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Synthesis of Carboxymethyl Polysaccharides and Their Moisture Absorption and Retention Abilities

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In this study, carboxymethyl hyaluronic acid, carboxymethyl starch and carboxymethyl chitosan were successfully prepared. The characterization of carboxymethyl hyaluronic acid was identified by IR and NMR techniques. The moisture absorption and retention abilities of these products were examined. Results showed that carboxymethyl hyaluronic acid, as well as carboxymethyl starch and carboxymethyl chitosan, had better moisture absorption and retention abilities both at 43 and 81 % relative humidity than the corresponding polysaccharide and hyaluronic acid. It is concluded that carboxymethylation could improve greatly the moisture absorption and retention abilities of polysaccharides and that carboxymethyl hyaluronic acid, carboxymethyl starch and carboxymethyl chitosan all would be very promising to be used as moisture absorption and retention ingredients instead of hyaluronic acid in cosmetics and in certain other fields.

Keywords: Carboxymethyl polysaccharides, Moisture absorption ability, Moisture retention ability, Hyaluronic acid.

INTRODUCTION

Chemical modification of polysaccharides is considered as one of the most important route to enhance the properties of biopolymers. Recent trends and strategies in research are geared towards functionalization of known materials and carboxymethylation of polysaccharides is one of the widely studied conversions that lead to development of new biomaterials with promising applications. Carboxymethylation was reported to be able to improve the moisture absorption and retention abilities of carbohydrate[1-3].

Hyaluronic acid is an important functional ingredient in cosmetics for its excellent moisture retention ability, but its price is very high for its limited output[1,4]. Consequently, exploring low cost and fine alternatives of hyaluronic acid is much attractive.

Although starch and chitosan cannot take the place of hyaluronic acid in cosmetics for their lower moisture absorption and retention abilities, the option in connection with their use in food products and cosmetics is still attractive, because of the abundant sources and their chemical, physical and biological properties[2,5-7]. Chemical modification of them may be a way to improve their moisture absorption and retention abilities aim to replace the use of hyaluronic acid in the area of cosmetics. In addition, design and synthesis of hyaluronic acid derivatives which helps to improve its moisture absorption and retention abilities will reduce the hyaluronic acid consumption and also have much potential.

Therefore, we prepared carboxymethyl hyaluronic acid, carboxymethyl starch and carboxymethyl chitosan and assessed their moisture absorption and retention abilities, aiming at improving the moisture absorption and retention abilities of polysaccharides and finding a low cost and fine alternative of hyaluronic acid.

EXPERIMENTAL

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

Synthesis of carboxymethyl polysaccharide: Carboxymethyl chitosan and carboxymethyl starch were prepared according to Chen *et al.*[8] and Cao *et al.*[9], respectively. Carboxymethyl hyaluronic acid was prepared as follow: 1 g hyaluronic acid was dispersed into 10 mL of 2-propanol at room temperature and 10 mol/L NaOH (2.52 mL) was added with stirring. After 1 h, 1.20 g chloroacetic acid was added and the reaction was carried out with stirring at 40 ºC for 3 h. The product was filtered and washed by MeOH for three times. After vacuum dried for 12 h at room temperature, carboxy-

methyl hyaluronic acid was prepared (Synthetic pathway was shown as Fig. 1).

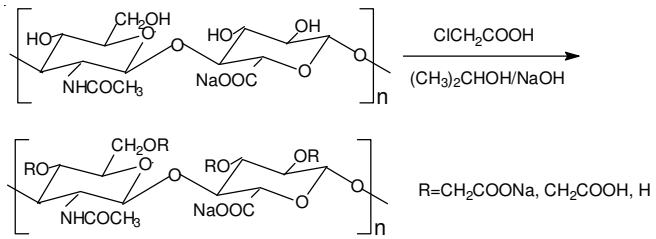

Fig. 1. Synthetic pathway for carboxymethyl hyaluronic acid

Characterization of carboxymethyl hyaluronic acid: 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 (500 MHz) NMR spectrometer in D_2O solvent.

