J Wood Sci (2010) 56:470–476
DOI 10.1007/s10086-010-1128-z

ORIGINAL ARTICLE

Zhenfu Jin · Youming Yu · Shunliu Shao · Jiewang Ye
Lin Lin · Kenji Iiyama

Lignin as a cross-linker of acrylic acid-grafted carboxymethyl lignocellulose

Received: August 3, 2009 / Accepted: April 7, 2010 / Published online: July 5, 2010

Abstract *Cunninghamia lanceolata* wood meal samples with different lignin contents after delignification with an acidic $NaClO_2$ system were carboxymethylated, and the degree of substitution (DS) and the distribution of the carboxymethyl (CM) groups were investigated by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Cellulose samples prepared from bleached kraft softwood pulp, food-grade konjac mannan, and commercial oat xylan (containing 10% arabinosyl and 15% glucosyl residues) were also investigated. The chemical shift of methylene protons in ^{1}H NMR spectra of CM groups of carboxymethyl konjac mannan and commercial oat xylan appeared in the same region as those of carboxymethylcellulose. The DS of carboxymethyl lignocellulose (CMLC) increased slightly from 1.36 to 1.48 with decreasing lignin content, but the water solubility of CMLC clearly increased with decreasing lignin content. It was suggested that the covalent linkages between lignin and cell-wall polysaccharides play the role of cross-linker in CMLC. Water absorbents were synthesized by graft-copolymerization of acrylic acid onto CMLC samples with different lignin contents. The highest level of water absorbency was obtained from CMLC containing 14% of lignin, suggesting the importance of lignin as the cross-linker.

Key words Carboxymethyl lignocellulose (CMLC) · Degree of substitution (DS) · Distribution of carboxymethyl (CM) groups · Lignin content · Cross-linker

Z. Jin (✉) · Y. Yu · J. Ye · L. Lin
School of Engineering, Zhejiang Forestry University, 88 North Huancheng Road, Linan, Zhejiang 311300, China
Tel. +86-571-63741607; Fax +86-571-63741607
e-mail: jinzhenfu@yahoo.com.cn

S. Shao
Institute of Ecology, Zhejiang Forestry Academy, Hangzhou, Zhejiang 310023, China

K. Iiyama
Japan International Research Center for Agricultural Science (JIRCAS), Tsukuba 305-8686, Japan

Introduction

There has been considerable interest in water-swellable superabsorbent polymers capable of absorbing and holding huge amounts of water. These polymers have found extensive commercial application as absorbents in personal care products such as infant diapers and feminine hygiene products. In addition, they have received considerable attention for a variety of more specialized applications, including soil improvers for use in agricultural and domestic situations, industrial dehydration agents, sensors, and drying preventives.[1] Absorbent polymers prepared from natural polymers such as cellulose and its derivatives have received increasing interest because they are environmentally friendly, biodegradable, and do not use fossil resources. Many efforts have been made to synthesize cellulose-based superabsorbing polymers and to improve their water absorbency.[2–7] Recently, modifications of hemicelluloses has also attracted a great deal of interest in the preparation of superabsorbing polymers.[8–17] Hemicelluloses consist of various heteropolysaccharides, which are generally branched polymers with comparatively low molecular weight. Monomeric units of carboxymethylated hemicelluloses also have two or three active hydroxyl groups that can be substituted by carboxymethyl groups.

The introduction of hydrophilic groups, i.e., carboxymethyl (CM) groups, and their cross-linker are the main reactions required to synthesize polysaccharide-based absorbent polymers.[18] The water solubility of carboxymethylcellulose (CMC) is due to the presence of CM groups. Higher water absorbency is achieved by a high degree of substitution (DS), but CMC is soluble in water when the DS is greater than 0.6.[19] The water absorbency increased with increasing DS, and water absorbency of the absorbent polymer was considerably low when the absorbents were synthesized in the absence of a cross-linker.[20]

Cross-linkers have to be used to prevent the dissolution of hydrophilic polymer chains in an aqueous environment. The cross-linking structure of a hydrogel decides both its dissolution and swelling capacities in an aqueous solution, so a moderate degree of cross-linking can enhance water absorbency. A higher density of cross-linker, which has more cross-linked points in polymeric chains, results in a rigid structure and a decrease in water absorbency because the structure is unable to expand.[3] Water absorbency decreases when the cross-linking density is below a moderate value because the cross-linked network structure in the polymer cannot form effectively, resulting a poorly cross-linked network that dissolves in water. Absorbent polymers are most commonly formed by free radical cross-linking polymerizations of hydrophilic acrylate monomers with small quantities of cross-linking agents containing two (or more) polymerizable double bonds.[1] Typical cross-linking agents such as *N,N′*-methylenebisacrylamide, triallylamine, ethylene glycol diacrylate, tetraethylene glycol diacrylate, trimethylolpropane triacrylate, and the methacrylate analogs of the aforementioned acrylates are usually used to synthesize cellulose-based absorbent polymers.[2,3] Lam et al.[11] reported that covalent linkages between lignin and cell wall polysaccharides act as a cross-linker of carboxymethyl lignocellulose (CMLC). Lignin, which is defined as the dehydrogenative polymer of hydroxycinnamyl alcohols, is the one of major structural components of the secondary plant cell walls of vascular plants. The covalent linkages between wall polysaccharides and lignin are important factors in the formation of the cell wall architecture, and have been previously well documented.[21,22] The presence of covalent linkages between polysaccharides and lignin affects strongly the water solubility of CMLC.[11]

