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Relationships between the molecular structure and moisture-absorption and moisture-retention abilities of carboxymethyl chitosan

II. Effect of degree of deacetylation and carboxymethylation

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Abstract

Carboxymethyl chitosans (CM-chitosan) of various degrees of deacetylation (DD 28–95%) and substitution (DS 0.15–1.21) were successfully prepared from *N*-acetylchitosans in NaOH of varying concentrations. Infrared spectroscopy (IR), elemental analysis, potentiometric titration, ^{13}C NMR, X-ray diffraction and gel-permeation chromatographic (GPC) techniques were used to characterize their molecular structures. The moisture-absorption (R_a) and -retention (R_h) abilities of CM-chitosan are closely related to the DD and DS values. Under conditions of high relative humidity, the maximum R_a and R_h were obtained at DD values of about 50%, and when the DD value deviated from 50%, R_a and R_h decreased. Under dry conditions, when the DD value was 50%, the R_h was the lowest. With the DS value increasing, R_a and R_h increased. However, further increase of the DS value above 1.0 reduced the increasing tendency of R_a and R_h, and even some decreases in R_a and R_h were observed. Intermolecular hydrogen bonds play a very important role in moisture-absorption and retention ability of CM-chitosan. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Carboxymethyl chitosan; Degree of deacetylation; Degree of substitution; Moisture absorption; Moisture retention

1. Introduction

In the last few years interest has increased considerably in the naturally occurring class of polymers known as the polysaccharides, owing to their abundance, friendliness to the environment, and potential to substitute for some petrochemicals.[1] Chitin, poly-β-(1 → 4)-*N*-acetyl-D-glucosamine, is the second most abundant natural polysaccharide and exists largely in the shells of crustacea and insects. Chitosan, poly-β-(1 → 4)-D-glucosamine, can be readily obtained from chitin by deacetylation with alkali. Despite much recent research into utilization of chitin and chitosan, poor solubility in neutral water and in common organic solvents have so far prevented either of them from enjoying widespread utilization.[2]

The conversion of chitosan into a water-soluble form can be achieved by means of the carboxymethylation reaction to obtain a derivative known as 'carboxymethyl chitosan (CM-chitosan)'. CM-chitosan is not only soluble in water, but has unique chemical, physical and biological properties such as high viscosity, large hydrodynamic volume, low toxicity, biocompatibility and film, gel-forming capabilities, all of which make it an attractive option in connection with its use in food products and cosmetics.[3,4]

Hyaluronic acid (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.[5] As CM-chitosan has a similar skeletal structure to HA, the moisture retention properties of CM-chitosan have received considerable attention. Matsumura et al. reported that CM-chitosan appeared to be more suitable than other chitosan derivatives for preparing HA-like substances.[6] Muzzarelli pointed out that a 0.25% CM-chitosan aqueous

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solution was comparable to a 20% aqueous solution of propylene glycal in terms of moisture-retention ability, and the viscosity was almost equal to that of HA.[3] However, published studies on the relationship between the moisture-retention ability of CM-chitosan and its molecular structural parameters are scarce. Such information is not only of academic interest, but is very important for applications. In our previous work,[7] moisture-absorption and retention of CM-chitosan with different substitution sites (6-*O*-CM-chitosan, 3,6-*O*-CM-chitosan, *N*-CM-chitosan) and molecular weights (2.6×10^3–2.48×10^5) were satisfactorily investigated. The results indicated that the 6-*O*-carboxymethyl group is a major active site for moisture-absorption and retention, and higher molecular weight helps to improve moisture-retention ability. 6-*O*-CM-chitosan with a molecular weight higher than 2.48×10^5 showed better moisture-retention ability than that of HA. In this paper, CM-chitosan of various degrees of deacetylation and substitution were successfully prepared. The relationship between degree of deacetylation and carboxymethylation of CM-chitosan and its moisture-absorption and retention ability were quantitatively investigated to seek a fundamental understanding of the moisture-retention properties of CM-chitosan.

