



Study of adsorption behaviors on a SiO₂ surface using alkyl cationic modified starches



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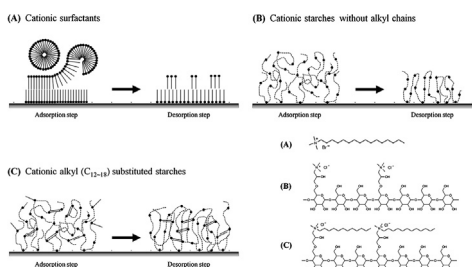
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HIGHLIGHTS

- Cationic alkyl starches were synthesized to observe the adsorption behavior by QCM-D.
- Adsorbed amount of cationic starches increased compared with cationic surfactants.
- Tendency for increased rigidity after desorption was observed in all cationic starches.
- Cationic alkyl starches showed more adsorbed amount and rigidity than cationic starches.

GRAPHICAL ABSTRACT



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ABSTRACT

Quartz crystal microbalance with dissipation monitoring (QCM-D) was performed in order to study the adsorption behavior of mono-electrolytes (cationic surfactants: C_{12–16} trimethyl ammonium bromide) and polyelectrolytes (cationic starches and cationic alkyl substituted starches). An adsorption step using surfactant or polymer solutions and a desorption step of rinsing with distilled water were adopted in order to observe the adsorption behavior. The adsorbed amount of all cationic starches increased compared with that of the cationic surfactants, and the adsorption gap between the adsorption and desorption processes was remarkably small. In addition, a tendency for increased rigidity after desorption was observed. In particular, the cationic alkyl (C_{12–18}) substituted starches had long alkyl chains as well as polymer backbones. In the results, the adsorbed layer of the cationic alkyl substituted starches increased more than the general cationic starches and exhibited more rigid properties. These results were attributed to the hydrophobic interactions among polymers originating from long alkyl chain substitutions.

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1. Introduction

Starch is one of the most abundant natural polymers in the world. Starch, which is readily obtained from natural grains, is environmentally biodegradable, renewable, and harmless to the human-body. Because it consists of a polymer structure such as dextrose linking, starch is a useful material that has many applications. Most importantly, from an industrial viewpoint, it is much cheaper than other polymer materials. Accordingly, starch is used

not only for food purposes but also in the textile and adhesives industries, paper-making, and cosmetics [1]. A well-known starch application is the synthesis of biodegradable (or biodestructible) polymers blended with biodegradable synthetic polymers, such as poly (ϵ -caprolactone) (PCL), poly (lactic acid) (PLA), and polyvinyl alcohol (PVOH) [2,3]. Furthermore, cationic modified starch is widely used to improve water solubility by controlling the surface charge of particles in aqueous solutions [4–6]. Due to the high molecular weight and cross-linking connecting structure of starch, it is not easily dissolved in water despite having many hydrophilic OH groups. Cationic modified starch is also used as a cellulose adhesive in paper-making industries and as an adsorbent for industrial wastewater treatment due to its water-soluble characteristics.

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The cationic nature of the modified starches also offers adsorption abilities in anionic materials, which can be exploited in practical applications [7,8].

As starch is harmless to the human body, environmentally friendly, and inexpensive, modified starch can be used in household and personal-care applications, as well as cosmetics. In terms of applications, the surface of skin, hair and cloth generally exhibits anionic characteristics. So, conditioning products such as fabric softener, hair rinse and hair treatment have used cationic surfactants and cationic polymers as main ingredients to attach them to skin, hair and cloth. Thus, cationic starches can provide efficient adsorption on their surfaces.

In this paper, the adsorption behaviors of various modified cationic starches are investigated. The study of adsorption behaviors is very difficult using skin, hair, and cloth directly, because the adsorbed amount is extremely small. Therefore, a SiO₂ cell was used as the anionic surface instead of skin, hair, or cloth; the adsorption study was undertaken using quartz crystal microbalance with dissipation monitoring (QCM-D). The QCM-D method has been developed in numerous previous research papers and allows comparison of the visco-elastic properties of each adsorption layer while also being used to measure the adsorbed amount and thickness of the adsorption layers [9–13,16–18].

In this study, three types of starches were used according to their molecular weight (starch-oligomer, soluble starch, and corn-starch) and cationic modification was conducted using the cationic reagents glycidyl trimethyl ammonium chloride (GTMAC) and glycidyl dimethyl alkyl (C_{12–18}) ammonium chloride [14,4]. The adsorption characteristics of a cationic substituted starch with a hydrocarbon alkyl chain were compared with those of a cationic starch without alkyl chains. This paper reports the results of this investigation in detail.