In this article, *Cunninghamia lanceolata* wood meal samples with different lignin contents were carboxymethylated to investigate the effect of lignin on the DS and distribution of carboxymethyl groups, and on the dissolving behavior of carboxymethylated products in water. The DS and the distribution of CM groups in CMLC were analyzed using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy.[9–11,23] Cellulose prepared from bleached kraft softwood pulp, food-grade konjac mannan, and commercial oat xylan (containing 10% arabinosyl and 15% glucosyl residues) was also investigated to identify chemical shifts in the region of anomeric and methylene protons of ^{1}H NMR of carboxymethylated monosaccharide residues. In addition, samples of carboxymethylated *C. lanceolata* wood meal with different lignin contents were graft-copolymerized with acrylic acid to analyze the water absorbance capacity and the role of lignin as cross-linkers.

Experimental

Materials

Wood shavings of an 18-year-old *Cunninghamia lanceolata* (Lamb.) Hook (cedar) were made available by a wood processing factory at Linan in Zhejiang province (29°56′N, 118°51′W), China. An air-dried sample was ground in a Wiley mill to pass a 0.42-mm sieve. The ground sample was extracted with ethanol–benzene (1:2, v/v) using a Soxhlet extractor.

The extract-free samples (10 g) were suspended in distilled water (1500 ml) and treated 2, 4, or 6 times with $NaClO_2$ (4 g) for 1 h at 70°C, together with 0.8 ml of acetic acid. The residue was filtrated with a fritted glass filtering crucible (1G4) and successively washed with distilled water to prepare samples with different lignin contents. Samples were dried for 2 days in a vacuum oven at 40°C.

Cellulose prepared from bleached kraft softwood pulp was kindly gifted by Nippon Pulp Chemicals Co., Japan, and commercial oat xylan (containing 10% arabinosyl and 15% glucosyl residues) was purchased from Sigma Chemical (St Louis, MO, USA). Konjac mannan (glucomannan) was commercial food-grade samples procured from a konjac product factory (Gunma Prefecture, Japan).

Determination of lignin content

The lignin contents of the extract-free ground samples were determined according to the Klason procedure.[24]

Preparation of carboxymethyl derivatives

Samples (5 g) were suspended in 2-propanol (100 ml) with 30% sodium hydroxide aqueous solution (6 g) and the reaction mixture was stirred for 1 h at 30°C. Monochloroacetic acid (7 g) was added and the temperature of the reaction bath was raised to 80°C. The etherification reaction was performed for 2 h. The product was neutralized with 80% acetic acid, collected by filtration, and then washed several times with ethanol/water (4:1 v/v) to remove inorganic salts followed by washing with absolute ethanol to dewater. The purified carboxymethylated product was dried in a vacuum oven overnight at 40°C.

Graft copolymerization

Graft copolymerization was carried out by the method of Suo et al.[3] with minor modifications. CMLC (1 g) and 10 ml of distilled water were charged into a separable three-necked round-bottom flask in a water bath maintained at 85°C for 30 min. Nitrogen gas was bubbled with stirring through the solution to remove dissolved oxygen. Acrylic acid (8 ml) and 30% NaOH (7 ml) were added followed by 0.04 g potassium persulfate ($K_2S_2O_8$) to initiate graft copolymerization for 2 h at 50°C. The product, graft copolymer, was dried for 20 h at 70°C and then ground in a Wiley mill to pass a 0.15-mm sieve.

Measurement of the water absorbency

Samples (0.2 g) were put into bags (20 × 10 cm) with a mesh size of 0.063 mm and immersed in 1 l of distilled water at room temperature until equilibrium was reached. Then the bags were hung up until no drop drained during 10 min. The water absorbency was then calculated from the following equation:

Water absorbency (g/g) = $(W_{sg} - W_{dg} - W_b)/W_{dg}$

where W_{sg}, W_{dg}, and W_b are the weights of the swollen gel, dry gel, and the bag, respectively.

