J Wood Sci (2015) 61:199–203
DOI 10.1007/s10086-015-1460-4

NOTE

# Solubilization of graminaceus plants in water by carboxymethylation

**Hao Ren · Shuang Qian · Shigetoshi Omori**

Received: 6 October 2014 / Accepted: 12 December 2014 / Published online: 21 January 2015


**Abstract** Graminaceus plants and their main components (lignin and cellulose) were carboxy methylated and compared with woody ones. The solubilities of carboxymethylated biomass, alkaline lignin, klason lignin, holocellulose, and α-cellulose were measured and the crystallinities of α-celluloses were also measured by X-ray diffraction. The main resistance factor to solubilization in water is thought to be the density in crystalline region of cellulose which was formed during long growth cycle in perennial plants.

**Keywords** Solubilization · Graminaceus plants · Carboxymethylation

## Introduction

The most popular carboxy methylation (CM) product could be carboxymethyl cellulose (CMC), which is applied to many different fields, such as medical, food, cosmetics, and other industrial application [1–5]. It is usually prepared from pure cotton cellulose or highly purified wood pulps by the method of Green [6]. When it is necessary to produce a large amount of CMC, people [7] tried to use something inexpensive to replace the high price raw materials. There are some studies which are about carboxymethylated wood meals, mechanical pulps, the soluble, and insoluble parts were fractionated and characterized [8, 9]. The authors also tried to use many kinds of sources besides wood meals, but most of the products were insoluble in water. Until now, nobody succeeded in dissolving woody materials in water by carboxymethylation. However, this fact is unsatisfactory; the point in this study is to do extension of raw materials from woody to non-woody materials, especially to focus on annual graminaceus plants, which might have less condensation and crystallization. It is expected that their CM products could be dissolved in water.

H. Ren (✉) · S. Qian
Department of Light Industry and Science, NanJing Forestry University, Nanjing 210037, Jiangsu, China
e-mail: renhaomie@hotmail.co.jp

S. Omori
College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13210, USA

## Experiment

### Preparation of raw materials

Air dried graminaceus plants [wheat straw(*Triticum Sativum*), rice straw(*Oryza Sativa*), reed (*Phragmites australis*), commercial horse hay (It is a mixture of herbaceous plants, sold by Valley View Stables, Syracuse, NY, US), corn(*Zea mays*).] were chopped around 2–3 cm length and ground to 30 meshes using Willey Mill and used as graminaceus plant raw materials. Air dried sugar maple (*Acer saccharum*) and western hemlock (*Tsuga heterophylla*) chips were ground to 30 meshes using Willey Mill and used as woody plant raw materials.

### Preparation of cellulose and lignin samples by soda pulping

The chopped plants were cooked with 2 % sodium hydroxide (plants to liquid ratio 1:7 w/v) at 121 °C, for 2 h using electric steam autoclave. The amount of plants used in each run was 300 g on an oven-dried basis. After cooling the cooked slurry, the pulp was filtrated and washed with

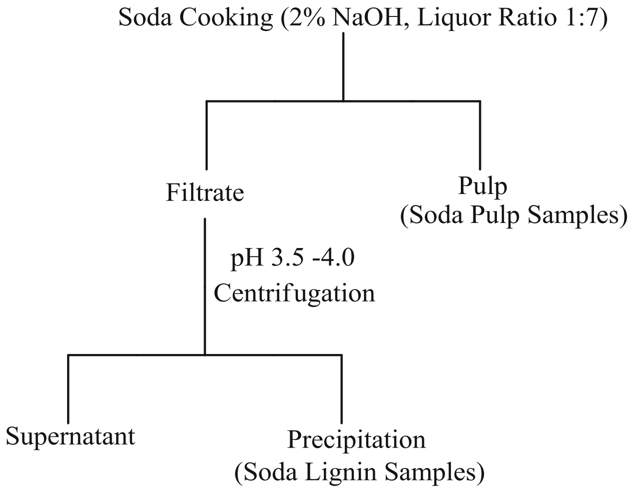


**Fig. 1** Preparation of plant soda pulps and lignins

hot water three times. The pulp was used as plants pulp sample. The filtrate and washing liquor were adjusted pH 3.5–4 and allowed to stand overnight (about 15 h). Then the mixture was centrifuged to remove the precipitates (PPT). The PPT was washed with water and used for plants lignin sample (Fig. 1).

### Kraft lignin from wood materials

The commercial hardwood and softwood Kraft lignins (Kp lignin) were purchased from LuoHe East China Lignin Industry, which were used as carboxymethylation raw materials.