2. Experimental

2.1. Materials

Chitosan was supplied by Yuhuan Ocean Biochemistry Co. Ltd., in Zhejiang province in China. The degree of deacetylation (DD) as determined by elemental analysis[8] was 0.93, and the molecular weight calculated from the GPC method was about 2.9×10^5. Standard pullulans for GPC were purchased from Showa Denko, Tokyo, Japan. All other chemicals were of reagent grade and used as received.

2.2. N-Acetylation of chitosan[9]

A solution of chitosan (20 g, DD 0.93) in aqueous 10% (w/w) HOAc (400 mL) was diluted with MeOH (1600 mL), and Ac_2O was added with stirring at room temperature. The reaction mixture was stored overnight at room temperature to give a rigid gel or clear solution. The gel was stirred with 0.5 M KOH in EtOH at room temperature overnight. The product was precipitated by addition of concentrated NH_4OH solution and filtered off. Each product was then washed neutral with 75% EtOH and Et_2O, and vacuum dried to give *N*-acetyl chitosan. Table 1 lists the N-acetylation conditions along with the degree of deacetylation (DD) for the chitosan samples obtained. The degree of deacetylation was shown to vary with the Ac_2O volume.

2.3. Carboxymethylation of chitosan

N-Acetylchitosan (10 g) suspended in NaOH (15 mL) was kept at −20 °C overnight. The frozen alkali chitosan was transferred to 2-propanol (100 mL), and $ClCH_2CO_2H$ was added in portions. After stirring at room temperature for 2 h, heat was applied to bring the reaction mixture to 60 °C for another 2 h. Next, HOAc was added to the mixture to adjust the pH to 7.0. The CM-chitosan salt was filtered and washed with EtOH. After dialyzing against deionized water for 3 days, the product was vacuum dried at room temperature. By

Table 1
N-Acetylchitosan of different degrees of deacetylation (DD)

Sample no.	[a] R_M	DD [c]	Elemental analysis						
			Found (%)			Calcd values (%)			DD [d]
			C	H	N	C	H	N	
[b] CH1	3.0:1	0.08	46.8	6.32	6.91	47.2	6.42	6.97	0.05
CH2	2.0:1	0.14	46.7	6.52	7.12	46.9	6.46	7.15	0.17
CH3	1.25:1	0.30	46.1	6.67	7.23	46.7	6.50	7.32	0.28
CH4	0.60:1	0.56	46.0	6.78	7.64	46.2	6.59	7.67	0.49
CH5	0.20:1	0.76	45.2	6.92	8.01	45.6	6.69	8.08	0.71
CH6	0.10:1	0.82	44.8	6.96	8.30	45.2	6.75	8.37	0.85
CH7	0.00:1	0.91	44.7	7.01	8.50	44.9	6.80	8.54	0.93

[a] R_M = mol ratio of Ac_2O to chitosan.
[b] CH = *N*-acetylchitosan.
[c] Determined by IR spectra.
[d] Determined by elemental analysis.

changing the alkali concentration, a series of CM-chitosans with various degrees of substitution (DS) were prepared.

2.4. Characterization

A Nicolet 170 SX FTIR spectrometer was used for the determination of the degree of deacetylation. Samples were insolubilized at pH 0.6 and prepared as KBr pellets (40 mg in 120 mg of KBr). The DD value was measured with the integrated intensity of the absorption at wavenumber of 1655 cm^{-1} (amide I band).[10] The elemental analysis was also applied to determine the DD value with an Elemental Analyzer-MOD 1106 (Italy).

The DS value of each sample was estimated from potentiometric titration.[11] The alkalimetric curves were recorded on a DELTA-320-S pH meter.

