Preparation and Moisture Absorption-Retention Ability of Chitosan Pyruvic Acid Derivatives

YUAN Wen-hui[1,2], YIN Xue-qiong[1,2], TU Wei-ping[1], LIN Qiang[1], CAO Yang[1]
(1. Key Laboratory of the National Ministry of Education for Tropical Biological Resources, Hainan 570228, China;
2. The Guangdong Provincial Laboratory of Green Chemical Technology, Guangzhou 510640, China)

Abstract: N-(1-carboxyethyl) chitosan (CET) was successfully prepared from chitosan and pyruvic acid (PA) under reducing conditions via aldimine formation. The chemical structure of the derivative obtained was determined by ^{1}H NMR. It was found ratio between pyruvic acid and glucose residue (RPT), reaction time, pH and molecular weight (M_w) of chitosan had great influence on the degree of substitution (DS). CET had similar moisture absorption-retention abilities with HA, and much better abilities than the original chitosan.

Key words: chitosan; carboxyethylation; moisture absorption; moisture retention
CLC number: O539 Document code: A Article ID: 0529-6579 (2007) S1-0329-02

Chitosan has been widely investigated and used in cosmetics, agriculture, food, medicine, biomaterial and other fields because of its good biocompatibility, biodegradability and special physicochemical properties. However, applications of chitosan are limited by its insolubility in water with pH higher than 6. Carboxyalkylation is one of the most popular ways to enhance chitosan's solubility in water[1].

1 Experimental

1 g chitosan was suspended in 80 mL stirred deioned water for 0.5 h. A sufficient quantity of PA was dropped into above suspension of chitosan. After chitosan reacted with PA for 8 h at pH 4.5, $NaBH_4$ solution was added to stirred chitosan solution slowly. Keep for 2 h, the pH value was adjusted to 6.5 by HCl. Then chitosan derivative was precipitated by 95% alcohol, then filtered, dialyzed, freezing dried to obtain white solid chitosan derivative. Chitosan with different Mw was modified with the same method. NMR[2], DS[3], Moisture absorption-retention abilities[4] were tested.

2 Results and Discussion

2.1 NMR spectra

^{1}H NMR spectrum of CET expressed the signal of CH_3 at 1.35 ~ 1.40 ppm, CH(CH_3)COOH of GlcNHR at 1.90 ppm, CH(CH_3)COOH of GlcNH$_2$ at 2.89 ppm, H-2 of GlcNHR at 3.14 ppm, H-3, 4, 5, 6 of GlcNHAc and NCH_2 3.40 ~ 4.00 ppm, H-1 of GlcNHAc, GlcNH$_2$, GlcNHR at 4.30, 4.64 and 4.83 respectively. The assignments were analogy with the reports for CET[2].

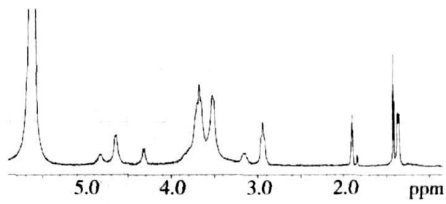

Fig. 1 ^{1}H NMR spectrum of CET

2.2 Effect of reaction conditions on DS

The degree of carboxyethylation vs the reaction time was shown in Tab. 1. It was shown that DS increased with the increase of reaction time and reached its maxium at 8 h.

Tab. 1 Effect of reaction time on DS

Time/h	1	4	8	12	20
DS/%	26.3	33.6	36.5	34.9	34.2

The effect of RPT on DS was shown in Tab. 2. With the increase of PA amount, the DS increased obviously before the ratio reached 6∶1. However, after

①收稿日期: 2007-01-10
基金项目: 广东省绿色化学产品技术重点实验室开放基金资助项目 (GC200606); 海南省教育厅资助项目 (Hj200557)
作者简介: 袁文 (1981年生), 男, 硕士研究生; 通讯联系人: 尹学琼; E-mail: yinxq7584@yahoo.com.cn

6∶1, the the DS changed a little.

Tab. 3 expressed that pH had obvious influence on the DS. DS increased with the increase of pH and at pH 4.5 the sample with highest DS was obtained.

