The moisture absorption and retention abilities of hyaluronan, chitosan, starch and their quaternary derivatives

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Abstract—Quaternary ammonium salt of hyaluronan (QHA), quaternary ammonium salt of starch (QS), and quaternary ammonium salt of chitosan (QCTS) were successfully prepared. Infrared spectroscopy (IR), $^1$H NMR and $^{13}$C NMR techniques were used to characterize the molecular structure of QHA. Results showed that QHA had better moisture absorption abilities than HA both at 43% and 81% RH. QS and QCTS had the same tendency. In addition, the three quaternized polysaccharides had better moisture retention abilities than their corresponding polysaccharides under three humidity conditions: 81% RH, 43% RH and dry condition. The –N+ (CH$_3$)$_3$ group played a very important role in moisture-absorption and retention ability of the quaternized polysaccharides. QCTS and QHA showed parallel or better $R_a$ and $R_h$ than that of HA, and had potential to use as moisture-retention ingredient, e. g., in cosmetics.

Key words—hydrophilic polymer; moisture absorption; moisture retention; quaternized modification

I. INTRODUCTION

Hyaluronan (HA), an important functional ingredient in cosmetics, is unique for its excellent moisture retention ability, but the total amount is limited, and the price is high [1, 2]. Chitosan is a unique natural cationic polysaccharide and it’s the second abundant nature polysaccharide after ellulose. It can improve the film-forming capability of cosmetics. As a non-toxic and renewable natural resource, chitosan and its derivatives have attracted considerable attention in connection with their use in food products and cosmetics [3-6]. However, it can not replace HA as the moisture absorption and retention ingredient in cosmetics because of its lower moisture retention ability.

Chen et al. reported that carboxymethyl chitosan had better moisture retention ability than chitosan [6, 7]. As appropriate modification could improve the moisture absorption and retention abilities of chitosan, we prepared quaternary ammonium salt of hyaluronan (QHA), quaternary ammonium salt of starch (QS) and quaternary ammonium salt of chitosan (QCTS), aiming at improving the moisture absorption and retention abilities of these polysaccharides.

II. EXPERIMENTAL

A. Materials

Chitosan was purchased from Qingdao Baicheng Biochemical Corp (China). HA and starch were purchased from Shandong Freda Biochem. Co. Ltd (China). The other reagents were all analytical grades and were used without further purification.

B. Synthesis of quaternized polysaccharides

QCTS and QS were prepared according to Lin [8] and Xiao [9] respectively. QHA was prepared as followed: 0.5 g HA was dispersed into 15 mL isopropanol at room temperature, and 2.0 mL NaOH (10 mol/L) was added with stirring. 0.5 ml 2, 3-epoxypropyl-trimethyl ammonium chloride (EPTMAC) was used as ethering agent, and the mass fraction was 69%. The reaction was carried out with stirring at 45°C for 7 h. The product was filtered and washed with ethanol for three times. After vacuum dried at room

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temperature, QHA was prepared. (Synthetic pathway was shown in Scheme 1).

Scheme 1. Synthetic pathway of QHA

C. Characterization of QHA

The IR spectra were measured on a Nicolet Magne-Avatar 360 instrument using KBr disks. The \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Apx 500 (500MHz) NMR spectrometer in D\(_2\)O solvent.

D. Measurement of moisture absorption abilities

Each sample was rubbed into powder and dried in oven at 100 °C for 4 h. 0.5 g samples were put into desiccators saturated with (NH\(_4\))\(_2\)SO\(_4\) (81% RH) and Na\(_2\)CO\(_3\) (43% RH) at room temperature, respectively. After 24 h and 48 h, weights of the samples were tested. The moisture absorption ability \((R_a)\) was evaluated by the percentage increase of weight:

\[
R_a(\%) = 100 \times \frac{(W_n - W_0)}{W_0}
\]

Where \(W_0\) and \(W_n\) were the weights of sample before and after were put into the desiccators, respectively.

