang, 2010) and their derivatives, have been used as crude materials for synthesizing green SAPs. Especially, the chitosan-based SAPs have excellent water absorbency, unique antibacterial activities, pH-, thermo- and ion-responsiveness abilities (Elkholy, Khalil, Elsabee, & Eweis, 2007; Jiang, Hua, & Tang, 2010; Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004). Ample literature reports and patents focused on the preparation, functional properties and application of the chitosan-based SAPs. It has been widely used to produce personal-care goods (baby diapers, feminine hygiene products, adult incontinence products),

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drug delivery, tissue engineering systems and so on (Duan, Liang, Cao, Wang, & Zhang, 2015; Giri, Thakur, Alexander, Ajazuddin, Badwaik, & Tripathi, 2012; Ladet, David, Domard, 2008; Yu et al., 2017).

However, chitosan with a typical degree of deacetylation (DDA) of more than 0.65 is very rare in the nature, except a few species such as some yeast, filamentous fungi and plants (Muzzarelli, Boudrant, Meyer, Manno, DeMarchis, & Paoletti, 2012; Pillai, Paul, & Sharma, 2009). This unique basic polysaccharide is usually derived from the partially N-deacetylation of chitin (the second most abundant biopolymer after cellulose widely exist in organisms) in concentrated alkaline solution (40–50%). Although, it has been a simple and mature production technology, the huge utilization alkali will still bring potential hazards, such as waste, cost, pollution, and endanger the local ecosystem, etc. The development of clean, green and efficient manufacturing technology for producing multipurpose chitosan-based materials is still one of the meaningful topics. If chitin can be used as the raw material to prepare multifunctional materials with outstanding performances, which can compare favorably with chitosan-based materials, it will have broader application prospects.

Due to the strong intra- and inter-molecular hydrogen bonds, chitin is insoluble in common solvents. Although the direct utilization of chitin is rather laborious, there is still plenty of researches focused on the preparation of multifunctional chitin-based materials, especially after the advent of the novel, green and efficient chitin solvent systems, such as alkali/urea and calcium solvent system. Chitin was completely dissolved in NaOH/urea aqueous solution, and a series of biocompatible chitin-based membrane, aerogels, fibers, hydrogels, and nanofibrous microspheres have been directly constructed, which could be used as adsorbent, catalysts, cell carriers, emulsifier, supercapacitors, and so on (Duan, Liu, He, & Zhang, 2014; Duan, Zhang et al., 2015; Duan et al., 2016; Tang, Chen, Duan, Lu, & Zhang, 2014; Wang, Liu, Shah, Li, & Li, 2015). Chitin can be also dissolved in calcium chloride dihydrate-saturated methanol. Then a biodegradable, non-toxic and cytocompatible multifunctionalized chitin hydrogel was obtained by controlling the regeneration method, which could be useful for biomedical, such as drug delivery with simultaneous imaging and biosensing, cell culture, tissue engineering, wound dressing, etc (Nagahama et al., 2008; Rejinold, Chennazhi, Tamura, Nair, & Rangasamy, 2011; Tamura et al., 2006; Tamura, Furuike, Nair, & Jayakumar, 2011). Chemical modification of chitin is one of the important pathways to improve its performance. Some chitin-based copolymers have been synthesized by grafting hydrophilic functional monomers (such as acrylamide, acrylic acid, methacrylic acid, L-lactide, succinic anhydride, etc.) onto the chitin backbones with excellent properties, including adsorbability, hygroscopicity, affinity, etc., which is promising to be used as glass cements, wound dressing, paraquat or metal ions adsorbent, superabsorbent polymers, and so on (Furlan, Fávere, & Laranjeira, 1996; Hsu et al., 2013; Liu et al., 2013; Tanodekaew et al., 2004).