Measurement of moisture absorption abilities: Each sample was rubbed in mortars into a powder and dried over in oven at 100 °C for 4 h. 0.5 g samples were putting into a saturated $(NH_4)_2SO_4$ desiccator (81 % relative humidity) and into a saturated Na_2CO_3 desiccator (43 % relative humidity) at room temperature, respectively. The moisture absorption ability (R_a) was evaluated by the percentage of weight increase of dry sample:

$$R_a\ (\%) = 100 \times (W_n - W_0)/W_0 \quad (1)$$

W_0 and W_n are the weights of the sample before and after putting it into the desiccators, respectively. Samples were consecutively tested at different time points.

Measurement of moisture retention abilities: The samples were rubbed in mortars into a powder and dried over in oven at 100 °C for 4 h. The wet samples were prepared by adding 10 % water to each sample and put into a saturated $(NH_4)_2SO_4$ desiccator (81 % relative humidity), a saturated Na2CO3 desiccator (43 % relative humidity) and a silica gel desiccator at room temperature, respectively. The moisture retention ability (RH) was evaluated by the percentage of residual water of wet sample:

$$RH\ (\%) = 100 \times (H_n/H_0) \quad (2)$$

H_0 and H_n are the weights of water in sample before and after being put into the desiccators at room temperature, respectively. Samples were consecutively tested at different time points.

RESULTS AND DISCUSSION

As shown in Fig. 2, the IR spectra of carboxymethyl hyaluronic acid showed new peak at 1741 cm^{-1}, which assigned to -COOH group. And the ^{1}H of -COOH group was also confirmed by the δ at 8.44 as shown in Figs. 3 and 4, there were four peaks at 172.24, 174.42, 177.94 and 180, which assigned to the -COOH (-COONa) groups and -CONHR groups. The above-mentioned results demonstrated that carboxymethyl hyaluronic acid was obtained.

The moisture absorption properties of carboxymethyl polysaccharides (carboxymethyl hyaluronic acid, carboxymethyl starch and carboxymethyl chitosan) were shown in Fig. 5. At both 43 % and 81 % relative humidity, R_a (%) of