E. Measurement of moisture retention abilities

0.5 g samples were rubbed into powder in mortars and dried in oven at 100 °C for 4 h. 0.05 g water was added to each sample. Samples were then put into silica gel, (NH\(_4\))\(_2\)SO\(_4\) and Na\(_2\)CO\(_3\) saturated desiccators, respectively. The moisture retention ability \((R_h)\) was evaluated by the percentage of residual water of wet sample:

\[
R_h(\%) = 100 \times \frac{(H_n / H_0)}{}
\]

Where \(H_0\) and \(H_n\) were the weights of water in sample before and after were put into the desiccators, respectively.

III. RESULTS AND DISCUSSION

The IR spectra of HA and QHA were shown in Fig. 1. As shown in Fig. 1, the IR spectrum of HA showed peaks assigned to the saccharine structure at 893 and 1150 cm\(^{-1}\). Characteristic peak of amine (N–H) vibration deformation appeared at 1628 cm\(^{-1}\). After quaternized, new peak appeared at about 1432 cm\(^{-1}\), which was assigned to the characteristic absorption of N–CH\(_3\). The \(^1\)H NMR and the \(^{13}\)C NMR spectra of QHA were shown in Fig. 2 and 3. The –N\(^+\) (CH\(_3\))\(_3\) group were confirmed by the \(\delta\) at 3.33 of \(^1\)H NMR spectrum in Fig. 2 and the \(\delta\) at 54.39 of \(^{13}\)C NMR spectrum in Fig. 3. The above-mentioned results demonstrated that QHA was obtained.
The moisture absorption properties of quaternized polysaccharides were shown in Fig. 4. Both at 43% and 81% RH, $R_a$ (%) of all the samples increased rapidly before 80 h, and then increased gradually. At 43% and 81% RH, $R_a$ of HA was 29.5% and 38% at 120 h, while $R_a$ of QHA was 63% and 78%. Both at 43% and 81% RH, QHA had greater moisture absorption capacity than its corresponding polysaccharide, HA. QCTS had the same tendency compared with chitosan. When RH was 43%, the moisture absorption index of chitosan and QCTS were 5.8-10% and 21-43% at 24-120 h, respectively. And when RH was 81%, the $R_a$ of chitosan and QCTS were 11.5-18% and 30.4-54%, respectively. For starch and QS, at 81% RH, the moisture absorption index was 19% and 45% at 120 h. And similarly, QS had better moisture absorption ability than that of starch. QHA had the best moisture absorption ability both at 43% and 81% RH among the samples tested, and QCTS showed better $R_a$ than that of HA and QS.

![Figure 4. Moisture absorption abilities of quaternized polysaccharides](image)

The moisture retention properties of quaternized polysaccharides were shown in Fig. 5. Both at 43% and 81% RH, the $R_h$ (%) of all the samples increased steadily at first, and then close to balance at 80-100 h. At 43% RH, $R_h$ of HA was 224.3% and 328% at the time point of 24 h and 120 h, while $R_h$ of QHA was 304.6% and 540%. At 81% RH, the $R_h$ of HA and QHA were 315.8-455% and 407.3-650% at 24-120 h, respectively. Under dry condition, the maximum $R_h$ of QHA was 41.31% at 24 h, and the minimum $R_h$ was 27% at 120 h, which was better than that of HA. QHA had greater moisture absorption capacity than HA under all the humidity conditions tested: at 43% RH, at 81% RH and in silica gel. QS and QCTS had the same tendency. Each quaternized polysaccharide was better in moisture retention ability than its corresponding polysaccharide at each combination of time and RH. QCTS showed parallel $R_h$ than that of HA under high relative humidity conditions (RH 81% and 43%), and QHA had the best moisture retention ability.

![Figure 5. Moisture retention abilities of quaternized polysaccharides](image)

All the quaternized polysaccharides had better moisture
absorption and retention abilities than their corresponding polysaccharides, indicating introduction of quaternary group was a convenient and effective method to give these polysaccharides their moisture absorption and retention abilities. Considering multifunction and low toxicity of these polysaccharides, researches on moisture absorption and retention abilities of their quaternary derivatives will be helpful to expand their applications in cosmetics and biomedicine. QCTS and QHA showed parallel or better $R_a$ and $R_h$ than that of HA, and had potential to use as moisture-retention ingredient, e. g., in cosmetics.

REFERENCES


