Carbohydrate Polymers 103 (2014) 285–293

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Synthesis of starch-g-p(DMDAAC) using HRP initiation and the correlation of its structure and sludge dewaterability

Shenghua Lv*, Ting Sun, Qingfang Zhou, Jingjing Liu, Huaidong Ding

College of Resource and Environment, Shaanxi University of Science & Technology, Xi'an 710021, China

ARTICLE INFO

Article history:
Received 6 November 2013
Received in revised form
11 December 2013
Accepted 12 December 2013
Available online 19 December 2013

Keywords:
Cationic starch
Horseradish peroxidase
Sewage sludge
Sludge dewatering

ABSTRACT

A new cationic starch used as a sludge dewatering agent was prepared by grafting copolymerization of degradation starch and dimethyldiallylammonium chloride (DMDAAC) using horseradish peroxidase/H_2O_2 initiation. Its chemical structure was characterized by FTIR, ^{1}H NMR, ^{13}C NMR, gel permeation chromatography, graft percent, and graft efficiency. The results indicated that its structure was built by grafting the DMDAAC oligomer onto the starch backbone as branched chains, with stronger hydrophobic regions and higher cationic degree. The specific resistance of the filtration and capillary suction time of the sludge conditioned with the cationic starch decreased distinctly, and the sludge water content could be reduced to 50.6% from 97.85%. The dewatering mechanism is proposed based on the surface tension, zeta potential, and microstructure of sludge, which involves stronger hydrophobic regions and cationic groups producing a porous structure within the sludge. The research results may provide valuable ideas for developing high-performance sludge dewatering agents.

1. Introduction

In recent years in China, together with the increasing pace of urbanization and industrialization, huge amounts of sewage sludge have been produced in municipal sewage and industrial effluent treatment. The sewage sludge has a high water content (WC; 95–98%), and has the nature of a hydrogel with greater fluidity, resulting in it being more difficult to further treat and re-use. Sludge dehydration should therefore be the first task for sludge treatment, and the WC of the sludge should be reduced to below 60% so that it can be further processed. Although there are various types of sludge dewatering equipment available, dewatering agents are still indispensable additives in the sludge dewatering process (Ali, Aeyed, & Seyed, 2013; Pal, Sen, Karmakar, Mal, & Singh, 2008). The most common dewatering agents are anionic polyacrylate, nonionic polyacrylamide, and cationic polyacrylamide (CPAM) (Lin et al., 2012; Noppakundilograt, Nanakorn, Jinsart, & Kiatkamjornwong, 2010; O'Shea, Qiao, & Franks, 2011). These dewatering agents have poor dewaterability, and may produce secondary contamination. In addition, their synthetic raw materials mainly depend on petroleum resources and inevitably face the threat of resource exhaustion. Therefore, many researchers have recently focused on the use of natural polymers, such as starch and chitosan, as biodegradable, renewable, and cost-effective materials for the synthesis of flocculants. The development of cationic starch, especially suitable for sewage flocculation and sludge dewatering, has received considerable attention (Krentz et al., 2006; Ma, Zheng, Tan, Liu, & Chen, 2013; Mishra, Mukul, Sen, & Jha, 2011; Wang et al., 2012). Cationic starch may be prepared by etherification or graft copolymerization of starch and cationic monomers (Anthony & Sims, 2013). The cationic monomers used for etherification are mainly 3-chloro-2-hydroxypropyltrimethylammonium chloride (CTAC) or 2,3-epoxypropyltrimethylammonium chloride (ETAC) (Zou, Zhao, Ge, Lei, & Luo, 2012). The etherifying reaction is carried out between chlorine of CTAC or epoxy groups of ETAC and hydroxyl groups of starch. The cationic monomers are bonded to the starch skeleton to form branched chains. At present, studies have mainly focused on improving the dewaterability by increasing the degree of substitution and graft efficiency (Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2008).