An HPLC instrument (Waters Co.) equipped with a TSK G5000 PWXL column (7.5 × 300 mm), P100 pump, RI-150 differential refractometer and Jiangshen Workstation was used for GPC analysis of weight-average molecular weight (M_w) of CM-chitosan. Each sample was dissolved in 0.1 mol/L aq NaCl, which was the eluent. The flow rate was 1.0 mL/min. The weight-average molecular weight (M_w) was calculated by the following equation:

$$\mathrm{Lg}\ (M_w) = -0.8540\ V_e + 10.0382 \qquad (1)$$

The ^{13}C NMR spectrum was recorded on a Mercury V_x300 spectrometer, and chemical shifts were determined by taking MeOH (δ 58.6) as the reference for ^{13}C NMR in D_2O at 323 K.

X-ray diffraction (XRD) of the samples was carried out a Dmax-Ray diffractometer. The X-ray diffraction patterns with CuKα radiation ($\lambda = 1.5404$ Å) at 40 KV and 30 mA were recorded in the range of $2\theta = 5–45°$.

2.5. Moisture absorption and retention test[6]

Prior to the moisture-absorption testing, the samples were dried over P_2O_5 in vacuo for 24 h. The water-absorption ability was evaluated by the percentage of weight increase of dry sample (R_a):

$$R_a\ (\%) = 100 \times (W_n - W_0)/W_0 \qquad (2)$$

Where W_0 and W_n are the weights of sample before and after putting it into a saturated $(NH_4)_2SO_4$ desiccator (81% relative humidity) and in a saturated K_2CO_3 desiccator (RH 43%) at 20 °C after 48 h of the test.

In the moisture-retention test, wet samples were prepared by adding 10% water to each sample. The moisture-retention ability was evaluated by the percentage of residual water of wet sample (R_h):

$$R_h\ (\%) = 100 \times (H_n/H_0) \qquad (3)$$

H_0 and H_n are the weights of water in sample before and after putting in the silica gel at 20 °C after 48 h of the test.

3. Results and discussion

3.1. Carboxymethylation of chitosan

A series of carboxymethylation reactions were conducted in this paper to determine the effect of the DD value of chitosan and alkali concentration on the carboxymethylation yield. As shown in Table 2, the degree of substitution of carboxymethyl groups had no relation with the DD value of chitosan. While alkali concentration can be thought as one of the most important factors to regulate carboxymethylation yield of chitosan as shown in Table 3. Work by Tokura and co-workers demonstrated that the DS value of CM-chitosan increased with NaOH concentration changing from 20 to 40%.[12] And in the present work, when NaOH concentration increased from 40 to 50%, the DS value increased from 0.15 to 0.63 at a DD value of 75%, and from 0.43 to 0.68 at a DD value of 90%. Whereas, further increase of NaOH concentration reduced the carboxymethylation reaction, and the DS value dropped to 0.57 and 0.46, respectively. A 50% NaOH solution seems to provide the optimum alkali concentration in the carboxymethylation process. At lower NaOH concentration, the rigid crystalline structure of chitosan was difficult to disrupt to ensure penetration of the $ClCH_2CO_2H$ into the interlocking polymer chains.[13] While a high alkali concentration above 60% promoted side reaction between NaOH and $ClCH_2CO_2H$,[14] and the $ClCH_2CO_2H$ concentration decreased accordingly. However, it was practically impossible to prepare CM-chitosan with a DS value higher than 1.0 by changing the NaOH concentration. In order to obtain highly substituted derivatives, further carboxymethylation of CM-chitosan (CMC-4 and CMC-7) were successfully performed with an NaOH concentration of 50%, and the DS values rose to 1.08 and 1.28, respectively.

When the NaOH concentration was 40 or 60%, a small part of the resulting products were not soluble, but they did swell in water. As shown in Table 3, CM-chitosan was water soluble at DS values above 0.45 when the DD was either 75 or 93%. Therefore, the critical DS value at which CM-chitosan becomes soluble in water may exist in the range of 0.4 to 0.45.

