Factors Influencing Molecular Weights of Methylcelluloses Prepared from Annual Plants and Juvenile Eucalyptus

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ABSTRACT: We studied the factors that influenced the molecular weights (M_w) of water-soluble methylcelluloses prepared from annual plants and juvenile eucalyptus. Miscanthus and cardoon stalks, and bleached pulps of abaca, jute, sisal, hemp, and flax were the annual plant materials studied. A higher concentration of NaOH solution during the impregnation led to a spring cardoon methylcellulose having a lower molecular weight. As the impregnation times increased, so did the molecular weights of the water-soluble methylcelluloses of spring cardoon. The impregnation conditions had less influence on the methylcelluloses of summer cardoon than on the methylcelluloses of spring cardoon. As the cooking times increased, so did the molecular weights of miscanthus methylcelluloses. A lower pulping severity increased the molecular weight of eucalyptus methylcellulose. The preliminary treatments (water soaking, premercerization, mercerization under pressure, and steam explosion) improved the molecular weights of water-soluble abaca methylcelluloses. The steam explosion method was the best of the preliminary treatments for the abaca pulp. Different species led to different molecular weights for methylcelluloses synthesized from ECF bleached pulps, and these were further improved by preliminary mercerization. The molecular weight of α-cellulose methylcellulose changed as the ratio of the methylation reagent was varied. To synthesize an optimum M_w of methylcellulose, the different raw materials can be chosen, the pulping parameters adjusted (including impregnation and cooking), the cellulose pretreated, and the methylcellulose conditions changed. The plant species is the decisive factor for the M_w of methylcellulose.
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Key words: annual plants; cellulose; eucalyptus; methylation; methylcellulose; molecular weight; preliminary treatments; pulps

INTRODUCTION

Methylcelluloses have been widely used as gels and fine chemicals in pharmaceuticals, foods, building, paints, ceramics, detergents, agriculture, polymerization, adhesives, cosmetics, and tobacco for many years.[1–3] They can be used as emulsifiers, medicines or medicine constituents, colloidal stabilizers, viscosity controllers, and flow controllers,[1–3] and they dissolve in cold water when their degrees of substitution are between 1.3 and 2.0.[4] For a given degree of substitution, the molecular weight of methylcelluloses is the decisive property that affects its solubility and applications.[2–4] High viscosity methylcelluloses are usually used as rheological controllers[2,3] while low-viscosity methylcelluloses are usually used in such pharmaceutical products as table coating additives.[2,3] Properties related to the molecular weight, such as the average molecular weight,[4,5] the polymolecularity,[5] and the average degree of polymerization[5] are the essential characteristics that affect the development and application of water-soluble methylcelluloses.[2,3,6] Current research into methylcellulose focuses on the novel elucidation of the gelation mechanism of methylcellulose solutions,[7,8] new applications,[9,10] synthesis in new homogeneous cellulose solutions,[11,12] and synthesis from such new resources as annual plant pulps.[13–16]

Methylcelluloses can be produced from cotton cellulose, wood, and annual plant pulps.[2,13–16] Mercerization in a concentrated NaOH solution causes the cellulose to swell, degrade, decrease the degree of crystallinity, and, most importantly, yield alkali cellulose, which is used to react with methyl halide to produce methylcellulose.[2,6] The reaction of alkali cellulose and methyl halide is carried out as a nucleophilic substitution through the interaction of the oxonium sodium hydroxide complexes on three accessible hydroxyls in the anhydroglucose unit.[6] When a bleached pulp is used to synthesize methylcellulose rather than a pure α-cellulose, the William etherification mechanism combined with the macro heterogeneous methylation of the pulp[17,18] causes the methylation to become inhomogeneous and incomplete, which is due to the difficulty of diffusion and penetration of methylation reagents, the inaccessible fibril interior, and the crystalline cellulose interior.[6,14,18]

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Thus, the synthesized methylcellulose often has a few un-reacted fibrils that can be seen in water solution, and considerable polymolecularity, which causes unexpected properties.[19]

