Preparations and Characterizations of Carboxymethylated Hydrophilic Macromolecular Composites Directly Derived from Weeds

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Abstract

Direct carboxymethylations for aliphatic hydroxyl groups in weeds such as Tall fescue (*Festuca arundinacea*, TF), Sweeping lovegrass (*Eragrostis curvula*, SL) and Canada goldenrod (*Solidago Canadensis*, CG) were carried out in 2-propanol / 30 % NaOH at 55 °C for 3.5 hrs. Under the typical conditions, carboxyletyleated TF (TF-CM), SL-CM and CG-CM were obtained at yields of 145%, 135% and 148% based on each dry weight of lignocellulosics, respectively. Although degrees of substitutions of these CM materials were only small values such as 0.08-0.11, almost all materials were easily dissolved into water. Structural features were investigated using FT-IR and UV-Vis. Viscosities of 1% (w/w) aqueous solutions or suspensions of CM derivatives were measured by vibrating viscometer under different temperatures and pH. Since there are differences on viscosities between TF and CG in spite of same degrees of substitution, properties were different due to different structures of plant tissues.

Key words: Lignocellulosics, Carboxymethylation, Weeds, Hydrophilic Composite

1. INTRODUCTION

Lignocellulose is well known as macromolecular composites in plant cell walls with lignin and carbohydrates such as cellulose and hemicellulose. This material is expected as circulating carbon resources with high recyclability based on both biodegradability and ability of regeneration through photosynthesis.

Lignocellulose has been utilized as essential materials for our lives such as fibers, ropes, roof materials and fuels since ancient periods. Within a few hundred years, chemical utilization of lignocellulose such as a paper pulp production has been discovered drastically. More recently, accumulated residue from both industrial and agricultural crops such as bagasse or empty fruit bunch of oil palm has been attracted as circulating organic materials because of crisis on depletion of fossil carbon resources. But it has been difficult to be utilized these raw materials as substitutions of petroleum or coals, because of low efficiency on transportation of these accumulation, which is one of the most important factors on the economic aspects on utilization as carbon resources. In addition, energy profit ratio (EPR), which is one of important indicators for values of resources, of these raw materials including lignocellulose is inferior to fossil carbon resources. For reasons mentioned above, it has been difficult to be utilized these accumulations of these herbal materials with both light weights and low energy densities as energy sources. Therefore, these materials should be utilized as raw materials for organic composites rather than as energy sources.

A weed is defined a natural herbal plant, which lives independent from human society. In general, there are only a few merits such as a raw material for medicines or for seasonal foods in local daily lives. Although these plants live in everywhere on the wet land space on the earth, only wild plants which live on the boundaries between nature and human society, such as on side spaces of traffic road, parks or public gardens can be utilized because of difficulty in harvest. Usually, these

plants produced negative influences on human activities. For example, wild animals and insects, which are often causes of traffic accidents, are usually invaded into road along the shade of these weeds. In addition, fire accidents along traffic roads and in the parks are also happened on dried weeds. Therefore, in a lot of cases in Japan, these wild plants are harvested at fixed intervals by local governments in order to keep a traffic safety and a clean environment. In almost all cases, the harvests activities are carried out by local offices using public budgets in Japan because several relating problems around these plans have been accepted as public risks, mentioned above. For example, Shobara city in Hiroshima prefecture in Japan, that is one of the typical local cities in Japan, has spent *ca.* 20 million yen per year in 2016 for harvesting wild plants living around public spaces or by the roadside. Though the harvests activities of these renewable raw materials are carried out every season, all plant materials were burned out as industrial wastes without any utilization. Since burning out of these lignocelluloses are both wastes of circulating materials by short-cut to CO₂ gas and wastes of public assets, these plant materials have been expected to be utilized.

Here, focusing on an EPR value of these harvests again, relatively high values are expected based on low costs of both conveyance and integration through public achievements. In fact, problems on material utilization of grass materials are these high costs based on low density compared to woody materials in both substances and energy. In addition, taking chemical utilization into considerations, grass materials have higher advantages than woody materials with rough lignocellulosic matrix in cell walls because of easy separation of components.

