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Synthesis of cationic alkylated chitosans and an investigation of their rheological properties and interaction with anionic surfactant

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ABSTRACT

Two methods were used to alkylate high M_W chitosan with glycidyltrimethylammonium chloride (GTAC) in order to produce chitosan derivatives that are water-soluble throughout the pH range. In addition, a novel chitosan derivative was created by alkylating one of the products with the GTAC analogue Quab 342 containing C12 alkyl chains. The phase behaviour and rheological characteristics of the chitosan derivatives were studied in the presence of anionic surfactant. The derivatives were found to form soluble complexes at low and high SDS concentrations and that the Quab 342 derivative was able to form gels.

1. Introduction

Chitin (poly β-(1→4)-*N*-acetyl-D-glucosamine) is found in arthropod shells (Mao, Guo, Sun, & Xue, 2017) and the cell walls of yeasts and fungi. It is the second most abundant natural polysaccharide after cellulose (Dutta, Dutta, & Tripathi, 2004), and it is in increasing demand as a raw material for many sophisticated applications in medicine, agriculture and other areas (Dutta et al., 2004; Hayes, Carney, Slater, & Bruck, 2008a; Kumar, Muzzarelli, Muzarelli, Sashiwa, & Domb, 2004; Pillai, Paul, & Sharma, 2009; Xia, Liu, Zhang, & Chen, 2011). Chitin's desirable properties include biocompatibility, biodegradability to normal body constituents, safety, non-toxicity, binding to mammalian and microbial cells, and antimicrobial activity against bacteria and fungi (Bellich, D'Agostino, Semeraro, & Gamini, 2016; Sahariah & Másson, 2017). These properties are shared by its acid-soluble derivative chitosan, which is prepared by removing at least 50% of the N-acetyl groups, and also by a wide variety of chemical derivatives.

Chitin is generally extracted from marine sources, such as shrimp shells and other shellfish by-products, although there is also interest in fungal and insect chitin (Sajomsang & Gonil, 2010). The extraction process (reviewed by Hayes, Carney, Slater, and Bruck (2008b) and Younes and Rinaudo (2015)) consists of demineralisation, deproteination, decolourisation, and in the case of chitosan, deacetylation. It generally involves strong acids and alkali, and may be extended to depolymerise the chitosan if low M_W products are desired (Mohammed, Williams, & Tverezovskaya, 2013). Alternatively a specific depolymerisation step may be added, such as ultrasound or enzyme hydrolysis (Lodhi et al., 2014).

Chemically, chitosan is a linear polyamine, basic, carrying reactive amino and hydroxyl groups, capable of chelating transition metal ions, and soluble in water below pH 6.5. Its hydroxyl and amino groups can be acylated or alkylated, which is very useful, because its uses under physiological conditions are limited by the fact that it precipitates when the pH is raised above 6.5 (e.g. Lim & Hudson, 2004; Snyman, Hamman, Kotze, Rollings, & Kotzé, 2002; Tungtong, Okonogi, Chowwanapoonpohn, Phutdhawong, & Yotsawimonwat, 2012). This problem can be solved by adding polar or charged groups to the polysaccharide backbone. Hydrophobic groups such as dodecyl moieties are also sometimes added to make chitosan soluble in organic solvents (Mourya & Inamdar, 2008), or enable it to bind to plastics as a biodegradable component (Kumar et al., 2004). Chemical derivatives of chitosan have been comprehensively reviewed by Mourya and Inamdar (Mourya & Inamdar, 2008) while Sahariah and Másson discuss their antibacterial activity (Sahariah & Másson, 2017).

One potentially extremely useful modification is to convert the 2-amino group into a quaternary amine (Mourya & Inamdar, 2008; Sahariah & Másson, 2017). The quaternary amine remains charged throughout the pH range and if the degree of substitution (D.S.) is high enough it can render even high M_W chitosans completely water-soluble. The simplest quaternised chitosan is N,N,N-trimethyl chitosan, synthesised by reductive alkylation (Guo et al., 2007), which has very promising antifungal (Snyman et al., 2002) and antibacterial activity (Sahariah & Másson, 2017). However, because the reductive methylation synthesis requires iodomethane and N-methyl pyrrolidine as a solvent, an alternative reaction which can be carried out in aqueous solution is often preferred. Glycidyl trimethylammonium chloride

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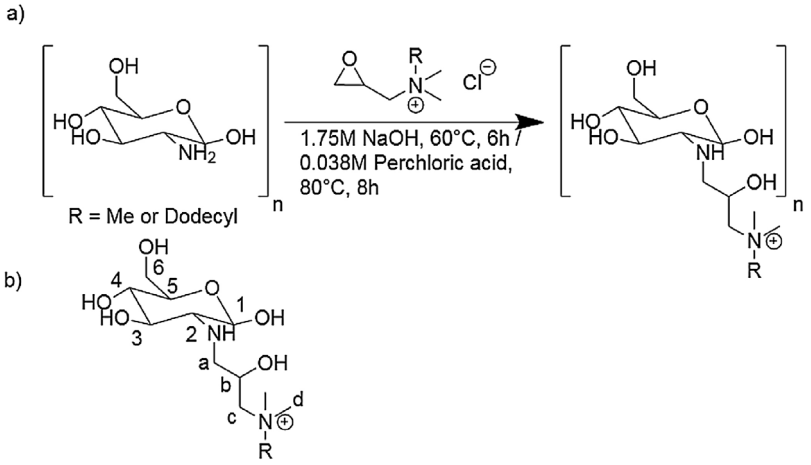

Fig. 1. (a) Reaction of GTAC or Quab 342 with chitosan monomer either by the high pH method: 1.75 M NaOH, 60 °C, 6 h or Ruihua method: 0.038 M perchloric acid, 80 °C, 8 h. (b) Location of protons on the GTAC- or Quab 342-alkylated glucosamine monomer (R = Methyl, R = Dodecyl, respectively).