The molecular weight of methylcellulose needs to be kept within a particular range by carefully choosing the raw materials and process parameters. In the present research, methylcellulose was prepared from plant stalks and bleached pulps. The experimental process consisted of impregnation, pulping, bleaching, mercerization, and methylation. Pulps of different plants have different morphological structures and chemical compositions,[20] so the methylcellulose produced from different species will have different properties even though the methylation conditions may be the same.[14] Therefore, the species is the most important factor in the production of methylcellulose.[14–16] Pulping conditions played a very important role in adjusting the properties of the pulp[13,19] (e.g., the lignin content, the degree of polymerization, the accessibility, and the degree of crystallinity). In addition, bleached pulps often have different chemical and physical compositions,[14] which determine whether the pulp needs preliminary treatments for its accessibility and reactivity to be improved.[6,14] When the accessibility of pulp is low, the pulp needs physical and chemical preliminary treatments.[6,14] During the heterogeneous methylation, the mercerization and methylation conditions also greatly influence the molecular weight of the synthesized methylcellulose.[2,6]

The present research investigates and discusses some of the factors that influence the molecular weight of water-soluble methylcellulose. Therefore, this research may contribute to find some methods for adjusting and controlling the molecular weights of methylcelluloses produced from annual plants and juvenile eucalyptus.

EXPERIMENTAL

Methylcelluloses and reagents

Methylcelluloses were prepared in the laboratory from α-cellulose, miscanthus stalks, cardoon stalks (harvested both in spring and in summer), eucalyptus chips, and Elemental Chlorine Free (ECF) bleached flax, hemp, jute, sisal, and abaca pulps.[13–16] The properties of these methylcelluloses are listed in Table I.[13–16] The detailed synthesis and characterization procedures of methylcelluloses were described in the papers of Ye and Farriol,[13,14] and Ye et al.[15,16] Such pretreatments as water-soaking, preliminary mercerization, mercerization under 15 bars pressure, and steam explosion were used to improve the accessibilities and reactivities of annual plant pulps.[14] About 5 g of pulp (oven-dried weight) was mercerized in excessive 40% (for cardoon, eucalyptus, and miscanthus pulps)[13,15,16] or 50% (for other annual plant pulps)[14] NaOH solution for 1 h at ambient temperature (about 20°C). The methylcellulose was synthesized from the mercerized pulp via double methylation with iodomethane in isopropanol for 22 h at 60°C.[13–16] The degree of substitution was determined by ^{13}C nuclear magnetic resonance (NMR). The water-soluble methylcellulose content was measured by dialysis or water extraction.[13–16] Each synthesized crude methylcellulose was a mixture of the water-soluble methylcellulose, the alkali-soluble methylcellulose, the trace unreacted cellulose, and the trace salts produced by acid neutralization.[13–16] The crude methylcellulose can be easily purified by washing with organic solvents to eliminate inorganic chemicals and by-products,[13–16] and by washing with hot water above the gelation temperature to obtain pure methylcelluloses.[2]

All chemical reagents were bought from the Sigma-Aldrich Company (Madrid, Spain) as reagent grades. These reagents were used without pretreatment.

Determination of the molecular weights

The apparatus of the size exclusion chromatography (SEC) combined with the high performance liquid chromatography (HPLC) was an Agilent 1100 series, which consisted of the G1311a quaternary pump, the G1322a degasser, the G1313a autosampler, the refractive index detector, and the G1316a column thermostat. The Agilent chemstation software for the LC and LC/MC system was used to control the HPLC apparatus. The SEC data were analyzed with the Agilent SEC data analysis software.

Solutions for chromatographic analyses were prepared quantitatively by distilled water extraction. The concentration of solution of water-soluble methylcellulose had to be in the range 0.2–0.4% and this was ensured by weighing a certain amount of methylcellulose on an electric balance. The amount of methylcellulose was calculated according to the water-soluble methylcellulose content of each synthesized methylcellulose sample in Table I. The weighed methylcellulose was then transferred into a 10-mL glass vial and 9 mL distilled water was added. The solution was stirred for 2 h at room temperature (about 20°C) and then the vial was placed in a refrigerator at 4°C and stored for 24 h. After this time, the vial was taken out of the refrigerator and the solution was stirred for another 2 h at room temperature (at 20°C). The suspended solution in the vial was centrifuged at 4000 rpm for 30 min. The upper clear liquid was removed with a syringe and filtered using a nylon membrane syringe filter of 13 mm $\wp$ with a diameter pore 0.2 μm. The filtered solution was injected into a 1.5-mL HPLC sample vial for SEC analysis.