Water extraction of carboxymethylated products

CMLC (2 g) was extracted five times (10 min each) with water (200 ml) with stirring at room temperature to yield water-soluble and -insoluble fractions. The water-insoluble fraction was washed with 80% (v/v) ethanol followed by absolute ethanol, and dried in the vacuum oven at 60°C. The water-soluble fraction was concentrated by a vacuum evaporator at 40°C and freeze dried.

Measurement of ^{1}H NMR spectra

Determination of DS and the distribution of CM groups using ^{1}H NMR spectroscopy was carried out according to the scheme of Ho and Kloslewlcz.[23] The carboxymethylated product (150 mg) was hydrolyzed with 25% (v/v) D_2SO_4 in D_2O solution (2 ml) for 90 min at 90°C. The hydrolysate was filtered by glass wool to remove precipitates, probably originating from lignin. The filtrate was directly collected into an NMR tube for ^{1}H NMR measurement. The ^{1}H NMR spectrum of the hydrolysate of carboxymethylated product in 25% (v/v) D_2SO_4 was recorded on a BRUKER-300 NMR Spectrometer (Bruker, Germany) operating at 300 MHz at 20°C. The sugar composition of carboxymethylated samples was estimated from signals of anomeric protons ranging 4.45 to 5.40 ppm of the ^{1}H NMR spectra by the procedure proposed by Lam et al.[10]

Measurement of IR spectrum

Fourier transform infrared (FTIR) spectra of the carboxymethylated products were recorded by the KBr disk method on an IR Prestige-21 Spectrometer (Shimadzu, Japan), using 64 scans and a resolution of 4 cm^{-1}.

Results and discussion

The DS and CM group distribution of carboxymethylated konjac mannan and commercial xylan

Commercial oat xylan, which contains arabinosyl (10%) and glucosyl (15%) residues, and konjac mannan (glucomannan) were carboxymethylated to investigate the DS characteristics and distribution of CM groups in comparison with those of carboxymethylcellulose (CMC) prepared from bleached kraft softwood pulp.

The ^{1}H NMR spectra of the anomeric proton region (4.45 to 5.40 ppm) of the hydrolysates of CMC, carboxymethylated konjac mannan (CMGM), and carboxymethylated commercial oat xylan (CMX) in 25% D_2SO_4 in D_2O solution are shown in Fig. 1.

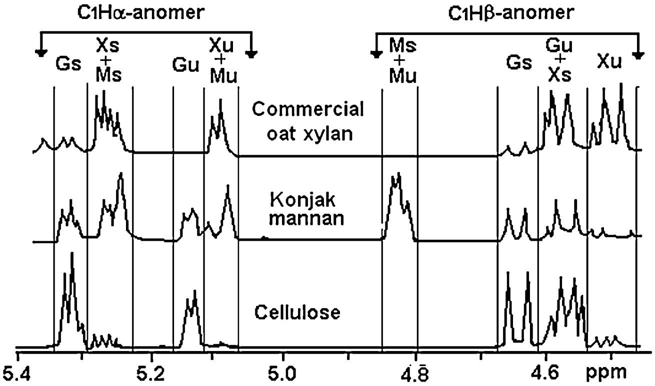

Fig. 1. ^{1}H NMR spectra of the anomeric proton regions of carboxymethyl cellulose (CMC), carboxymethyl konjac mannan (CMGM), and carboxymethyl commercial oat xylan (CMX) after hydrolysis in 25% D_2SO_4 for 90 min at 90°C. *G*, *M*, and *X*: glucosyl, mannosyl, and xylosyl residues, respectively. *s* and *u* refer to substituted (with CM groups) and unsubstituted hydroxyl groups, respectively, at the C2 position of monomeric sugar residues in the hydrolysates

Table 1. Carboxymethylated sugar composition of carboxymethylcellulose (CMC), carboxymethylated konjac mannan (CMGM), and carboxymethylated commercial oat xylan (CMX)

	Carboxymethylated sugar composition (%)			
	Mannose	Xylose	Glucose	Arabinose
CMC	–	10.2	89.6	–
CMGM	57.9	–	42.6	–
CMX	–	76.4	(23.6)	

Parentheses indicate that both carboxymethylglucose and carboxymethylarabinose were involved

It is well documented that the signals of α-anomeric protons appear in the lower field region (5.00–5.40 ppm) compared to β-anomeric protons (4.45–4.90 ppm).[10,23] Carboxymethylated sugar compositions in hydrolysates of CMC, CMGM, and CMX were calculated using the integral of anomeric protons at corresponding chemical shifts (Fig. 1) based on the equations proposed by Lam et al. (Table 1).[10] The hydrolysate of CMGM, carboxymethylated food-grade konjac mannan, was composed of mannosyl and glucosyl residues at a ratio of mannosyl : glucosyl of 1.36 : 1. The sugar composition of the hydrolysate of CMX was 76% xylosyl and 24% others (probably both glucosyl and arabinosyl) residues based on the calculation using the equations of Lam et al.,[10] which agreed well with the sugar composition in the original oat xylan, data for which was provided by Sigma Chemical (75% xylose, 15% glucose, 10% arabinose).