Because of excessive alkali in the reaction system, deacetylation couldn't be prevented. As shown in Tables 2 and 3, the DD values of all the *N*-acetylchitosan samples increased after the carboxymethylation reaction to different extents. Deacetylation proceeded to about 20–30% when the DD value of *N*-acetylchitosan

Table 2
CM-chitosan of different degrees of deacetylation (DD)

Sample no.	DD (CH [a])	DS (CMC [b])	DD [c] (CMC)	M_w ($\times 10^5$) of CMC				Elemental analysis						
				$M_{w,ag}$	$M_{w,s}$	N_{ap}	R_w/%	Found (%)			Calcd values (%)			DD [d]
								C	H	N	C	H	N	
CMC-1	0.08	0.60	0.28	7.48	0.38	19.7	72.6	45.2	6.14	5.99	46.0	6.02	6.10	0.20
CMC-2	0.14	0.67	0.31	8.24	0.36	22.9	81.82	45.0	6.10	5.95	45.8	5.98	6.06	0.26
CMC-3	0.30	0.65	0.53	13.2	0.37	35.7	84.0	44.8	6.14	6.27	45.4	6.05	6.35	0.48
CMC-4	0.56	0.63	0.74	11.92	0.41	29.1	66.1	44.5	6.21	6.58	44.9	6.11	6.64	0.68
CMC-5	0.76	0.67	0.87	4.8	0.36	13.3	35.7	39.9	6.78	6.09	44.5	6.13	6.79	0.85
CMC-6	0.82	0.66	0.91	1.8	0.39	4.6	24.5	44.0	6.23	6.86	44.3	6.15	6.91	0.92
CMC-7	0.93	0.68	0.95	1.59	0.39	4.1	27.6	39.9	6.87	6.24	44.2	6.15	6.91	0.95

[a] CH = *N*-acetylchitosan.

[b] CMC = CM-chitosan.

[c] Determined by IR spectra.

[d] Determined by elemental analysis.

Table 3
CM-chitosan of different degrees of substitution (DS)

Sample no.	DD [c] (CH [a])	NaOH Conc	DS (CMC [b])	DD [c] (CMC)	M_w ($\times 10^5$) of CMC				Elemental analysis						
					$M_{w,ag}$	$M_{w,s}$	N_{ap}	R_w/%	Found (%)			Calcd values (%)			DD [d]
									C	H	N	C	H	N	
[e] CMC-4-1	0.56	40%	0.15	0.52	/	/	/	/	46.0	6.31	7.20	46.2	6.27	7.23	0.58
[e] CMC-4-2		60%	0.29	0.50	/	/	/	/	45.4	6.38	7.02	45.7	6.33	7.07	0.52
CMC-4-3		40%	0.46	0.69	3.86	0.35	11.3	50.2	44.6	6.33	6.80	45.2	6.23	6.89	0.63
CMC-4-4		60%	0.57	0.74	4.63	0.38	12.2	54.6	44.6	6.23	6.72	44.9	6.16	6.77	0.70
CMC-4-5		50%	0.63	0.73	11.92	0.41	29.1	66.1	44.5	6.21	6.61	44.9	6.12	6.67	0.70
CMC-4-6		50% (twice)	1.08	0.78	14.87	0.38	39.1	89.8	39.6	6.54	5.50	44.1	5.86	6.12	0.88
[e] CMC-7-1	0.93	40%	0.43	0.93	/	/	/	/	44.2	6.40	7.36	44.5	6.35	7.41	0.93
CMC-7-2		40%	0.45	0.94	1.23	0.37	3.3	12.5	44.2	6.39	7.34	44.4	6.36	7.37	0.93
CMC-7-3		60%	0.46	0.95	1.37	0.39	3.5	13.9	44.0	6.40	7.31	44.4	6.33	7.38	0.95
CMC-7-4		50%	0.68	0.95	1.59	0.39	4.1	27.6	39.9	6.87	6.24	44.2	6.15	6.91	0.94
CMC-7-5		50% (twice)	1.21	0.95	12.55	0.38	33.0	90.1	39.7	6.41	5.44	43.8	5.80	6.00	0.95

[a] CH = *N*-acetylchitosan.
[b] CMC = CM-chitosan.
[c] Determined by IR spectra.
[d] Determined by elemental analysis.
[e] Insoluble part of CMC.