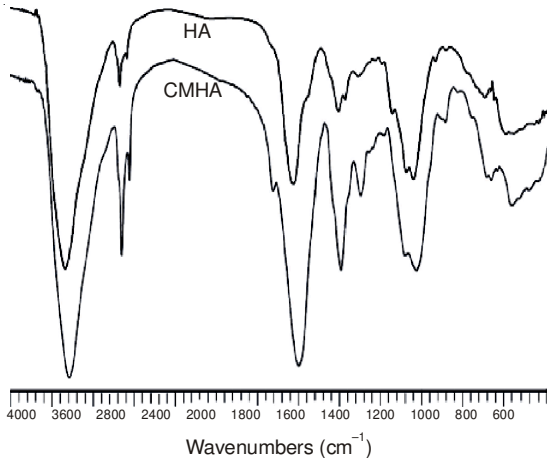

Fig. 2. IR spectra of hyaluronic acid and carboxymethyl hyaluronic acid

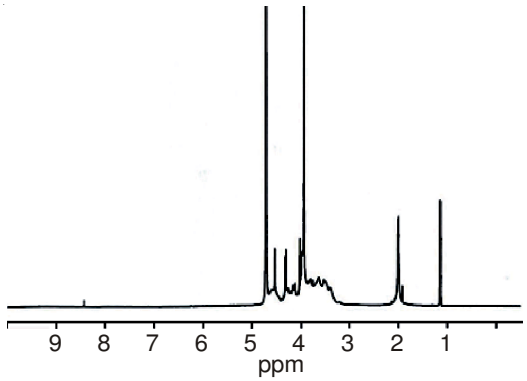

Fig. 3. ^{1}H NMR spectrum of carboxymethyl hyaluronic acid

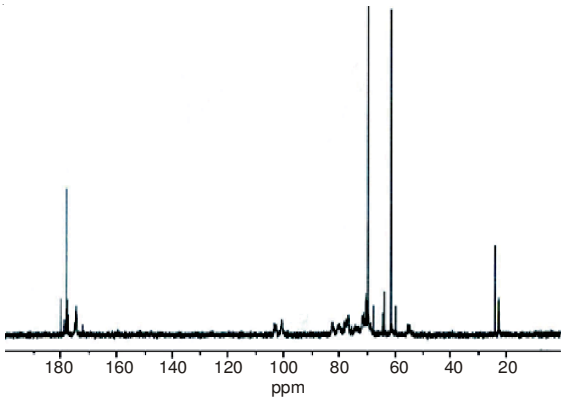

Fig. 4. ^{13}C NMR spectrum of carboxymethyl hyaluronic acid

of each sample increased as time prolonging and reached a steady state after 104 h. At 43 % relative humidity, the R_a values of carboxymethyl hyaluronic acid, hyaluronic acid, carboxymethyl starch, S, carboxymethyl chitosan and CTS were 67.34, 27.09, 46.54, 13.63, 57.57 and 13.16 % at the end of the experiment, respectively. And at 81 % relative humidity, the R_a values of carboxymethyl hyaluronic acid, hyaluronic acid, carboxymethyl starch, S, carboxymethyl chitosan and CTS were 82.24, 36.49, 69.72, 14.78, 55.21 and 15.54 % at the end of the experiment, respectively. This indicated each carboxymethyl polysaccharides had better moisture absorption abilities than the corresponding polysaccharide. Carboxymethyl hyaluronic acid, carboxymethyl chitosan and carboxymethyl starch are all have higher moisture absorption abilities than hyaluronic acid both at 43 % relative humidity and 81 % rela-

TABLE-1
MOISTURE RETENTION ABILITIES OF CARBOXYMETHYL POLYSACCHARIDES (%)

Sample No.	Relative humidity[a] 43 (%)		Relative humidity 81 (%)		Silica gel	
	24 h	48 h	24 h	48 h	24 h	48 h
Hyaluronic acid[b] (HA)	278.24	320.72	331.41	395.81	58.50	38.00
Carboxymethyl hyaluronic acid[c] (CMHA)	322.10	456.91	397.33	559.36	58.54	43.33
Chitosan[d] (CTS)	165.24	182.35	195.48	210.05	52.71	32.51
Carboxymethyl chitosan[e] (CMCS)	309.18	433.33	366.60	504.26	54.11	40.58
S[f]	156.80	167.96	193.14	200.98	54.85	33.96
Carboxymethyl starch[g] (CMS)	250	310.10	312.5	387.96	56.30	42.72

[a]Relative humidity; [b]Hyaluronic acid; [c]Carboxymethyl hyaluronic acid; [d]Chitosan; [e]Carboxymethyl chitosan; [f]Starch; [g]Carboxymethyl starch

tive humidity and among them carboxymethyl hyaluronic acid is the highest one.

The moisture retention properties of carboxymethyl polysaccharides were shown in Table-1. At both 43 and 81 % relative humidity, each RH value of carboxymethyl hyaluronic acid, S, carboxymethyl starch, carboxymethyl chitosan, CTS and hyaluronic acid was above 100 % all the time during the experiment, which indicated that they acted as moisture absorption ingredients under the two humidity conditions. The RH values of carboxymethyl hyaluronic acid and carboxymethyl chitosan were higher than those of hyaluronic acid at both 43 and 81 % relative humidity all the times and among them the RH value of carboxymethyl hyaluronic acid was the highest one, even could reach 559.36 % at 48 h. The RH value of each compounds decreased in varying degrees under a silica gel environment and was below 100 % all the time, it was different from in the condition of at 43 and 81 % relative humidity. At 48 h the RH value of carboxymethyl hyaluronic acid, carboxymethyl chitosan and CTS was 43.33, 40.58 and 42.72 % under a silica gel environment respectively, while the RH value of hyaluronic acid was just 38 % in the same condition. In Table-1, we can also find that the RH values of each carboxymethyl polysaccharides were much higher than the corresponding polysaccharide, which demonstrated that carboxymethylation improved the moisture retention abilities of hyaluronic acid, S and CTS greatly. These phenomena confirm that carboxymethylation was the effective way to improve the moisture absorption and retention abilities of carbohydrate and the carboxymethyl polysaccharide such as carboxymethyl hyaluronic acid, carboxymethyl chitosan and carboxymethyl starch had the great potential to be used as substitutes of hyaluronic acid in certain fields (for example, in cosmetics) as the moisture absorption and retention ingredients.