### Preparation of holocellulose

The holocelluloses of graminaceus plants and wood were prepared by applying Shibazaki et al's method [10]:

A 2-g sample was treated with 200 mL of 7 % sodium chlorite aqueous solution with a couple drops of acetic acid at 70–80 °C for 1 h and then filtrated and washed with water.

### Preparation of α-celluloses

α-Celluloses were prepared followed by the method of Japan Wood Research Society [11].

A 1 g of oven dried (oven temperature was setting on 105 °C) holocellulose prepared above was put in a 200-mL beaker then 25 mL of 17.5 % sodium hydroxide solution was added at 20 °C and left standing for 4 min. The wetted sample was dispersed for 5 min. The container was covered with petridish and left standing. After 30 min of sodium hydroxide addition, 25 mL of water were added and stirred for 1 min then left standing for another 5 min. Then reaction mixture was filtrated with 1G3 glass filter, and washed with water within 5 min.

### Carboxy methylation of samples

The CM method used in this study was a little modified method of Green [1]. A 1 g of oven-dried sample was suspended in 50 mL of 2-Propanol under stirring and 13 mL of 30 % sodium hydroxide was added to it, taking 30 min, and continued stirring for additional 1 h at room temperature. Then a 3.5 g of Monochloroacetic acid (MCA) sodium salt was added within 30 min. After the addition of MCA it was heated up to 55 °C for 3.5 h under stirring. After cooled down to room temperature it was washed with 150 (30 × 5) mL of 80 % methanol followed by pure methanol.

### Measurement of crystallinity by X-ray diffraction

The diffraction patterns were obtained from radiation generated by the copper target of Rigaku Ultima IV (Rigaku Corporation, Japan) set at 40 kV and 30 mA with the detector placed on a goniometer. Data were acquired in $2\theta$ scale from 10$^{o}$ to 80$^{o}$, scanning rate is 5 $^{o}$/min. The degree of crystallinity was calculated based on the method in Segal et al.'s paper [12].

## Result and discussion

### Carboxy methylated graminaceus plant

The appearance of wood and graminaceus plant looks very different. Wood is a big, hard, and perennial plant, while a graminaceus plant is small, soft, and annual. When we compared these two objects, the graminaceus plant looks to

**Table 1** The solubility of plant CM

| Sample Name | Solubility (+, −, ±)[a] | Color |
|---|---|---|
| Wheat straw CM | + | Colored |
| Rice straw CM | + | Colored |
| Reed CM | + | Colored |
| Commercial horse hay CM | + | Colored |
| Corn stem CM | + | Colored |
| Bleached[b] wheat CM | + | Colorless |
| Bleached[b] rice straw CM | + | Colorless |
| Sugar maple meal CM | − | Colored |
| Western hemlock meal CM | − | Colored |

*CM* carboxy methylation, *bleached* Holocellulose treatment in experiment section

[a] + soluble, − insoluble, ± not sure

be solubilized in water by carboxymethylation compared with woody materials. The graminaceus plants were treated followed by the methods cited in the experimental sections and their solubility was tested (Table 1). As expected, the CM graminaceus plant was dissolved in water and showed brown color, while CM wood was partially dissolved and colored. This phenomenon indicated that they are obviously different from each other. Lignin is not the main reason for a non-dissolvable situation.

Carboxy methylated graminaceus plant holocellulose

A brown color CM plant (Table 1) could not be accepted in practical use but it is removable in solvent precipitation technique depending on the utilization purposes. The carboxy methylation treatment to holocellulose (bleached plant) was attempted to do in this study, which were prepared according to the methods in experimental section. As shown in Table 1, CM holocelluloses (bleached plants) were completely water soluble products; they showed very clear and colorless status in water. Therefore, brown color in the product materials of CM plant themselves could be derived from lignin.

Carboxy methylated soda pulps

The soda pulps from graminaceus plant prepared according to the method in soda pulping experiment section were carboxymethylated and their solubility in water was tested (Table 2). As shown in Table 2, the nice colorless CM products were resulted from non-bleached plant pulps. During the CM process the colored impurities were removed from product into solvents. It showed that the plant soda pulps are possible to use as a raw material without bleaching for carboxymethylation. This will benefit for CM products makers.

Carboxy methylated alkaline lignin

The soda lignins from soda cooking of graminaceus plant (Fig. 1) and kraft lignins from wood and commercial lignin were carboxymethylated according to CM method in experiment section then solubility tests were done. The results showed that all of the experimental samples were dissolved in water and showed brown color (Table 3). This result supported that the brown color in CM graminaceus plant products came from lignin.