A modified SEC condition was used.[5] The eluant was 0.05*M* NaCl solution, which was prepared with

TABLE I
Some Properties of Crude Methylcelluloses[13,16]

Material	Methylcellulose (MC)	Water-soluble MC content (%)	DS at C2	DS at C3	DS at C6	Total DS
Cardoon 1	MD27	66.83	—	—	—	—
Cardoon 2	MD28	81.52	—	—	—	—
Cardoon 3	M020	62.59	0.41	0.25	0.34	1.00
Cardoon 4	MD30	27.02	0.47	0.44	0.42	1.33
Cardoon 5	MD31	15.20	0.38	0.15	0.12	0.65
Cardoon 6	MD32	7.10	0.37	0.12	0.10	0.59
Cardoon 7	MD33	15.96	0.32	0.11	0.09	0.52
Cardoon 8	MD34	23.25	0.28	0.10	0.08	0.46
Eucalyptus 2	MD35	82.14	0.41	0.20	0.20	0.81
Eucalyptus 3	MD36	59.59	0.38	0.22	0.16	0.76
Eucalyptus 4	MD37	82.82	0.44	0.21	0.21	0.86
Eucalyptus 5	MD38	81.84	0.40	0.19	0.23	0.82
Eucalyptus 6	MD39	83.49	0.53	0.28	0.26	1.07
α-cellulose	MD17	32.40	—	—	—	—
α-cellulose	MD15	39.88	0.48	0.32	0.25	1.05
α-cellulose	MD18	34.19	0.50	0.39	0.27	1.16
α-cellulose	MD21	71.89	0.52	0.36	0.29	1.17
α-cellulose	MD23	75.61	0.56	0.36	0.36	1.28
Miscanthus 1	MD25	22.1	0.20	0.09	0.17	0.46
Mscanthus 2	MD22	69.2	0.33	0.16	0.21	0.70
Miscanthus 3	MD24	84.1	0.40	0.34	0.32	1.06
Miscanthus 4	MD19	53.6	0.43	0.36	035	1.14
Miscanthus 4	MD26	93.4	0.67	0.38	0.47	1.52
Flax_non[a]	MD45	11.03	—	—	—	—
Hemp_non[a]	MD41	16.67	—	—	—	—
Sisal_non[a]	MD44	18.82	—	—	—	—
Abaca_non[a]	MD55	12.50	—	—	—	—
Jute_non[a]	MD42	18.48	—	—	—	—
Flax_pre[b]	MD58	56.52	0.65	0.36	0.43	1.45
Hemp_pre[b]	MD59	3.73	—	—	—	—
Sisal_pre[b]	MD46	7.41	—	—	—	—
Abaca_pre[b]	MD47	51.72	0.63	0.33	0.40	1.36
Jute_pre[b]	MD57	0.64	—	—	—	—
Abaca_water[c]	MD48	18.75	0.33	0.17	0.22	0.72
Abaca_l5[d]	MD54	14.63	0.37	0.18	0.25	0.80
Abaca_steam[e]	MD53	49.23	0.40	0.30	0.32	1.02

[a] Non-treated pulp.
[b] Preliminarily mercerized pulp.
[c] Water-soaked pulp.
[d] Mercerized pulp under a pressure of 15 bars.
[e] Steam-exploded pulp.

distilled water and filtered with an Albet® polytetrafluoroethylene (PTFE) membrane filter of 47 mm φ and a pore diameter of 0.2 μm. The eluant was degassed by an online degassing system, the G1322a degasser. The flow rate was 1 mL/min. The temperature of the G1316a column thermostat was set at 25°C. Samples were automatically injected using the G1313a autosampler. Two columns were used in series: a size exclusion chromatography column (Tosohaas, Tsk Gel G 3000 Pwxl, 7.8 mm id ×30 cm) and a guard column (Tosohaas, Tsk column guard Pwxl).