(GTAC) alkylates the amino groups via its epoxide ring and it already carries a quaternary amine group. The GTAC alkylation is well studied, and typically carried out under neutral conditions at temperatures of 70 °C – 100 °C (Kim, Lee, Lee, & Park, 2003; Lim & Hudson, 2004; Nam, Kim, & Ko, 1999; Ruihua, Bingchao, Zheng, & Wang, 2012), and the resulting quaternised chitosan also has antimicrobial activity (Kim et al., 2003; Lim & Hudson, 2004; Nam et al., 1999; Sahariah & Másson, 2017).

With its wide solubility range, quaternised chitosan has obvious potential applications in a broad range of commercial products, including pharmaceuticals, neutraceuticals, cosmetics and personal care products. As Dutta et al. point out, chitosan can form a clear elastic skin on hair (which is negatively charged), and it can form gels in aqueous alcohol solvents (many types of cosmetics, skincare products and pharmeuticals are applied as gels) and furthermore, high M_W chitosans do not pass through the skin barrier (Dutta et al., 2004). If quaternised chitosans share all these chitosan traits, they would be desirable components for these formulations. In the case of shampoos it would also be desirable for the chitosans to have foaming and emulsifying properties, either by themselves or when combined with surfactants in a formulation.

This study was undertaken to synthesise quaternised chitosans with high D.S. using GTAC. Two synthetic methods were attempted. (1) Heterogeneous GTAC alkylation at high pH to alkylate both the amino and hydroxyl groups on the chitosan backbone. Our first hypothesis was that at high pH, the 3- and 6-hydroxyl groups may be alkylated as well, increasing the D.S. and the charge density by up to three times. (2) Homogeneous GTAC alkylation in dilute perchloric acid by Ruihua's method (Ruihua et al., 2012). In addition, a second alkylating agent was tested: Quab 342, a GTAC analogue which carries a dodecyl chain in place of one of the quaternary amine's methyl groups.The second hypothesis was that this quaternised chitosan derivative (with hydrophobic groups in addition to the positively charged substituents) would have enhanced rheological characteristics due to intermolecular hydrophobic interaction and that the interactions could be enhanced by the presence of anionic surfactants. Hydrophobically associating polymers, which are predominately non-ionic or anionic, are finding increasing application in commercial formulations in many industrial sectors and since the formulations invariably include surfactants a knowledge of the polymer-surfactant interactions is important (Goddard & Ananthapadmanabhan, 1998; Langevin, 2009; Williams, 2003).

2. Materials and methods

2.1. Materials

High molecular weight chitosans Chitopharm™ S (S#2265, 17% Degree of Acetylation, DA) and Chitopharm™ L (L#2272, 16% DA) were supplied by Chitinor AS, Norway. Quab 342 (3-chloro-, 2-hydroxypropyl-*N,N,N*-dimethyllaurylammonium chloride) was a gift from Croda Ltd UK. Glycidyl trimethylammonium chloride (GTAC) was obtained from Sigma–Aldrich; sodium dodecyl sulphate and all other chemicals were from Sigma–Aldrich or Fisher.

2.2. Alkylation of chitosan with Quab reagents

For the high pH GTAC alkylation reaction, the following method was used: 20 g of high molecular weight chitosan S#2265 was suspended in 400 g deionised water under mechanical stirring. 35 g sodium hydroxide pellets were dissolved in 100 g distilled water, which was then added dropwise to the chitosan slurry. The vessel was then purged with inert nitrogen gas and the temperature raised to 60 °C. 12.08 g of GTAC was added via a pressure equalising funnel over 20 min at 0, 2 and 4 h. At 6 h the sample was allowed to cool, and neutralised with 32% HCl. The sample (G-2265) was subsequently washed with isopropanol.

To produce the G- and GQ-chitosan samples, the method of Ruihua et al. (Ruihua et al., 2012) was employed. 5 g of chitosan L#2272 was suspended in 750 ml ultrapure water, and dissolved by dropwise addition of 4.75 ml perchloric acid, with stirring. The sample was then heated to 60 °C, with mechanical stirring. 12.5 g of GTAC was added at 0, 30 and 60 min, then the temperature was raised to 80 °C and the reaction continued for 8 hours. For the G-chitosan, the product was then extracted by precipitation in acetone. For the GQ-chitosan, the pH was raised to 11.2 with 1 M NaOH and the alkylation procedure was repeated, using Quab 342 reagent in place of GTAC. The reactions are shown in Fig. 1.

2.3. Characterisation of derivatised chitosans

FT-IR spectra of chitosans and chitosan derivatives were measured by the KBr disc method on a Perkin Elmer Spectrum RX1 FT-IR Spectrophotometer. Proton NMR spectra were recorded in D_2O on a Bruker Spectrophotometer at 400 MHz, 298.2 K, 256 scans and the fid files were analysed in MestReNova 9.0 software for Windows. Noise was removed by apodisation along t1 (Exponential 0.3 and Gaussian 5.0) and background correction by Whitaker Smoother. Phase