Carboxy methylated klason lignin

Klason lignins (KL) were prepared from graminaceus plants and woods, respectively, according to the method of Experimental Manual of Woody Material Science edited by Japan Wood Research Society [9] then were carboxymethylated by the method mentioned in experiment section and the solubility was tested and recorded (Table 4). It was expected that at least graminaceus plant KL could be dissolved in water. Surprisingly, none of the tested samples was dissolved in water. This result showed that lignin condensation happened during the sulfuric acid treatment process so that chemical agents became hard to penetrate into lignocellulosic materials.

**Table 2** The solubility of CM alkaline pulps

| Sample name | Solubility (+, −, ±)[a] | Color |
|---|---|---|
| Soda pulp (Wheat) CM | + | Colorless |
| Soda Pulp (Rice) CM | + | Colorless |
| BKP (commercial) CM | − | Colorless |

*CM* carboxy methylation, *BKP* bleached kraft pulp

[a] + soluble, − insoluble, ± not sure

**Table 3** The solubility of CM alkaline lignin

| Sample name | Solubility (+, −, ±)[a] | Color |
|---|---|---|
| Wheat soda lignin CM | + | Colored |
| Rice soda lignin CM | + | Colored |
| Commercial hardwood Kp Lignin CM | + | Colored |
| Commercial softwood Kp lignin CM | + | Colored |

*CM* carboxy methylation, *Kp lignin* kraft lignin

[a] + soluble, − insoluble, ± not sure

**Table 4** The solubility of CM klason lignin (KL)

| Sample Name | Solubility (+, −, ±)[a] | Color |
|---|---|---|
| Wheat straw KL CM | − | Colored |
| Rice straw KL CM | − | Colored |
| Reed KL CM | − | Colored |
| Sugar maple KL CM | − | Colored |
| Western hemlock KL CM | − | Colored |

*CM* carboxy methylation, *KL* klason lignin

[a] + soluble, − insoluble, ± not sure

Carboxy methylated α-cellulose

α-Cellulose was prepared by the method in experiment section and the result was recorded in Table 5. The solubilization of graminaceus plants' α-cellulose is not clear (± in Table 5), it may be similar to the crystallization of organic compounds, which was soluble in a mixture status but when it is getting pure, a crystal compound would be produced. In the case of CM graminaceus plant, raw materials contained hemicellulose and amorphous

**Table 5** The Solubility of CM α-Cellulose

| Sample Name | Solubility (+, −, ±)[a] | Color |
|---|---|---|
| Wheat straw α-Cellulose CM | ± | Colorless |
| Rice straw α-cellulose CM | ± | Colorless |
| Sugar maple α-cellulose CM | − | Colorless |
| Western hemlock α-cellulose CM | − | Colorless |
| BKP α-cellulose CM | ± | Colorless |

*CM* carboxy methylation, *BKP* bleached kraft pulp

[a] + soluble, − insoluble, ± not sure

**Table 6** Crystallinity of α-cellulose

| Samples | Degree of crystallinity (%) |
|---|---|
| Western hemlock | 55.91 |
| Sugar maple | 53.91 |
| Wheat straw | 49.95 |
| Rice straw | 36.59 |
| BKP (commercials) | 31.69 |

*BKP* bleached kraft pulp

cellulose, so that the CM products were a mixture of CM-hemicellulose and CM-cellulose, and even included some CM-lignins. In above cases, α-cellulose was dissolved in water after carboxymethylation. However, when α-cellulose were separated and purified, the CM α-cellulose showed difficulty to be fully dissolved in water. As a result, the solubility of CM α-cellulose (graminaceus plants) in the water became unclear. On the other hand, CM α-celluloses (both from hardwood and softwood) are still insoluble in water clearly. The reason is thought to be based on the big crystallinity differences between annual plant and perennial wood. Therefore, when doing CM treatment, the penetration of solvent between graminaceus and woody plants showed very different. The cellulose crystal of graminaceus is relatively flexible, but wood is very tight [13]. This resulted in the large solubility difference between CM graminaceus and woody plants. If lignin is tightly blocked into the IPN (Interpenetrating Polymer Network) structure in plant cell wall (e.g., woody perennial plant), CM treatment on lignocellulosics would be impossible. Without breaking through their cellulose crystal lock, the chemical penetration is impossible. That is to say, residual lignin resisted remove from highly purified wood pulp.

On the other hand carboxymethylated bleached kraft pulp (BKP) showed the relative flexibility (Table 5) because of the drastic treatment back ground: pulping and severe multiple stage bleaching processes. As a result the crystal density would be decreased.

### The crystallinity of α-cellulose

The crystallinity of woody α-cellulose is higher than graminaceus plant α-cellulose (Table 6), all of which are calculated basing on Fig. 2, but the difference of crystallinity between 53.91 and 49.95 % would not be reflected to solubility significantly. The effect to solubility of CM α-cellulose is not the crystallinity but would be related to its density and solvent penetration.