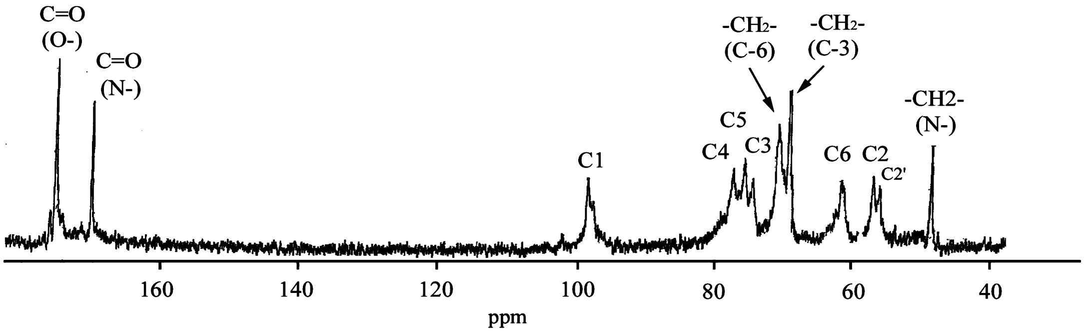

Fig. 1. ^{13}C NMR spectrum of CM-chitosan (CMC-7).

was lower than 0.56, but to about 10% when original DD value was 60 to 80%. Whereas further deacetylation became difficult when the DD of *N*-acetylchitosan was above 0.9. Increasing alkali concentration and further carboxymethylation promoted deacetylation.

IR spectra of CM-chitosans with various DD and DS values showed characteristic absorptions due to the –COOH group at 1737 cm^{-1}, confirming a successful carboxymethylation.[15,16] The strong absorptions at 1654, 1560 and 1314 cm^{-1} in the spectrum CMC-1 are assigned to the amide I, II and III vibration bends,[17] indicating existence of a large number of acetyl groups. With the DD value increasing, the three absorption bends decreased dramatically, and the amide II and III stretching bends disappeared completely at DD value of 0.95, whereas the absorption assigned to $-NH_3^+$ at 1519 cm^{-1} appeared.[14] With the DS value increasing, the –COOH stretching bends together with the $-CH_2$ and C–O–C stretching vibration at 2930 and 1242 cm^{-1} increased accordingly. When the DS value was higher than 0.68, the C–O stretching bend at 1030 cm^{-1} corresponding to the primary hydroxyl group disappeared, indicating that the carboxymethyl groups are mainly substituted at the OH-6 position.[7] Further evidence supporting a successful carboxymethylation of chitosan is provided by the ^{13}C NMR spectrum of a sample of CMC-7 in Fig. 1. The signals for –*COOH substituted on –OH and –NH are obvious at 173.5 and 170.0 ppm. The three chemical shifts at 70.9, 69.3 and 48.7 ppm are assigned to $-^*CH_2COOH$ groups substituted on OH-6, OH-3 and NH-2, indicating that there are three possible sites for the carboxymethylation of chitosan and that the product prepared was *N*,*O*-CM-chitosan.[18] On account of the signal intensity, it is also suggested that the OH-6 is the major site for formation of CM-chitosan. The X-ray diffraction pattern of insoluble CM-chitosan (CMC-4-1) exhibited two characteristic peaks at $2\theta = 10.4$ and 19.8°, which coincided with the pattern of the L-2 polymorph of shrimp chitosan reported by Satio and Kim.[19,20] When the DS value was above 0.46, the peaks at $2\theta = 10.4°$ decreased gradually and disappeared when the DS value was above 0.63. When the DS value was higher than 1.08, CM-chitosan became amorphous.[21] It indicates that the carboxymethylation reaction first took place preferentially in the amorphous region and then proceeded very moderately from the edge to the inside of the crystalline region.[22] Thus the chitosan in the amphorous region was carboxymethylated first to give a water-soluble fraction, and the DS value was high. While in the crystalline region, the DS value was rather low, and the product was insoluble in water. With further carboxymethylation the crystalline structure was destroyed, and the crystallinity disappeared.