The signals of methylene protons (–CH_2–) of CM groups in hydrolysate of CMC were observed in the range 4.13–4.43 ppm, and the methylene protons gave four sharp and intense signals in the region, which can be assigned to CM groups at C_3, $C_{2\alpha}$, $C_{2\beta}$, and C_6 from the lower field to higher field, respectively.[9,23] By analogy with CMC, signals of methylene protons of CM groups in CMGM and CMX appeared in the same region of chemical shifts (Fig. 2). Petzold et al.[13] reported that the methylene proton of CM groups of hydrolysate of carboxymethyl xylan gave four sharp and intense signals in the same chemical shift range. Carboxymethylated arabinan gave signals in the same region of chemical shift, and the DS and the substitution at different positions were determined by means of ^{1}H NMR.[15] Thus it was suggested that DS and the distribution of CM groups in all carboxymethylated cell wall polysaccharides can also be determined using the ^{1}H NMR method.

The DS and distribution of CM groups at the C_2 (DS_2), C_3 (DS_3), and C_6 (DS_6) of CMC, CMGM, and CMX were calculated as follows;

$$DS_2 = B_2/A;\ DS_3 = B_3/A;\ DS_6 = B_6/A;\ DS = DS_2 + DS_3 + DS_6,$$

where A is the integral value of anomeric signals in the region between 4.45 and 5.40 ppm, and B_2, B_3, and B_6 are one-half of the integral values of methylene signals in the regions between 4.25 and 4.39 ppm, 4.39 and 4.43 ppm, and 4.13 and 4.18 ppm, respectively.

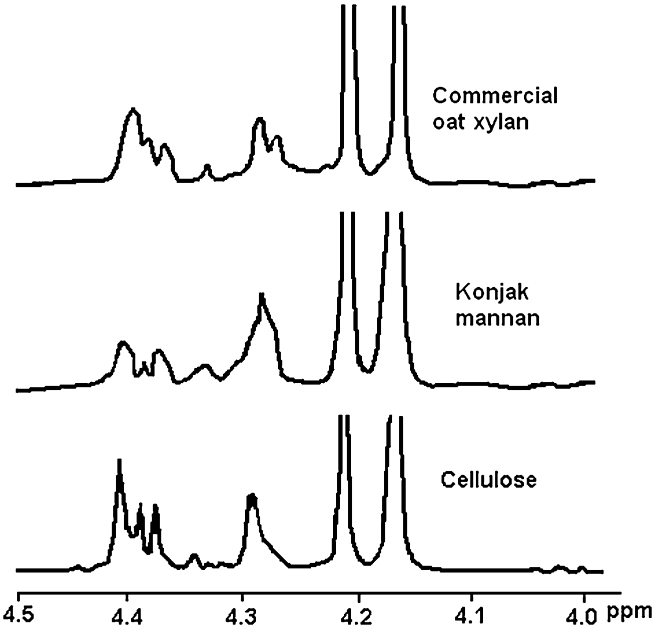

Fig. 2. ^{1}H NMR spectra of methylene protons of carboxymethyl groups of CMC, CMGM, and CMX after hydrolysis in 25% D_2SO_4 for 90 min at 90°C. The signal around δ 4.2 ppm is assigned to methylene protons of glycolic acid,[9] which is a by-product of carboxymethylation

The DSs of CMGM and CMX were lower than that of CMC (Table 2). The distribution of CM groups at the C2, C3, and C6 positions of CMC was in the ratio 0.81 : 0.27 : 0.50, indicating that the relative reactivity of the hydroxyl groups was in the order OH(2) > OH(6) > OH(3) under present experimental conditions. CMGM gave a different distribution pattern, OH(6) > OH(2) > OH(3), than that of CMC (Table 2), probably because of the difference in the formation of hydrogen bonding at the C6 position of mannosyl residues. CMX, containing 15% glucose and 10% arabinose, appeared in the same distribution trend as CMC (Table 2).