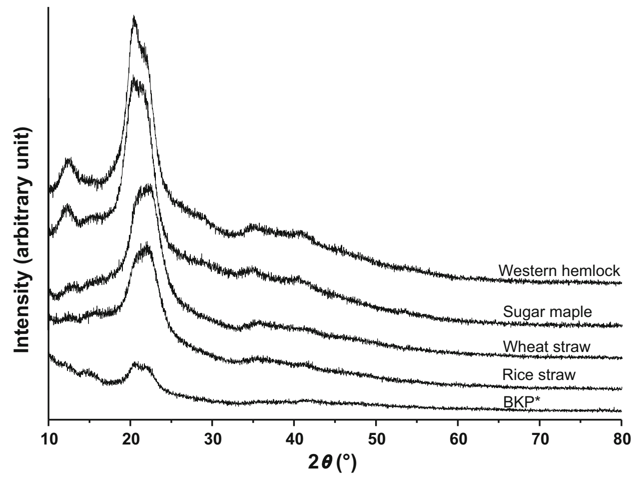


**Fig. 2** XRD spectra of α-cellulose (*BKP** bleached kraft pulp)

## Conclusion

Graminaceus plant can be made soluble in water by carboxymethylation directly but its solution is brown color which was derived from lignin. The removal of brown color must be required to take away the lignin from CM graminaceus plants depending on the usage. By pretreatment of graminaceus plant with sodium chlorite, the brown color can be removed from the product. The graminaceus plant soda lignins and kraft wood lignins can be solubilized in water by carboxymethylation but any KL could not be solubilized because of the solvent penetration problem caused by condensation of sulfuric acid treatment. The main reason CM wood meal is insoluble in water is not lignin but cellulose crystal which blocks the solvent penetration.

**Acknowledgments** Financial support for this study provided by the Natural Science Foundation of JiangSu Province (BK2012420), National Natural Science Foundation of China (No. 51203075), NanJing Forestry University Young Talent Funding (No. 163105701 and No. 163105017) is gratefully acknowledged.

## References


1. Kariman MES (2007) Application of polyvinyl alcohol (PVA)/carboxymethyl cellulose (CMC) hydrogel produced by conventional crosslinking or by freezing and thawing. J Macromol Sci Pure Appl Chem 44:619–624
2. Chen X, Liu JH, Feng ZC, Shao ZZ (2005) Macroporous chitosan/carboxymethylcellulose blend membranes and their application for lysozyme adsorption. J Appl Polym Sci 96:1267–1274
3. Dai RY, Wu G, Li WG, Zhou Q, Li XH, Chen HZ (2010) Gelatin/carboxymethylcellulose/dioctyl sulfosuccinate sodium microcapsule by complex coacervation and its application for electrophoretic display. Colloids Surf A 362:86–89
4. Diftis N, Kiosseoglou V (2003) Improvement of emulsifying properties of soybean protein isolate by conjugation with carboxymethyl cellulose. Food Chem 81:1–6
5. Leach RE, Burns JW, Dawe EJ, SmithBarbour MD, Diamond MP (1998) Reduction of postsurgical adhesion formation in the rabbit uterine horn model with use of hyaluronate/carboxymethylcellulose Gel. Fertil Steril 69:415–418
6. Green JW (1963) *O*-Carboxymethylcellulose. Methods in Carbohydrates Chemistry, vol III. Academic press, New York, pp 322–326
7. Chien SN, Ren H, Aoyagi M, Lai YZ, Amidon ET (2010) Fractionation of wood polymers by carboxymethylation-influence of reaction conditions. J Biobased Mater Bioenergy 4:40–45
8. Lam BTLT, Iiyama K, Nakano J (1985) Preparation of carboxymethylcellulose from refiner mechanical pulp, 3: Degree of substitution and distribution in carboxymethylcellulose. Mokuzai Gakkaishi 31:475–492
9. Jin ZF, Yu YM, Shao SL, Ye JW, Lin L, Iiyama K (2010) Lignin as a cross-linker of arcrylic acid-grafted carboxymethyl lignocellulose. J Wood Sci 56:470–476
10. Shibazaki H, Kuga S, Onabe F (1994) Mechanical properties of paper sheet containing bacterial cellulose. Jpn Tappi 48:93–102
11. Japan Wood Research Society (1999) Laboratory Manual of woody material science. Bun'eido Publish Co., Tokyo, pp 92–97
12. Segal L, Creely JJ, MartinJr AE, Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. Text Res J 29:786–794
13. Gu F, Wang WX, Jing L, Jin YC (2013) Sulfite-formaldehyde pretreatment on rice straw for the improvement of enzymatic saccharification. Biore Tech 142:218–224