Carboxymethylation (CM reactions) is one of the most useful reactions on hydroxyl groups for derivations of hydrophilic macromolecules. These hydrophilic macromolecules based on cellulosic materials such as carboxymethylcellulose (CMC) have been attracted as

Fig. 1 Scheme for carboxymethylation of (a) cellulose and (b) lignin. This scheme shows that only a half of hydroxyl groups in cellulose are reacted in (a). R = H, Ar or alkyl groups.

industrial materials such as chemicals, food additives, molds, paints, adhesives. In general, high quality paper pulps from woods have been used as raw materials for CMC. In addition, CM reactions have also utilized as one of major techniques to increase hydrophilicity of hydrophobic macromolecules such as lignins. For example, carboxymethylated lignin materials have also been investigated to improve properties. CM reactions of lignophenols, which are designed phenolic native lignin derivatives, have been developed for medical reagents such as inhibitors for HIV or swelling hydrophilic gels [1-2]. For these reasons, chemical utilization of weeds live along traffic roads or in public spaces was tried through direct CM reactions for these lignocellulose without pulping process.

Recently, Chien *et al* has reported trials on fractionation of macromolecular compositions in Aspen (*Populus tremula*) and Norway spruce (*Picea abies*) through CM reactions [3]. Moreover, Ren *et al* reported detail spectroscopic analyses for CM derivatives of agricultural grass materials [3]. In addition, Ren *et al* also reported phenolic moieties in lignin precursors showed relatively low reactivity for CM reactions [4]. Therefore, investigation for physical properties of direct CM materials is required information of influences of phenolic hydroxyl groups.

In this study direct CM reactions for lignocellulosics in three weeds, Tall fescue (*Festuca arundinacea*), Sweeping lovegrass (*Eragrostis curvula*) and Canada golden rod (*Solidago canadensis*) and investigations on physical properties of resulting CM derivatives in aqueous solutions or water dispersions were carried out using vibration viscometer under different temperatures, pH and concentrations.

2. EXPERIMENTAL

2.1. Sampling of wild grass materials

Tall fescue (TF, *Festuca arundinacea*) was collected on July 14th 2014 at a field along prefectural road No.442 in Nanatsuka-cho (N:34.5°, E:132.6°), Shobara city, Hiroshima, Japan. And both Weeping lovegrass (WLG, *Eragrostis curvula*) and Canada golden rod (CG, *Solidago canadensis*) were also collected on November 12th 2014 at the same location. Only stems of these plants were well dried at r.t. and used for synthesis. These stems were cut and then were well crushed by Labomillcer (Osaka Rika Co, JAPAN). Resulting powders of lignocellulosics were separated using SUS mesh (250 μ m). The 60 mesh-passed samples were used for experiments.

2.2. Analysis for fundamental chemical compositions

To evaluate fundamental chemical compositions in stems of plants, several parameters were estimated following JIS standards in duplicate experiments. The parameters were corresponded to humidity, ash, cold water extraction, hot water extraction, extraction by 1% alkaline aq. solutions, extraction by ethanol-benzene(1:2, v:v) under reflux, amounts of holocellulose, lignin contents, α - and β -cellulosic moieties of these materials.

2.3. Synthesis of carboxymethylated lignocellulosics

CM reactions for grass materials were carried out following a typical procedure as below [3, 6-9]. Defatted powder (60 mesh passed) of lignocellulosics (1.0 g) was added into 100 mL three necked-round bottom flask, and then 15.0 mL of 2-propanol was poured and stirred well at room temperature. After 30 min stirring, 20.0 mL of 30 % NaOH was added. After a reaction mixture was heated up to 55°C, 100 mg (1.1 mmol) of monochloroacetic acid was gradually added within 30 min. After 3.5 hrs, the reaction mixture was washed out using 80% MeOH aq. Resulting precipitate was washed by 80 % MeOH aq using centrifugation (5 °C, 3 500 rpm, 20 min). After air drying and vacuum drying on P₂O₅, a sodium salt of CM derivative was obtained as a yellow powder. A yield of CM-Na was determined by the defatted powder. The adequate synthesis conditions were investigated under different conditions such as reaction temperatures (10°C, 40°C, 55°C), concentrations of NaOH (7.5%, 15% and 30%) and reaction times (5 min, 60 min and 120 min). In addition, a CM reaction for holocellulose of TF was also prepared through the same procedure.