3.2. Molecular weight

The GPC chromatograms of CM-chitosan contained two peaks, indicating the occurrence of aggregation. The peaks at the low-elution volume correspond to the aggregates with high weigh-average molecular weight ($M_{w,ag}$), and the others correspond to single chains with low weight-average molecular weight ($M_{w,s}$). The apparent aggregation number (N_{ap}) was estimated by the formula $N_{ap} = M_{w,ag}/M_{w,s}$. As shown in Table 2, the M_w of single chains of all CM-chitosan samples were $3-4 \times 10^4$ regardless of the DD and DS values. But for aggregates, the aggregation number increased until a DD value of 53%, and reached maximum at N_{ap} of 35.7 and then deceased rapidly to N_{ap} of 4.1 at DD value of 95%. At the same time, as demonstrated in Table 3, with the DS value increasing, the aggregation number increased accordingly. Especially when the DS increased from 0.68 to 1.21, a sharp increase in N_{ap} from 4.1 to 33.0 could be observed at the DD value of 90%. The same order can be observed for the weight ratio of aggregates to single chains (R_w). From our previous work,[23] aggregation of CM-chitoan is mainly attributed to interchain interactions, and intermolecular hydrogen bonds play a very important role. It seems that when the DD value of CM-chitosan is about 50%, the intermolecular hydrogen bonds in CM-chitosan chains are the strongest, and the higher the degree of carboxymethylation, the stronger the intermolecular interaction force. Yui and Imada[24] and Chanzy and co-workers[25] reported that the chitosan chain is an extended 2-fold helix conformation. Two adjacent polymer chains run along the *a*-axis, and are linked to each other by N-2···O-6 hydrogen bonds, which makes a sheet structure parallel to the *ac*-plane. When carboxymethyl groups are substituted mainly on the OH-6 of chitosan, a stronger hydrogen bonding (O=C–O···NH) could form between molecular chains due to conjugative effect of carbonyl groups,[26] which results in a strong tendency for aggregation. While when the DD value was about 50%, an alternative distribution of acetylated and nonacetylated glucosamine units makes the chain stiffer and more extended as reported by Karim and co-workers.[27] Therefore the nitrogen, which acts as a proton donor, is exposed to O=C–*O– of an adjacent molecular to form aggregates easily. It is assumed that when the DD value is about 50%, or when the DS value is high enough, the CM-chitosan chains are likely to be held together by intermolecular hydrogen bonds linking the nitrogen atoms to COOH of an adjacent parallel along the *a*-axis to form a spacious network.[25]

3.3. Moisture-absorption and retention properties

The moisture-absorption and retention ability of CM-chitosan obviously depends on the DD and DS value. As shown in Table 4, when RH was 81%, the moisture-absorption ability increased until the DD value of 53%, reached the maximum at 60.8% and then decreased rapidly to 45.0% at the DD value of 95%. When RH was 43%, the maximum R_a (40.1%) was also obtained at a DD value of 53%, when the DD value deviated from 53%, the R_a value decreased. However, the order of moisture-retention ability of CM-chitosan in silica gel was the opposite: the lowest R_h was obtained at a DD value of 53%, and when the DD deviated from 53%, R_h increased. It should not be neglected to note that these orders are closely related to those of the aggregation number of molecular chains and weigh ratio of aggregates to single chains of CM-chitosan with different DD values. This strongly suggests that the driving force for aggregates, i.e., the intermolecular hydrogen bonds of molecular chains, which affects the interaction between water and polymer chains directly, may be a very important factor to regulate moisture-absorption and retention ability of CM-chitosan. Under high relative humidity conditions (RH 81% and 43%), water molecules are accessible to the surface of the sugar residues and readily develop hydrogen-bond interactions with the CM-chitosan molecular chains. As a result, they intervene between chains or chain sheets in the network.[28] When the DD value was about 50%, the aggregation number and the weight ratio of aggregates to single chains were the largest, which means that most molecular chains are bonded together by intermolecular hydrogen bonds to form a spacious network structure; thus, water molecules are kept inside more easily, whereas in the case of dry conditions (in silica gel), moisture in the polymer network will diffuse to the environment. When the DD value was 53%, most of the –COOH and $–NH_2$ groups were occupied by interchain interactions between CM-chitosan molecular chains, which decreased the hydrogen bonds between such hydrophilic groups and water. Thus moisture is released more quickly. When the RH was 43%, all samples showed better R_a and R_h than HA. When RH was 81%, the R_a of CM-chitossan with DD value of 53% was better than that of HA. While in silica gel, CM-chitosan with a DD value of 0.95 demonstrated better moisture-retention ability.