RESULTS AND DISCUSSION

Effect of the pulping conditions

Chemical pulping is a very important step in the production of dissolving pulps for cellulose derivatization.[19] The pulping eliminates most of the lignins and hemicelluloses, which reduces most impurities and increases the voids in the cellulose.[6,14,19] The chemical pulping further breaks up the aggregated fibrils and microfibrils, which increases the accessible surface for reagents to penetrate and react with the cellulose.[6,14,19] The present pulping process consisted of impregnation and steam pulping (or steam cooking).[13,15,16]

Effect of the impregnation conditions

The main impregnation parameters of spring cardoon are listed in Table II.[15] All the experiments on spring cardoon were carried out at the same pulping severity (2.96). The pulping severity, *p*-factor, was calculated by the following eq. (1)[21]:

TABLE II
Main Impregnation Parameters of Spring Cardoon Methylcelluloses

Methylcellulose	NaOH concentration (%)	Retention time (h)
MD27	20	2
MD28	30	1
MD20	30	1.5
MD30	30	2

$$P = \log(R_o) = \log\left(\int_0^t exp\left(\frac{T-100}{14.75}\right)dt\right) \quad (1)$$

R_0: the severity of steam pulping; T: reaction temperature, (°C); t: retention time, (min).

The molecular weights of water-soluble methylcelluloses are listed in Table III. MD27 and MD30 stalks had the same impregnation retention time while the MD27 stalk was impregnated at a lower concentration of NaOH solution. The MD30 had a lower M_w and DPw than MD27 had. A higher concentration of the impregnation NaOH solution led to a lower molecular weight of the methylcelluloses synthesized because the 30% NaOH solution degraded the cellulose more than the 20% NaOH solution during the impregnation.[6,19]

The MD28, MD20, and MD30 stalks were impregnated at the same concentration of NaOH solution but at increasing impregnation times. When the impregnation time was longer, the methylcellulose properties were better. Their M_w and DPw increased at longer impregnation retention times. This phenomenon can be explained by the mechanism of impregnation and methylation reaction.[13,16] When the stalk is impregnated for a longer time, more NaOH solution diffuses and penetrates into the inner capillaries and voids of the stalks, which is vital for the fibrillation and delignification of pulping.[13] After the pulping and bleaching, the accessibility of the pulp is better. In addition, more lignin is removed; more voids and capillaries are created; more aggregated microfibrils are separated. Thus, the reactivity of the pulp is better, which favors and facilitates the diffusion of the methylation reagent and NaOH solution in the bleached pulp. The methylation of the bleached pulp is a typical topochemical reaction[15,18] with the hindrance of not only residual lignins and hemicelluloses, but also the special physical morphology structures of bleached pulps.[6,15–18] At the beginning of the methylation, the chemicals rapidly diffuse and penetrate into the accessible amorphous region and the exterior part of the fibrils.[15–18] The lignin and hemicellulose, uncooked fibrils, and aggregated microfibrils restrict the comparatively slow diffusion and penetration of reagents into the inner part of the fibrils where further methylation can proceed.[15] Therefore, the surface of the fibers is converted, and the amorphous cellulose of the fiber is methylated. In the concentrated NaOH solution and in the topochemical methylation, the cellulose of the surface and the amorphous region are degraded much more than cellulose of the inner portion of fiber.[15] Therefore, the molecular weight was low when the impregnation time was short.[15] This meant that the impregnation effect was worse and that the molecular weights of synthesized methylcelluloses were low.[6,15]

TABLE III
Molecular Weights of Water-Soluble Methylcelluloses Prepared from Spring Cardoon

Methylcellulose	M_n[a]	M_w[b]	P_d[c]	DP_w[d]
MD28	8021	54,543	6.8	291
MD20	25,980	140,880	5.4	752
MD30	40,174	175,360	4.4	937
MD27	34,471	218340	6.3	1166

[a] Number–average molecular weight.
[b] Weight–average molecular weight.
[c] Polymolecularity.
[d] Weight–average degree of polymerization.