Effect of lignin on DS and distribution of carboxymethylated lignocellulose

The major components of wood meal are cellulose, hemicellulose, and lignin. The contribution of the hydroxyl groups of lignin to the DS of CM groups is significantly low.[9,10] The main structural feature of the hemicelluloses appearing in softwoods is galactoglucomannan, which is built up by a (1–4)-linkage linear backbone of partially acetylated β-D-glucopyranose and β-D-mannopyranose units.[25] *C. lanceolata* wood meal was delignified with $NaClO_2$ either 2, 4, or 6 times under acidic conditions for 1 h each at 70°C. The lignin content of the delignified wood meal is shown in Table 3. Even after treatment with $NaClO_2$ 6 times, 4.1% of lignin still remained. This result can be explained by the presence of linkages between lignin and cell wall polysaccharides. Covalent linkages between cell wall polysaccharides and lignin have been previously well documented.[11,21,22] Covalent linkages between cell wall polysaccharides and lignin are important factors in the formation of the cell wall architecture.[22] Lam et al.[11] concluded that lignins in softwood mainly bonded chemically or physically to cell wall polysaccharides, including cellulose, while lignin in hardwood linked to hemicelluloses on the basis of the results of carboxymethylation of softwood and hardwood.

C. lanceolata wood meal samples with different lignin contents were carboxymethylated to investigate the effects of lignin content on DS and the distribution of CM groups

Table 2. Degree of substitution and distribution of carboxymethyl groups of carboxymethylated samples calculated by the ^{1}H NMR method

	Distribution of carboxymethyl groups			Degree of substitution (DS)
	C2	C3	C6	Total
Commercial cellulose	0.81	0.27	0.50	1.58
Konjac mannan	0.60	0.20	0.67	1.47
Commercial xylan	0.75	0.25	0.29	1.29
Cunninghamia lanceolata				
Original	0.55	0.19	0.63	1.36
Treated 2 times[a]	0.50	0.18	0.62	1.30
Treated 4 times	0.47	0.21	0.75	1.43
Treated 6 times	0.56	0.18	0.73	1.48

[a] Number of $NaClO_2$ treatments for delignification of *C. lanceolata* wood meal

Table 3. Effect of lignin content of *C. lanceolata* wood meal on water solubility of carboxymethylated *C. lanceolata* wood meal and water absorbency of grafted copolymer of carboxymethylated *C. lanceolata* wood meal

	Original	2 times[a]	4 times[a]	6 times[a]
Klason residue (lignin content) (%)[b]	31.4	19.2	14.0	4.1
Yield of water-soluble fraction (%)[c]	20	72	83	100
Water absorbency (g/g)	566	604	944	694

[a] Number of $NaClO_2$ treatments for delignification of *C. lanceolata* wood meal
[b] Of *C. lanceolata* wood meal before carboxymethylation
[c] Of carboxymethylated *C. lanceolata* wood meal

in CMLC. The ^1H NMR spectra of hydrolysates of CMLC containing different lignin contents are shown in Fig. 3. The DS of CMLC increased slightly from 1.36 to 1.48 with decreasing lignin content, probably because of the release of hydroxyl groups binding to lignin by the delignification. There were no significant changes of DS values at the C2 and C3 positions for different lignin contents, but higher DS at the C6 position of highly delignified CMLCs suggested that lignin might link to the C6 position of hexosans (Table 2).

Characteristics of CMLCs with different lignin contents were also examined by FTIR. Bands observed in the 1200–1000 cm^{-1} region were assigned to C–O stretching and O–H bending of cellulose and hemicellulose units. These bands are not independent vibrational modes because they couple with the vibrations of adjacent groups and are sensitive to hydrogen bonding.[26] The CMLCs of original wood meal samples and samples treated 2 times with $NaClO_2$ displayed two absorption bands in the 1200–1000 cm^{-1} region, while the CMLCs treated 4 and 6 times with $NaClO_2$ had one band, which became more pronounced with decreasing lignin content (Fig. 4), suggesting that hydrogen bonds were cleaved and substituted by CM groups. The C=C stretching band of lignin aromatic rings occurs in the 1520–1500 cm^{-1} region and asymmetric Ar–O–C stretching vibration appears in the 1275–1220 cm^{-1} region.[27] These characteristic bands of lignin in the FTIR spectra decreased with decreasing lignin content, and no band was observed in the highly delignified samples (Fig. 4).

Effect of lignin content on dissolving behavior of carboxymethylated lignocellulose

CMLC samples with different lignin contents were extracted thoroughly with water at room temperature to prepare water-soluble and -insoluble fractions. C–O stretching and O–H bending bands, which are characteristic bands of cellulose and hemicellulose, occurred in the 1200–1000 cm^{-1} region. The water-insoluble fraction displayed similar spectra to that of CMLC before water extraction, but no characteristic bands of lignin in the 1520–1500 and 1275–1220 cm^{-1} regions were observed in spectra of the water-soluble fraction, suggesting that the water solubility of carboxymethyl derivatives is fundamentally related to the presence of lignin (Fig. 5).