Conclusion

Each carboxymethyl polysaccharide (carboxymethyl hyaluronic acid, carboxymethyl chitosan and carboxymethyl starch) showed better moisture absorption and retention abilities than its corresponding polysaccharide at each combination of time and relative humidity. It indicated that carboxymethylation was a convenient and effective method to enhance both moisture absorption and retention abilities for hyaluronic acid, CTS and S. The carboxymethyl polysaccharide carboxymethyl hyaluronic acid, carboxymethyl-chitosan and carboxymethyl starch had the great potential to be used as substitutes of hyaluronic acid in certain fields (for example, in cosmetics) as the moisture absorption and retention ingredients.

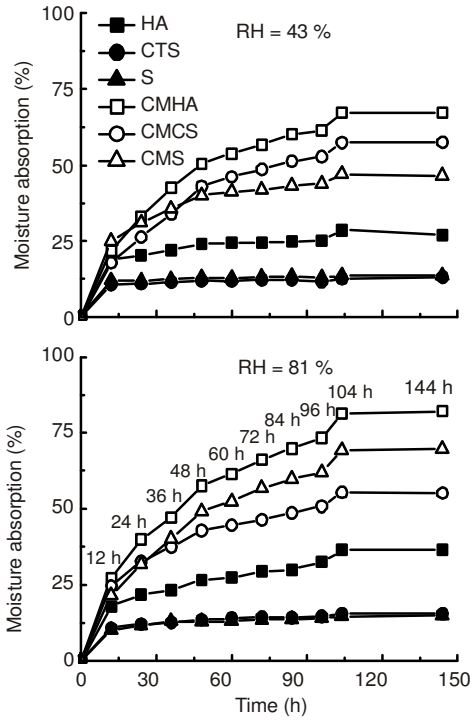

Fig. 5. Moisture absorption abilities of carboxymethyl polysaccharides

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REFERENCES

1. L.Y. Chen, Y.M. Du and X.Q. Zeng, *Carbohydr. Res*., **338**, 333 (2003).
2. L.Y. Chen, Y.M. Du, H. Wu and L. Xiao, *J. Appl. Polym. Sci*., **83**, 1233 (2002).
3. L.Y. Chen, Y.M. Du, L. Xiao and C.Q. Zuo, *Chinese J. Appl. Chem*., **18**, 5 (2001).
4. D. Bakoš, M. Soldan and I. Hernandez-Fuentes, *Biomaterials*, **20**, 191 (1999).
5. R.A.A. Muzzarelli, *Carbohydr. Polym*., **8**, 1 (1988).
6. G.M. Pavlov, E.V. Korneeva, S.E. Harding and G.A. Vichoreva, *Polymer*, **39**, 6951 (1998).
7. F. Shahidi, J.K.V. Arachchi and Y. Jeon, *J. Trends Food Sci. Technol*., **10**, 37 (1999).
8. L.Y. Chen, Y.M. Du and Y. Liu, *J. Wuhan Univ. (Nat. Sci. Ed.)*, **46**, 191 (2000).
9. L.Q. Cao, S.M. Xu, S. Feng, F. Yue and J.D. Wang, *CChina Surfact. Deterg. Cosmet.*, **34**, 97 (2004).