TABLE IV
Impregnation Conditions of Summer Cardoon Methylcelluloses

Methylcellulose	NaOH concentration (%)	Time (h)	Temperature (°C)
MD31	20	1	22
MD32	20	1	60
MD33	30	1	22
MD34	30	1	60

The impregnation conditions for the summer cardoon stalks were different from those of spring cardoon (see Table IV).[15] The molecular weights of summer cardoon methylcelluloses are listed in Table V. The molecular weights of the summer cardoon methylcelluloses were similar. When the impregnation solution was 30% NaOH, the MD33 and MD34 had almost the same molecular weights. This indicated that the temperature had little influence on the molec-

TABLE V
Molecular Weights of Water-Soluble Methylcelluloses Prepared from Summer Cardoon

Methylcellulose	M_n	M_w	P_d	DP_w
MD32	27,731	146,890	5.3	785
MD34	29,432	156,590	5.3	836
MD33	29,967	158,550	5.3	847
MD31	35,059	168,020	4.8	897

TABLE VI
Cooking Conditions of Miscanthus Methylcelluloses

Methylcellulose	Cooking time (min)	Temperature (°C)
MD25	4	180
MD22	8	180
MD24	15	180
MD19	26	180
MD26	26[a]	180

[a] Higher volume of iodomethane used in methylation.

TABLE VIII
Steam-Pulping Conditions of Eucalyptus Methylcelluloses

Methylcellulose	Reaction time (min)	Temperature (°C)	Pulping severity
MD36	8	180	3.26
MD35	16	180	3.56
MD37	24	180	3.74
MD38	16	190	3.85
MD39	24	190	4.03

ular weight when the stalk was impregnated in the 30% NaOH solution. When the impregnation solution was 20% NaOH, the molecular weight of the MD31 sample was higher than that of the MD32 sample, indicating that the temperature had some influence on the molecular weight when the stalk was impregnated in the 20% NaOH solution. Based on these data, the alkaline concentration and the temperature of impregnation had very little influence on the molecular weights of methylcelluloses prepared from summer cardoon stalks.

Effect of the cooking times

The cooking conditions of the miscanthus stalks are listed in Table VI.[16] The molecular weights of water-soluble miscanthus methylcelluloses are listed in Table VII. Their cooking times greatly influenced the molecular weights of the miscanthus methylcelluloses obtained. Shorter cooking times led to pulps with higher lignin and hemicellulose contents.[13,15,16] The shorter cooking times degraded the cellulose less and produced fewer voids and capillaries.[13] What is more, the micro-fibrils of pulps with shorter cooking times aggregated much more than those of the pulps with longer cooking times.[13,15,16] Therefore, pulps with low accessibilities and reactivities were produced using shorter cooking times. Because of the topochemical methylation mechanism,[15,17,18] the methylation was hindered by the shorter cooking time. On the other hand, when the cooking time was longer, the surfaces, voids, and capillaries of the pulps were much more accessible. In addition, the methylation reagents had more opportunity to diffuse and penetrate into the inner part of the fibers and react with the alkali cellulose.[15] Therefore, the molecular weights of methylcelluloses were higher when the cooking times were longer. However, too long a cooking time degraded the cellulose during the cooking.[22] Therefore, an optimum cooking time needed to be tested.

TABLE VII
Molecular Weights of Water-Soluble Methylcelluloses Prepared from Miscanthus

Methylcellulose	M_n	M_w	P_d	DP_w
MD25	7888	20,685	2.6	110
MD22	12,482	99,063	7.9	529
MD19	44,072	190,330	4.3	1017
MD24	33,524	205,960	6.1	1100
MD26	55,050	222,470	4.0	1188

When the cooking temperature was the same and the cooking time increased from 4 to 26 min, the molecular weights of water-soluble miscanthus methylcelluloses increased from 20,685 to 222,470. The MD25 sample, which was cooked for only 4 min, had a very low molecular weight and degree of polymerization. The MD24 and MD19 samples, which were cooked for 15 and 26 min, respectively, had similar molecular weights and degrees of polymerization. The MD26 sample was particularly interesting. It was synthesized with a greater amount of methylation reagent than the MD19 sample, although the two samples had the same cooking time, which indicated that the methylation condition had some influence on the molecular weight of water-soluble methylcelluloses.

The molecular weights of miscanthus methylcelluloses increased as the cooking time increased. Therefore, if the molecular weight of methylcelluloses was to be higher, the pulping severity also had to be higher. Since the MD26 sample had a degree of polymerization of 1188, the cooking and methylation conditions of MD26 might be optimum for the miscanthus stalks.

Effect of the cooking temperatures

The cooking conditions for the eucalyptus chips are listed in Table VIII.[15] The molecular weights of eucalyptus methylcelluloses are listed in Table IX. Although the cooking conditions for the eucalyptus chips were quite different, the molecular weights of the water-soluble methylcelluloses in four samples (MD35, MD36, MD37, and MD38) were almost the same.