It is well known that CMC with a DS of CM groups lower than 0.5 is water insoluble, while CMC is soluble in water

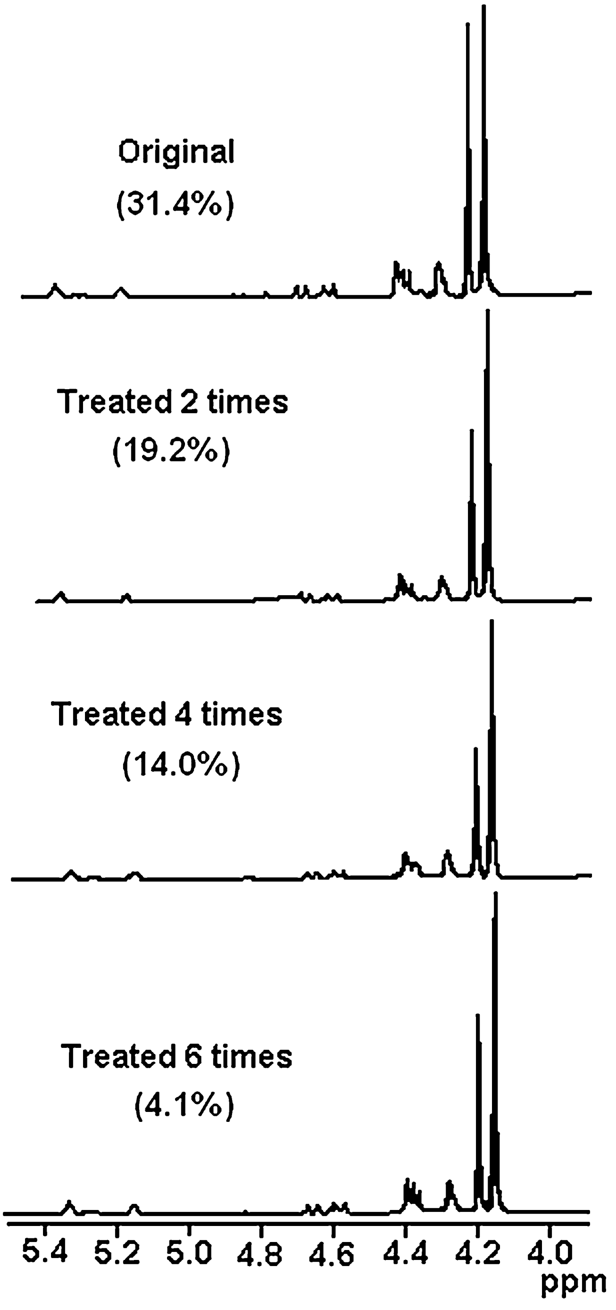

Fig. 3. ^1H NMR spectra of carboxymethylated *Cunninghamia lanceolata* wood meal prepared from wood meal samples with different lignin contents (*percentages*) resulting from treatment with $NaClO_2$. Lignin contents were 31.4%, 19.2%, 14.0%, and 4.1% of the samples, as treated with acidic $NaClO_2$ 2, 4, and 6 times for 1 h at 70°C, respectively. The signal around δ 4.2 ppm is assigned to methylene protons of glycolic acid,[9] which is a by-product of carboxymethylation

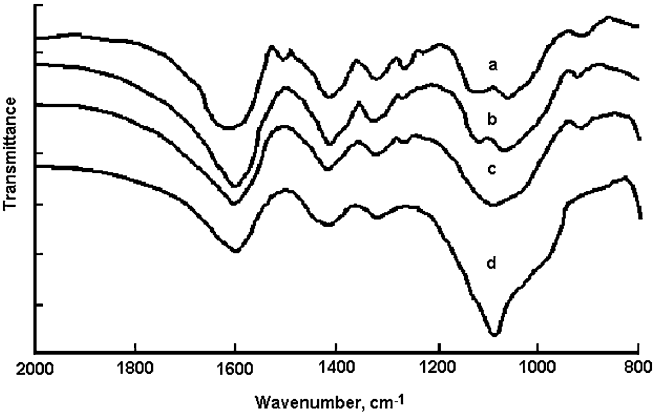

Fig. 4. Fourier transform infrared (FTIR) spectra of carboxymethylated *C. lanceolata* wood meal samples containing different lignin contents. Lignin contents were *a*, 31.4%; *b*, 19.2%; *c*, 14.0%; and *d*, 4.1% of the original, as treated with acidic $NaClO_2$ 2, 4, and 6 times for 1 h at 70°C, respectively