In spite of this, the investigation for the preparation of multifunctional materials by physical or chemical modification of chitin is still far less than that of chitosan. The only difference between chitin and chitosan is that the DDA and molecular weight (Mw) are different. Some researchers have been concerned that the use of chitosan in diverse areas is directly related to the DDA and Mw of the polymer. It has been reported that the DDA and Mw influenced the physicochemical and biological properties of chitosan, such as thermal decomposition property, thermosensitivity, gelation, emulsifying ability, cytocompatibility, biodegradability, wound healing, and so on (Ko, Shin, Choi, Park, & Woo, 2011; Li & Xia, 2011; Zhou et al., 2008). However, there are few systemic researches concerned about the effects of DDA and Mw on the synthesis and properties of chitin-based SAPs. In previous study, we synthesized a transparent homogeneous chitin-based acrylate SAP under NaOH/urea solution with excellent water absorption capacity, but the presence of urea leads to the difficulty in figuring out the mechanism of the graft copolymerization between acrylic acid and chitin (Liu et al., 2013). In the following work, chitin is immediately dissolved in the NaOH aqueous solution via freezing-thawing treatment for two times without adding urea or any other reagents, and a series of chitin-based SAPs were obtained directly through utilizing the static solution polymerization method without nitrogen protection. The graft copolymerization mechanism, the effects of the DDA and Mw on the synthesis and properties of chitin-based SAP were also be discussed.

2. Materials and methods

2.1. Materials

Shrimp chitin was purchased from Zhejiang Golden·Shell Pharmaceutical Co., Ltd. (PRC), with a DDA of $4.70 \pm 0.65\%$ calculated according to the following equation: $DDA = [1 - (w_C/w_N - 5.14)/1.72] \times 100\%$, where w_C/w_N is the ratio of carbon to nitrogen (Tang et al., 2014), which was determined based on the CHN elemental analysis (Elementar vario EL cube, Germany). The viscosity-average molecular weight was more than 7.47×10^5 g/mol, measured in an Ubbelohde viscometer (Einbu, Naess, Elgsaeter, & Vårum, 2004). Acrylic acid monomer (AA, AR) was supplied by Shanghai Reagent Corp. (Shanghai, China), and it was filtered with a G4 glass sand core crucible without further purification before use. The ammonium persulfate (APS, AR), *N*,*N*'-methylenebisacrylamide (MBA, CP) and all other commercially available solvents or reagents were of analytical grade, and were used directly without further purification. Unless otherwise specification, the deionized water (the electrical conductivity is 17.50 μS/cm) was used throughout the experimental process. Running water (the electrical conductivity is 218 μS/cm) is potable water in Chizhou city (China). The physiological saline and artificial urine was prepared according to the literature (Liu et al., 2013).

2.2. Preparation of chitin solution

According to Fig. 1, chitin powder was dispersed in 40 wt% NaOH aqueous solution, after freezing-thawing-cyclic (FTC) treatment for two times, and the alkali-chitin mixture was diluted by iced-water with stirring, frozen in a domestic refrigerator (LW-120HB, Haier, China) at −18 °C overnight again and thawed at room temperature (RT), then a homogeneous transparent chitin solution was obtained. The chitin solution was stored at −18 °C before it was used for additional treatment. After thawing at RT, the chitin solution was kept at 25 °C, 30 °C and 35 °C for a specified time (Supplemental Table S1, column "treating time"), respectively, and a series of chitin solution with a variety of DDA and Mw were prepared by the homogeneous deacetylation treatment. The apparent viscosity was monitored by an NDJ-8S viscometer (Shanghai Ping Xuan Scientific Instrument Co., Ltd.), using the No. 4 spindle and rotating at 12 rpm. A minor portion of chitin solution was taken out and used for structural analysis (Liu et al., 2013).

To obtain a series of chitin samples with similar DDA but varied Mw, chitin (20 g) was suspended in 2 mol/L aqueous hydrochloric acid (100 mL), treated by an ultrasonic cleaner (JK-250DB, Hefei Kinnic Machinery Manufacture CO., LTD., China) for 0, 1, 2, 3, 4, and 5 h, respectively. Then it was filtered and continuously washed with water, until there is no residual Cl^- detected by $AgNO_3$, and dried at 40 °C under vacuum.

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