Table 4
Moisture-absorption and -retention abilities of CM-chitosan with different DD values

Sample no.	DD [d] (CMC [a])	R_a/% (dry sample)		R_h/% (wet sample)
		RH [b]81%	RH43%	silica gel
CMC-1	0.28	46.3	31.3	59.5
CMC-2	0.31	55.5	37.5	59.0
CMC-3	0.53	60.8	40.0	55.9
CMC-4	0.74	52.9	36.9	64.8
CMC-5	0.87	49.4	33.4	65.8
CMC-6	0.91	47.6	33.0	70.5
CMC-7	0.95	45.0	32.7	75.2
HA [c]	/	56.2	24.8	72.8

[a] CMC = CM-chitosan.
[b] RH = relative humidity.
[c] HA = hyaluronic acid.
[d] Determined by IR spectra.

As shown in Table 5, all CM-chitosan samples showed better R_a and R_h than chitosan, indicating introduction of the carboxymethyl group is a convenient and effective method to give chitosan its moisture-retention ability. With an increase in DS, in moisture-absorption and retention ability of CM-chitosan increased accordingly. Especially with the DS value changing from 0.4 to 0.6, R_a and R_h values increased rapidly. However, further increasing of the DS value from 0.6 to 1.2, the increasing rate of the R_a and R_h value slowed down, and even some decrease in R_a and R_h values were observed when the DS value was above 1.0. This can be explained that with increasing carboxyl groups, on one hand, hydrogen bonds between water and COOH groups increased, while on the other hand, the intermolecular hydrogen bonds between CM-chitosan molecular chains increased at the

Table 5
Moisture-absorption and -retention ability of CM-chitosan with different DS values

Sample no.	DD	DS (CMC [a])	R_a/% (dry sample)		R_h/% (wet sample)
			RH [c]81%	RH43%	Silica gel
CMC-4-1	About 70%	0.15	17.7	19.6	39.6
CMC-4-2		0.29	18.5	20.0	42.5
CMC-4-3		0.46	25.0	25.4	45.8
CMC-4-4		0.57	38.5	29.6	56.2
CMC-4-5		0.63	53.8	38.4	57.5
CMC-4-6		1.08	50.5	35.0	70.0
CMC-7-1	About 90%	0.43	29.6	23.6	46.7
CMC-7-2		0.45	32.1	25.3	50.0
CMC-7-3		0.46	39.3	27.1	53.3
CMC-7-4		0.68	46.1	33.6	63.2
CMC-7-5		1.21	53.2	37.2	59.2
[b] CH-4	0.56	/	25.8	20.0	40.8
CH-7	0.93	/	15.0	11.8	31.0

[a] CMC = CM-chotisan.
[b] CH = chitosan.
[c] RH = relative humidity.

same time, which helps to bond large amounts of water and retain them in a spacious network. While, when the DS value was higher than 1.0, the hydrogen bonds between the molecular chains of CM-chtosan increased sharply, which was proved by a rapid increase of aggregation number and weight ratio of aggregates to single chains as known in Table 3. Thus the hydrogen bonds between –COOH and water were weakened and resulted in a slowdown of the increasing rate of R_a and Rh, and even some decreasing R_a and R_h. CM-chitosan with the DS value from 0.6 to 1.0 showed equal or better R_a and R_h than that of HA, and has potential to use as moisture-retention ingredient, e.g., in cosmetics.

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