Tab. 2 Effect of RPT on DS

RPT	1	2	4	6	8	10
DS/%	26.5	30.7	36.5	40.5	41.5	42.2

Tab. 3 Effect of pH on DS

pH	3.5	4	4.5	5
DS/%	25.6	32.3	40.5	34.6

Five kinds of chitosan with different M_w: 6 000 (a), 50 000 (b), 200 000 (c), 570 000 (d), and 970 000 (e) were modified to get CET. The effect of M_w on DS was shown in Tab. 4. With the increase of M_w, the DS decreased. Chitosan with lower Mw was easier to be carboxyethylated.

Tab. 4 Effect of CT M_w of DS

M_w	a	b	c	d	e
DS/%	54.2	52.7	48.4	45.5	40.5

2.3 Moisture absorption-retention Activity

Tab. 5 Moisture absorption activities (Ra) of (RH 81%)

Time/h	6	12	24	36	72
CTS	8.9	13.0	17.0	17.4	17.5
PCTS	11.9	17.4	25.6	30.3	37.1
HA	14.1	21.6	30.9	35.2	40.7

Moisture absorption and retention activity of chitosan, CET (DS 45%) and HA were determined at RH 81%, 43% respectively (as shown in Tab. 5 and 6). Tab. 5 shew CET had similar Ra with HA and much better moisture absorption ability than chitosan.

Tab. 6 shew CET had better moisture acitivity than chitosan, but a little lower than HA, and at 24 h of CET, chitosan, and HA were 135.2%, 101.3% and 150.5%, respectively. That meaned residual moisture in the samples did not decrease but increased, and all the samples had good moisture retention activity.

Tab. 6 Moisture retention activity (Rh) of samples (in saturated K_2CO_3, RH 43%, 20℃)

Time/h	6	12	24	36	72
CTS	100.4	101.1	101.3	101.4	101.4
PCTS	117.6	128.6	135.2	140.1	141.3
HA	127.5	139.8	150.5	156.3	163.2

3 Conclusion

CET was successfully achieved from chitosan and pyruvic acid via aldimine formation. CET expressed much better moisture absorption-retention activities, and had similar moisture absorption-retention ability with HA. Chitosan has abundant natural resources. Therefore, CET has the potential to substitute HA in many fields.

References:

[1] SASHIWA H, SHIGEMASA Y, ROY R. Novel N-Alkylation of chitosan via michael type reaction [J]. Chem Lett, 2000, 29 (8): 862—863.

[2] SKORIK Y A, GOMES C A, VASCONCELOS M T, et al. N-(2-Carboxylethyl) chitosans: regioselective synthesis, characterisation and protolytic equilibria [J]. Carbohydr Res, 2003, 338 (3): 271—276.

[3] MUZZARELLI R A A, TANFANI F, EMANUELLI M, et al. N-carboxymethylidene chitosans and N-carboxymethylchitosans: Novel chelating polyampholytes obtained from chitosan glyoxylate [J]. Carbohydr Res, 1982, 107 (1): 199—214.

[4] CHEN L Y, DU Y M, ZENG X Q. Relationships between the molecular structure and moisture-absorption and moisture-retention abilities of carboxymethyl chitosan II. Effect of degree of deacetylation and carboxymethylation [J]. Carbohydr Res, 2003, 338 (4): 333—400.

壳聚糖丙酮酸衍生物的合成及吸湿保湿性能

袁 文[1,2], 尹学琼[1,2], 涂伟萍[2], 林 强[1], 曹 阳[1]

(1. 海南大学热带生物资源教育部重点实验室, 海南 海口 570228;
2. 华南理工大学广东省绿色化学产品技术重点实验室, 广东 广州 510640)

摘 要: 以丙酮酸改性壳聚糖制备了 N-(1羧乙基)壳聚糖 (CET), 用 ^{1}H NMR 电位滴定等方式对产物进行了表征。研究发现, 丙酮酸与糖元比例、反应时间、 pH和壳聚糖相对分子质量 (M_w) 对产物取代度 (DS) 影响较大, 最佳丙酮酸与糖元比例、反应时间、 pH分别为 8∶1, 8 h, 4.5. 随壳聚糖 M_w降低, DS增加。 CET比壳聚糖的吸湿保湿明显增加, 并呈现与 HA类似的吸湿保湿性能。

关键词: 壳聚糖; 羧乙基化; 吸湿; 保湿

中图分类号: Q539