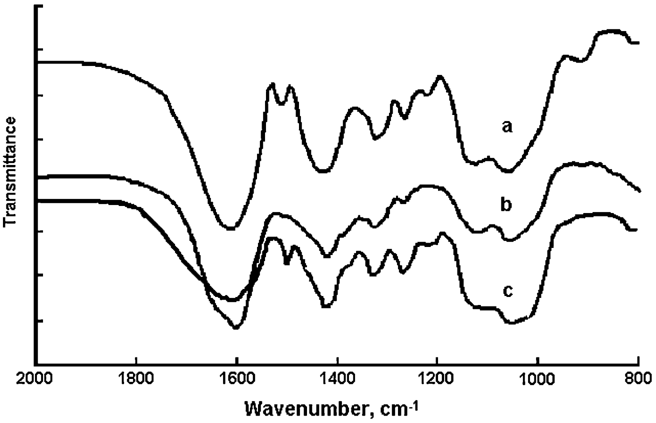

Fig. 5. FTIR spectra of carboxymethylated *C. lanceolata* wood meal (*a*) and its water-soluble (*b*) and -insoluble (*c*) fractions

when DS is greater than 0.6.[19] The DS values of CMC, CMGM, and CMX were 1.58, 1.47 and 1.29, respectively, and they dissolved completely in water to produce clear, high-viscosity liquids (Table 2). On the other hand, although the DS of CM groups of CMLC containing 31.4% of lignin was 1.36, the yield of the water-soluble fraction was only 20% (Table 3). The yields of the water-soluble fraction of CMLCs increased with decreasing lignin content. These results suggest that lignin acted as a cross-linker among polysaccharides through linkages between cell wall polysaccharides and lignin and that these linkages related fundamentally to the solubility of CMLC, as proposed by Lam et al.[11]

Effect of lignin on water absorbency

Water absorbents were synthesized by grafting acrylic acid onto CMLC samples with different lignin contents. Cross-linkers are used in hydrogels to prevent the dissolution of hydrophilic polymer chains in an aqueous environment. CMLC containing 14% of lignin insolubilized in water by graft-copolymerization with acrylic acid gave the highest water absorbency of 944 g/g, but the water absorbency decreased with further delignification, probably because of the difficulty of the formation of an effective cross-linked network structure in the copolymer when using heavily delignified CMLC (Table 3). In general, the cross-linking structure of a hydrogel decides both its dissolution and swelling capacities in an aqueous solution, therefore a moderate degree of cross-linking is suitable for the enhancement of absorbency of the resulting hydrogel.[3] CMLC containing 31.4% of lignin grafted with *N,N*-methylenebisacrylamide as a cross-linker was also synthesized. The water absorbency of grafted copolymer synthesized by *N,N*-methylenebisacrylamide was lower compared with that produced using acrylic acid as a cross-linker. The cross-linking, in addition to the linkages between lignin and polysaccharides, would cause a higher cross-linking density to form a tight network, resulting in lower levels of water absorbency (data not shown). CMLC with a lignin content of 14% was optimum as cross-linker for water absorbency. CMLC samples with lower or higher lignin contents would result in decreased water absorbency.

Conclusions

1. In ^1H NMR spectra, the hydrolysates of CMGM and CMX appeared at the same region of chemical shifts for methylene protons of CM groups (4.13–4.43 ppm), and also for anomeric protons (4.45–5.40 ppm), as those of the hydrolysate of CMC.
2. The DS levels of CMLCs increased slightly from 1.36 to 1.48 with decreasing lignin content, probably because of the release of hydroxyl groups binding to lignin by the delignification. There were no significant changes of DS levels at the C2 and C3 positions with lignin content, but higher DS levels at the C6 position of highly delignified CMLCs suggested that lignin may link to the C6 position of hexosans.
3. The covalent linkages between cell wall polysaccharides and lignin acted as a cross-linker in CMLC. CMLC samples containing 14% of lignin proved to be optimum as a cross-linker for water absorbency. Samples with lower or higher lignin contents would cause lower or higher cross-linking densities, resulting in lower levels of water absorbency.

Acknowledgments This work was completed with the financial support of the Agricultural Key Research Project of Zhejiang Province, China (2006C12069).

References

1. Kinney AB, Scranton AB (1994) Formation and structure of cross-linked polyacrylates. In: Buchholz FL, Nicholas NA (eds) Superabsorbent polymers, science and technology. ACS Symposium Series No.573, Chicago, pp 2–26