When cationic starch is prepared by grafting copolymerization, the cationic comonomers are diallyldimethylammonium chloride (DMDAAC) or 3-(methacryloylamino)propyltrimethylammonium chloride (Ochoa et al., 2007). DMDAAC alone cannot form a polymer due to its self-inhibition; generally, acrylamide (AM) is used as a comonomer to form a copolymer with DMDAAC. CPAM is actually a copolymer of AM and DMDAAC (p(AM-*co*-DMDAAC)). Therefore, cationic starch is actually p(AM-*co*-DMDAAC) grafted on the starch

* Corresponding author. Tel.: +86 029 86168291; fax: +86 029 86168291.
E-mail addresses: Lvsh@sust.edu.cn, lvsh630603@yahoo.com (S. Lv).

0144-8617/$ – see front matter
http://dx.doi.org/10.1016/j.carbpol.2013.12.036

skeleton to form starch-g-p(AM-*co*-DMDAAC). In recent years, improving the flocculation effect and dewaterability by increasing grafting percent (GP) and grafting efficiency (GE) using a suitable initiator has become a hot topic of research. Gamma irradiation and complex initiation by $Ce(SO_4)_2$–$K_2S_2O_8$ or $CO(NH_2)_2$–$(NH_4)_2S_2O_8$ have been investigated and have exhibited a significant effect (Lv et al., 2013).

The determination of the molecular structure of cationic starch is another difficult issue in this research field. Although there are many advanced structural measurement techniques, such as FTIR, NMR, and MS, its accurate molecular structure is still difficult to confirm due to the complexity of polymerization and the difficulty in separation of products. Nowadays, the molecular structure of cationic starch can usually be characterized by the FTIR, ^{1}H NMR, and ^{13}C NMR spectra of feature groups and structure (Randal & Shogren, 2013; Tawaki, Uchida, Maeda, & Ikeda, 2005).

Starch-g-p(AM-*co*-DMDAAC) has been used in sewage flocculation and exhibited a good flocculation effect and cost effectiveness (Pal, Sen, Karmakar, Mal, & Singh, 2008). However, using starch-g-p(AM-*co*-DMDAAC) as a sludge dewatering agent can lead to the sludge forming a sticky gel, meaning that the sludge WC cannot be reduced to below 60%. Therefore, improving the dewaterability of cationic starch has become an urgent and arduous task. The solution to this problem should be sought from the working mechanism of flocculation and sludge dewatering. Flocculation is a process of adsorption and bridging coagulation. The starch-g-p(AM-*co*-DMDAAC) with long molecular chains and strong cationic groups could produce strong adsorption and coagulation, so it has stronger flocculation effects in sewage treatment. Sludge dewatering is a process of water repelling and drainage, which differs distinctly from that of sewage flocculation. Formation of hydrophobic regions within the sludge and further development into a porous structure in a mechanical dehydrating process is the main feature of the mechanism. The hydrophobic regions and porous structure are the synergetic result of hydrophilic/hydrophobic regions and cationic groups. Therefore, the ideal sludge dewatering agent has not only hydrophilic groups for solubility and dispersion, but also stronger hydrophobic groups for forming the hydrophobic regions for building drainage channels. In starch-g-p(AM-*co*-DMDAAC), the hydrophobic groups and cationic groups are separated by hydrophilic nonionic AM units, so the hydrophobic groups cannot connect to form hydrophobic regions. Therefore, the self-structure of starch-g-p(AM-*co*-DMDAAC) leads to its poor dewatering capacity.

Based on the analysis above, a new cationic starch with an ideal molecular structure for sludge dehydration was designed and prepared by grafting oligomeric p(DMDAAC) onto the starch skeleton using a horseradish peroxidase (HRP) initiation system. The oligomers are bonded to the starch as branched chains, which consist of five- or six-membered rings of DMDAAC. The ring-structure units connected directly may form large hydrophobic regions and strong cationic regions. This molecular structure is designed specifically for improving the sludge dewaterability of the cationic starch. The special structure can only be built by HRP initiation. HRP is a kind of enzyme-mediated initiator, its outstanding features being a unique initiation mechanism and structural controllability, as well as moderate reaction conditions and high reaction efficiency (Anthony & Sims, 2013; Lv, Gong, & Ma, 2012). The molecular structure was demonstrated by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The sludge dewaterability was investigated using the specific resistance of filtration (SRF), capillary suction time (CST), and dewatering ratio of sludge. The working mechanism was probed by investigation of the surface tension, zeta potential, pore structure, and SEM images of the sludge.