The cooking times were the same for MD37 and MD39 pulps. The MD39 pulp was cooked at a higher temperature than the that of the MD37 pulp. The

TABLE IX
Molecular Weights of Water-Soluble Methylcellulose Prepared from Eucalyptus

Methylcellulose	M_n	M_w	P_d	DP_w
MD39	17,570	104,790	6.0	560
MD35	23,591	127,270	5.4	680
MD37	19,778	133,830	6.8	715
MD38	25,967	147,160	5.7	786
MD36	27,592	160,010	5.8	855

MD39 had a lower molecular weight than that of the MD37, which indicated that it had degraded much more than that of MD37 at a higher cooking temperature.

When the cooking time was the same for the MD35 and MD38 pulps, the MD38 sample was cooked at a higher temperature than that of the MD35. The MD35 had a lower molecular weight than MD38 because of the topochemical methylation mechanism.[17,18] Eucalyptus is a hardwood and its pulping severity is usually higher than that of annual plants.[15] A low cooking temperature or pulping severity leads to a low accessibility and reactivity of the pulps.[15] Therefore, the low accessibility and reactivity of the MD35 pulp restricted the synthesis of methylcellulose to having a higher molecular weight.[6]

When the cooking temperature was 190°C, MD38 had a higher molecular weight than MD39. This indicated that a longer cooking time led to a higher degradation. When the cooking temperature was 180°C, MD36 had a higher molecular weight than MD35 and MD37, which both had similar molecular weights even though the MD35 and MD37 pulps were cooked for 16 and 24 min, respectively. The cooking condition of MD36 may be the optimum and synthesized methylcellulose with a higher molecular weight than other cooking conditions did.

Effect of the pretreatments

The effects of the abaca pulp pretreatments were compared. The molecular weights of water-soluble abaca methylcelluloses are listed in Table X. When the abaca pulp was not pretreated, its molecular weight and degree of polymerization were the lowest, and its polymolecularity was the highest of the five methylcelluloses. Mercerization under pressure and the water soaking method improved and increased the molecular weights and degrees of polymerization. What is more, these two methods also reduced the polymolecularity. The preliminary mercerization degraded the abaca pulp and improved its accessibility and reactivity.[14] The effect of the preliminary mercerization was better than that of mercerization under pressure and water soaking. The steam explosion method was the best of these four preliminary treatment methods. It increased the molecular weight and degree of polymerization 144% more than the nonpreliminary treatment method.

Why did the molecular weights increase after different pretreatments? The pretreatments did not increase the molecular weights of cellulose; on the contrary, they usually degraded it.[4] For example, mercerization under pressure degraded the cellulose molecule and increased the uniform distribution of NaOH solution in the voids and capillaries of the abaca pulp.[6] The preliminary mercerization and the steam explosion also had similar degradation functions.[4,22] The pretreatments improved the molecular weight of water-soluble methylcelluloses because they increased the accessibility and reactivity of the abaca pulp.[14] When the accessibilities and reactivities of pulps were improved, the synthesized methylcelluloses had much better properties[6,14] (including higher molecular weights).

The increases of the molecular weights of the water-soluble methylcelluloses can be explained by the topochemical methylation mechanism of bleached pulp.[17,18] Firstly, the methylation reaction concentrates on the accessible region of the fiber, where the molecular weight of cellulose is degraded to be lower than that of the interior of fibers and cellulose crystals.[17,18] The methylation reagent cannot diffuse, penetrate, or reach the interior to react because of the lower accessibility.[6,17,18] Therefore, the methylation is limited to the surface and outside of the fibers and the synthesized methylcelluloses had a lower molecular weight without any pretreatments. Even the simplest water soaking had a great effect on the molecular weight of synthesized methylcellulose.[14]

TABLE X
Molecular Weights of Water-Soluble Methylcelluloses Prepared from Abaca Pulp

Methylcellulose	Preliminary treatments	M_n	M_w	P_d	DP_w
MD55	None	16,753	100,140	6.0	535
MD54	Mercerization under pressure	28,087	136,380	4.9	728
MD48	Water soaking	30,132	139,560	4.6	745
MD47	Preliminary mercerization	52,776	213,890	4.1	1142
MD53	Steam explosion	79,373	243,950	3.1	1303