2. Experimental

2.1. Materials

Starch-oligomer (dextrose equivalent 10; Mw 4000; poly dispersity 3.2 by GPC) and corn-starch were obtained as commercial products from DAESANG Corporation (South Korea). Soluble starch (Mw 7.1 × 10⁴; poly dispersity 2.8 by GPC; extra pure grade) was purchased from Samchun Pure Chemical Co., Ltd. (South Korea). Glycidyl trimethyl ammonium chloride (GTMAC; technical grade; purity > 70%) was purchased from Sigma-Aldrich (Korea). N-dodecyl-N-dimethylamine, N-tetradecyl-N-dimethylamine, N-hexadecyl-N-dimethylamine, and N-octadecyl-N-dimethylamine were obtained from TCI (Tokyo, Japan). Dodecyl trimethyl ammonium bromide, tetradecyl trimethyl ammonium bromide, and hexadecyl trimethyl ammonium bromide were also purchased from TCI (Tokyo, Japan).

2.2. GTMAC (C₁) substituted starch synthesis

The cationic starches (starch-g-GTMAC and starch-g-C₁) were synthesized according to the method reported by Bendoraitiene [6]. Three types of starch, i.e. starch-oligomer (DE10, Mw 4000), soluble starch (Mw 7.1 × 10⁴), and corn-starch, were used to synthesize the cationic starches.

Dried starch was added to a reaction vessel containing a mixture of distilled water, GTMAC (C₁), and aqueous sodium hydroxide (1N solution). The reaction solution was then mixed until it became homogeneous. The reaction proceeded at a temperature of 45 °C for 24 h. After being cooled to room temperature, the reaction solution was precipitated in excess isopropyl alcohol (IPA). Finally, the filtered product was purified via washing with IPA three times.

The final powder product was then dried in a vacuum oven at 45 °C for 8 h. The molar ratio of the reactants was anhydroglucose (AGU):GTMAC:NaOH:H₂O = 1:(0.1–0.5):0.04:1.

2.3. Glycidyl dimethyl alkyl ammonium chloride (C_{12–18}) substituted starch synthesis

Solutions of glycidyl dimethyl dodecyl ammonium chloride (GDMDAC, C₁₂), glycidyl dimethyl tetradecyl ammonium chloride (GDMTAC, C₁₄), glycidyl dimethyl hexadecyl ammonium chloride (GDMHAC, C₁₆), and glycidyl dimethyl octadecyl ammonium chloride (GDMOAC, C₁₈) were prepared as intermediates for the cationic alkyl grafting reaction with N-dimethyl-N-alkyl (C_{12–18}) amine and epichlorohydrin. In this paper, the data and conditions of the N-dimethyl-N-alkyl (C_{12–18}) amine and epichlorohydrin reaction are excluded.

Starch-oligomer, soluble starch, and starch (soluble)-g-C₁ were used to synthesize the alkyl cationic starches. The reaction conditions and molar ratios were the same as those employed in the GTMAC grafting experiments.

The overall synthesis scheme of the cationic starches is shown in Fig. 1.

2.4. Evaluation of the degree of substitution

An elementary analysis (C, H, N) and Cl[−] potentiometric titration with AgNO₃ were performed in order to evaluate the nitrogen and chlorine content in cationic starches [15]. In the elementary analysis (EA), the degree of substitution (DS) was calculated from the ratio of nitrogen and carbon content. For products containing a small amount of nitrogen, potentiometric titration of Cl[−] was performed as well as the EA in order to improve the accuracy of the analysis.

The molar ratio of nitrogen content and Cl[−] content was the same, as the quaternization reagents such as GTMAC, GDMDAC, GDMTAC, GDMHAC and GDMOAC contained 1 nitrogen with 1 chlorine as a counter ion.

The degree of substitution is defined by the following equation [13]:

$$DS(\%) = \frac{\text{mole number of N(or Cl)}}{\text{total mole number of AGU}} \times 100 \quad (1)$$

2.5. Surface tension and critical micellar concentration (CMC)

The surface tension of an aqueous cationic starch solution was measured by an equilibrium surface tensiometer (ThermoCahn, RADIANT Series 300). The measurement was conducted at 25 °C in 0.1 wt% concentration using a pH 7.0 buffer solution.

CMC of cationic surfactants and alkyl substituted cationic starch-oligomers was measured at 25 °C using a Du Nuoy ring tensiometer with a platinum ring (Kruss K100, Germany).

2.6. Particle size and zeta potential

The particle size and zeta potential of the aqueous starch (DE10)-g-C₁₈ solution were measured at 25 °C as a function of DS by using a zeta potential analyzer (Otsuka ELS-800, Japan). The particle size measurement was carried out in a 1.0 wt% concentration with distilled water and the zeta potential measurement was performed with 0.5 wt% concentration without any pH adjustment. The dilute cationic starch solutions were measured at pH 6.9–7.5. Distilled water was used instead of a 7.0 buffer solution to remove interference of ionic strength. Because the intensity of light scattering was weak under 1500 cps at starch (DE10)-g-C_{12–16} series, the measurement was carried out only for the starch (DE10)-g-C₁₈ series.

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