2. Xiao Y, Meshitsuka G (2001) Development of high-retention water absorbent from cellulosic materials: water absorbent from bleached kraft pulp. J Wood Sci 47:394–399
3. Suo A, Qian J, Yao Y, Zhang W (2007) Synthesis and properties of carboxymethyl cellulose-graft-poly(acrylic acid-*co*-acrylamide) as a novel cellulose-based super absorbent. J Appl Polym Sci 103:1382–1388
4. Pushpanalar V, Langford SJ, Ahmad M, Lim YY (2006) Optimization of reaction conditions for preparing carboxymethylcellulose from sago waste. Carbohydr Polym 64:312–318
5. Ramos LA, Frollini E, Heinze T (2005) Carboxymethylation of cellulose in the new solvent dimethyl sulfoxide/tetrabutylammonium fluoride. Carbohydr Polym 60:259–267
6. Capitani D, Porro F, Segre AL (2000) High field NMR analysis of the degree of substitution in carboxymethylcellulose sodium salt. Carbohydr Polym 42:283–286
7. Adinugraha MP, Marseno DW, Haryadi (2005) Synthesis and characterization of sodium carboxymethylcellulose from Cavendish banana pseudo stem (*Musa cavendishii* Lambert). Carbohydr Polym 62:164–169
8. Ebringerova A, Hromadkova Z, Hribalova V (1995) Structure and mitogenic activities of corn cob heteroxylans. Int J Biol Macromol 17:327–331
9. Lam TBT, Iiyama K, Nakano J (1985) Preparation of carboxymethylcellulose from refiner mechanical pulp. III. Degree of substitution and distribution in carboxymethylcellulose. Mokuzai Gakkaishi 31:8–13
10. Lam TBT, Iiyama K, Nakano J (1985) Preparation of carboxymethyl-cellulose from refiner mechanical pulp IV. Analyses of carboxymethylated polysaccharides by the use of ^{1}H-NMR. Mokuzai Gakkaishi 31:14–19
11. Lam TBT, Iiyama K, Nakano J (1985) Preparation of carboxymethyl-cellulose from refiner mechanical pulp V. Physical and chemical associations among cellulose, hemicellulose and lignin in wood cell walls. Mokuzai Gakkaishi 31:475–482
12. Parvathy KS, Susheelamma NS, Tharanathan RN, Gaonkar AK (2006) A simple non-aqueous method for carboxymethylation of galactomannans. Carbohydr Polym 62:137–141
13. Petzold K, Schwikal K, Gunther W, Heinze T (2006) Carboxymethyl xylan – control of properties by synthesis. Macromol Symp 232:27–36
14. Ren JL, Sun RC, Peng F (2008) Carboxymethylation of hemicelluloses isolated from sugarcane bagasse. Polym Degrad Stabil 93: 786–793
15. Saghir S, Iqbal MS, Hussain MA, Koschella A, Heinze T (2008) Structure characterization and carboxymethylation of arabinoxylan isolated from Ispaghula (*Plantago ovata*) seed husk. Carbohydr Polym 74:309–317
16. Schmorak J, Bishop CT, Adams GA (1957) Constitution of a degraded polysaccharide from wheat bran. Can J Chem 35: 108–114
17. Yu HQ, Huang YH, Ying H, Xiao CB (2007) Preparation and characterization of a quaternary ammonium derivative of konjac glucomannan. Carbohydr Polym 69:29–40
18. Baumann H, Richter A, Klemm D, Faust V (2000) Concepts for preparation of novel regioselective modified cellulose derivatives sulfated, aminated, carboxylated and acetylated for hemocompatible ultra thin coatings on biomaterials. Macromol Chem Phys 201:1950–1962
19. Su K (2003) Cellulose ether. In: Yan R (ed) Water-soluble polymer (in Chinese). Chemistry Industry, Beijing, pp 343–518
20. Kuwabara S, Kubota H (1996) Water-absorbing characteristics of acrylic acid-grafted carboxymethylcellulose synthesized by photo grafting. J Appl Polym Sci 60:1965–1970
21. Iiyama K, Lam TBT, Stone BA (1994) Covalent cross-links in the cell wall. Plant Physiol 104:315–320
22. Koshijima T, Watanabe T (2003) Location of lignin moieties along polysaccharide chains in lignin-carbohydrate complexes. In: Timell TE (ed) Association between lignin and carbohydrates in wood and other plant Tissues. Springer-Verlag, Berlin, pp 61–89
23. Ho FFL, Kloslewlcz DW (1980) Proton nuclear magnetic resonance spectrometry for determination of substituents and their distribution in carboxymethyl cellulose. Anal Chem 52:913–916
24. Yoshihara K, Kobayashi T, Fuji T, Akamatsu I (1984) A novel modification of Klason lignin quantitative method (in Japanese). Kamipa Gikyoshi 38:466–475
25. Dekker RFH (1985) Biodegradation of the hemicelluloses. In: Higuchi T (ed) Biosynthesis and biodegradation of wood components. Academic, Orlando, pp 189–256
26. Silverstein RM, Webster FX (1997) Spectrometric identification of organic compounds (6th edn). John Wiley, New York, pp 71–143
27. Hergert HL (1971) Infraspectra. In: Sarkanen KV, Ludwig CH (eds) Lignins: occurrence, formation, structure and reactions. Wiley-Interscience, New York, pp 267–297