TABLE XI
Molecular Weights of Water-Soluble Methylcelluloses Prepared from Cellulose

Methylcellulose	CH_3I/AHG[a]	M_n	M_w	P_d	DP_w
MD17	4.51	14,339	102,170	7.1	546
MD21	18.06	30,422	159,620	5.2	853
MD23	22.57	28,585	181,540	6.4	970
MD18	13.54	34,070	199,500	5.9	1066
MD15	9.03	42,884	220,340	5.1	1177

[a] Mole ratio of iodomethane and AHG (AHG stands for anhydroglucose).

Effect of the methylation conditions

α-Cellulose can be considered as pure cellulose having no lignin or hemicellulose adhered to the surface of elementary fibrils.[23] A bleached pulp is usually impure cellulose, with a certain amount of hemicellulose and lignin adhered to the surface of elementary fibrils.[23] Hemicellulose is an amorphous polysaccharide with a low degree of polymerization, but higher accessibility, and higher reactivity than the cellulose.[24] Hemicellulose and the coexisting lignin compete with the cellulose to be mercerized and methylated. The aggregated fibrils hinder the diffusion of chemical reagents onto the surface of interior cellulose fibrils.[6] Therefore, the bleached pulp has less accessibility and reactivity than the α-cellulose.[16]

The molecular weights of water-soluble methylcelluloses prepared from the α-cellulose (see Table XI) are controlled by the mechanism and kinetics of the methylation.[2,3,6] Because the synthesis of the MD17 sample used the lowest amount of chemical methylation reagent, the molecular weight of the MD17 sample was the lowest among these synthesized methylcelluloses. The methylation concentrates on the accessible surface of fibrils.[17,18] The surface cellulose of fibrils has more opportunity to be reacted and to be degraded in a concentrated NaOH solution.[17,18] Therefore, the molecular weight of MD17 methylcellulose was the lowest and the polymolecularity was the highest. When the mole ratio of iodomethane and anhydroglucose was higher and same quantity of alkali charge was used in the methylation, the iodomethane had more opportunity to diffuse and penetrate into the interior of fibrils. The alkaline solution has difficulty in diffusing and penetrating into the interior of fibrils.[17,18] Thus, the celluloses in interior fibrils usually have higher molecular weights in the methylation process. When the iodomethane reacts with the celluloses that have higher molecular weights, the synthesized methylcelluloses also have higher molecular weights. Therefore, water-soluble methylcelluloses of higher molecular weights and higher degrees of polymerization are synthesized because of more methylation reagents.

The MD15 had the highest molecular weight. The degree of substitution and water-soluble methylcellulose content of MD15 were lower than those of MD18, MD21 and MD23 were. This indicates that the reagent ratio of the MD15 was optimum for the molecular weight, but should be higher to improve the yield of water-soluble methylcellulose and the degree of substitution.[16]

Effect of the harvest time of the cardoon

Two different cardoon harvest times were compared: spring and summer. The molecular weights are listed in Table III and V. We used only the dry stalk from the summer harvest but the total biomass from the spring harvest, including the stalk, leaves, and capitula.[15] Therefore, the spring cardoon pulp had more impure components than did the summer cardoon pulp. The pulping severity of the summer cardoon, which was cooked at 170°C for 4 min, was lower than that of the spring cardoon, which was cooked at 180°C for 4 min.[15]

Because of the impure components and low pulping severity,[15] the methylation of the spring cardoon pulp was greatly influenced by the impregnation conditions. The methylation of the summer cardoon pulp, on the other hand, was influenced very little by the

TABLE XII
Molecular Weights of Water-Soluble Methylcelluloses Prepared from Pulps Without Pretreatments

Methylcellulose	Material	DP_v of pulp	M_n	M_w	P_d	DP_w
MD55	Abaca	1928	16,753	100,140	6.0	535
MD41	Hemp	948	17,438	112,400	6.4	600
MD42	Jute	1413	23,906	161,640	6.8	863
MD44	Sisal	998	14,171	167,180	11.8	893
MD45	Flax	1165	40,584	202,880	5.0	1084