2. Experimental

2.1. Materials

HRP, with an activity of 2900 U mg^{-1} and M_w of 3000, and thermostable α-amylase, with an activity of 10,000 U mg^{-1} and maximum suitable temperature of 94 °C, were bought from Beijing Biosynthesis Biotechnology Company (Beijing, China). Cornstarch was supplied by the Xi'an Starch Factory (Xi'an, China). Hydrogen peroxide (H_2O_2, 30 wt%), DMDAAC, sodium bicarbonate ($NaHCO_3$), toluidine blue indicator, potassium polyvinyl sulfate (PVSK), and methanol were supplied by the Xi'an Chemical Reagent Factory (Xi'an, China).

The municipal sewage and sludge came from the aerated grit chambers and secondary settling tanks, respectively, of urban sewage treatment plants (Xi'an, China). The important parameters of the sewage sludge were as follows: pH 7.53; zeta potential, −24.3 mV; SRF, 7.53×10^{13} m kg^{-1}; CST, 76.53 s; water content, 97.85%; total solids, 2.15%; organic matter, 53.6% dry basis; total nitrogen content, 2.79% dry basis; and total phosphorus, 2.61% dry basis.

The control samples were CPAM and starch-g-p(AM-*co*-DMDAAC). CPAM was prepared by copolymerization of 20 g of AM and 15 g of DMDAAC using $(NH_3)_2S_2O_8$ initiation. The cationic degree (CD) was 41.5%. The M_w and M_n were 85,427 and 72,395, respectively. Starch-g-p(AM-*co*-DMDAAC) was synthesized by graft copolymerization of 10 g of starch, 10 g of AM, and 19 g of DMDAAC using $Ce(SO_4)_2$–$K_2S_2O_8$ initiation. The CD was 39.4%, and M_w and M_n were 164,562 and 127,567, respectively.

2.2. Preparation of starch-g-p(DMDAAC)

Amounts of 25 g of starch and 0.01 g of thermostable α-amylase were placed into a three-neck round-bottom flask with 75 g of deionized water under stirring. Then, the mixture was heated and kept at 90 °C for 2 h. This was then cooled to 35 °C, with the product being degraded starch. Then, 25 g of DMDAAC was added to the degraded starch solution and the pH value adjusted to 7.0 with $NaHCO_3$, with the temperature being kept at 45 °C. Then, a certain amount of HRP was added at once, and H_2O_2 was added dropwise for 1 h. After adding the H_2O_2, the reaction was continued at 45 °C for 6 h. The final product was starch-g-p(DMDAAC).

2.3. Structural characterization of starch-g-p(DMDAAC)

2.3.1. FTIR and NMR spectra

FTIR spectra were obtained using an EQUINOX-55 FTIR spectrometer (Bruker, Germany). The samples were purified by precipitation and washing with methanol.

The ^{1}H NMR and ^{13}C NMR spectra were obtained using an INOVA 400 MHz spectrometer (AVANCE III, Switzerland). The samples were purified, dried, and then dissolved in deuterated dimethyl sulfoxide (DMSO).

2.3.2. Gel permeation chromatography

M_w, M_n, and polydispersity index (PDI) were measured using a gel permeation chromatograph (model 2414, Waters, USA). Sodium azide solution (0.10 mol L^{-1}) was utilized as the carrying phase at a flow rate of 1 mL min^{-1} at 40 °C. The standard sample was poly(ethylene glycol). The samples were purified following the same procedure as before.

2.3.3. Cationic degree

The CD was determined by colloid titration. Cationic starch (0.02 g) was accurately weighed in a 250 mL Erlenmeyer flask with 100 mL of deionized water. Then, the solution pH value was