TABLE XIII
Molecular Weights of Water-Soluble Methylcelluloses Prepared from Preliminarily Mercerized Pulps

Methylcellulose	Material	DP_v of pulp	M_n	M_w	P_d	DP_w
MD46	Sisal	998	16,642	134,700	8.1	719
MD59	Hemp	948	6075	142,210	23.4	760
MD57	Jute	1413	98,077	144,230	14.7	770
MD52	Flax	1165	32,469	206,310	6.4	1102
MD47	Abaca	1928	52,776	213,890	4.1	1142

impregnation conditions. Thus, the leaves and capitula of spring cardoon must be removed before the pulping so that the quality of pulp for synthesizing methylcelluloses can be improved.[15]

Although the spring cardoon was cooked at a higher pulping severity,[15] the methylcelluloses synthesized from its pulp had much higher molecular weights than those synthesized from summer cardoon pulp. This indicated that the pulping severity of the summer cardoon needed to be increased to improve the molecular weights of the synthesized methylcelluloses. A higher pulping severity of the summer cardoon improved the accessibility and reactivity of the pulp.[6,13,14] Therefore, the molecular weights of the methylcelluloses were also higher.

Effect of the species

Effect of the species on the M_w

Five ECF bleached pulp methylcelluloses of different molecular weights (see Table XII) were synthesized under the same methylation conditions.

The abaca pulp had the highest original degree of polymerization and the lowest molecular weight of water-soluble methylcellulose. This means that the accessibility and reactivity of the abaca pulp were lower than those of other pulps were.[14] The degrees of polymerization of hemp and abaca methylcelluloses were similar as were those of jute and sisal methylcelluloses. The flax methylcellulose had the highest molecular weight and the lowest polymolecularity. These data show that the reactivities and accessibilities of flax and sisal pulps were the highest of the five pulps.[14] The abaca pulp needed to be activated to improve the molecular weight of the synthesized methylcelluloses. The jute and hemp pulps also had low accessibilities and reactivities. The methylcellulose of sisal pulp had a polymolecularity of 11.8, which meant that one part of the pulp was highly degraded while another part was only slightly degraded. The flax pulp was the best material for producing higher molecular weight methylcellulose without pretreatment.

Effect of the species on the pretreatments

Table XIII shows the molecular weights of the methylcelluloses prepared from five pulps that had been treated by preliminary mercerization,[4] an effective method for improving the accessibility and reactivity of the abaca pulp. After this preliminary treatment, the molecular weights of abaca methylcellulose (MD47) and hemp methylcellulose (MD59) were higher, which demonstrated that higher accessibility and reactivity could help to increase the molecular weight of synthesized methylcelluloses.[6,14] The degree of polymerization of the flax methylcellulose (MD52) was similar to that of MD45, which was synthesized from flax pulp without preliminary mercerization. The sisal methylcellulose (MD46) and jute methylcellulose (MD57) had lower molecular weights than sisal and jute methylcelluloses synthesized by the conventional mercerization method without pretreatment. This indicated that preliminary mercerization could not be used with sisal or jute pulps to improve the molecular weights. Less severe pretreatments, such as water soaking and steam explosion, can be used to improve their accessibilities and reactivities.[14] The abaca and hemp pulps needed preliminary mercerization to improve the accessibilities and reactivities, which in turn improved the molecular weights of the methylcelluloses obtained. The flax pulp did not need preliminary mercerization because its accessibility and reactivity were sufficient for it to be methylated.[14] After the preliminary treatment, the polymolecularity of the hemp and jute methylcelluloses increased considerably, which showed that some of their pulp was considerably degraded while another portion was only slightly degraded during the synthesis.

CONCLUSIONS

The water-soluble methylcelluloses with intermediate molecular weights were prepared from juvenile eucalyptus and annual plants. The effect that the impregnation times, the impregnation temperatures, the alkali charge of impregnation, the cooking times, the pulping severity, the pretreatments, and the charge of methylation reagents have on the molecular weights of synthesized methylcelluloses depends on the species. The present research shows that the species is a decisive factor in the production of methylcellulose. However, the pulping, the cellulose pretreatments and the methylation conditions can adjust the molecular

weights of the synthesized methylcellulose. Therefore, the present research may be used to control and optimize the quality of methylcelluloses.

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