2.4. Degree of substitution (DS)

A degree of substitution (DS) of a CM material was determined using a reverse titration. After a CM material was washed by MeOH with conc. HCl, carboxyl groups of TF-CM with acid form were titrated using 1.0 M NaOH with pH meter (F-21 pH meter with 9621C pH electrode, Horiba Co.). The DS value was calculated all materials as cellulose.

2.5. Viscosity of dispersions of CM derivatives.

Aqueous dispersions or solutions (1%, w./w.) of CM-materials including commercial CMC and CM holocellulose of TF were prepared and used for experiments. Measurements of viscosity were carried out using vibrating viscometer (VM-1A, YAMACO Co.) at 10, 25 and 40 °C. Viscosity (mPa s) was divided by density of solutions or dispersions.

3. RESULTS AND DISCUSSIONS

3.1. Chemical compositions of lignocellulosics

Chemical compositions of TF, WLG and CG were summarized in Table1. There were large differences in amounts of extractives and ash. On the contrary, it was found that there were only small differences in macromolecular contents, such as carbohydrates and lignin. In addition, amounts of α -cellulose, which composed of crystal form of cellulose, were almost same amounts. This result implied that macromolecules and their composites show similar properties such as solubility and viscosity. Due to these results, 60 mesh

Table1 Chemical compositions of weed materials

	Tall Fescue/%	Weeping Lovegrass/%	Canada Goldenrod/%
Humidity	8.1	7.8	7.8
Cold water extractives	15.8	3.5	0.7
Hot water extractives	27.7	6.0	6.1
1% NaOH extractives	48.6	39.5	27.0
EtOH-benzene extractives	11.2	0.8	0.8
Ash	4.7	1.5	1.2
Holocellulose	77.4	79.3	89.7
α -cellulose	44.1	40.3	43.0
β -cellulose	2.9	1.8	1.8
Total Lignin Contents	18.6	23.8	22.3
Acid soluble Lignin	1.5	1.5	3.3
Klason Lignin	17.1	22.3	19.0

Duplicate measurements were carried out for all experiments.

passed grass meals (particle size < 250 μm) of lignocellulosics after removal of extractives were used for synthesis. In addition, not only α -cellulose but both β - and γ - cellulose moieties were included in the materials, which including several hemicellulose such as xylan. As results of 1 % NaOH extraction showed, a part of hemicellulose was extracted and removed through hydrolysis under a mild alkaline condition. As GC has more abundant lignin contents for about 4% than TF, it was implied that it was hard to be isolated from lignocellulosic carbohydrates.

3.2. Characteristics and properties of CM derivatives

Results of direct CM reactions on TF, WLG and CG under different conditions were summarized in Table2. The reaction condition of Run1, which showed 143% yield, was a typical condition ([NaOH] = 20%, T = 55 $^{\circ}\text{C}$, t = 210 min). In a case of a glucoside monomeric part in cellulose with three free aliphatic hydroxyl groups (C2-OH, C3-OH and C6-OH), an ideal yield of CM derivatives with only one -OH group which was converted into a carboxymethyl group showed about 158% yield as sodium salts in calculation. Also, a monomeric part in a native lignin molecule has only one aliphatic hydroxyl groups such as C9-OH (C γ -OH) will be reacted because of only low amounts of -OH in native lignin and low reactivity of phenolic -OH for CM reactions [5]. In addition, based on Table1, there were 80% of carbohydrates and 20 % of lignin in TF

Table2 Reaction conditions and yields of carboxymethylation for Tall fescue, Weeping lovegrass and Canada goldenrod materials.

Run	NaOH / %	Temp. / $^{\circ}\text{C}$	Reaction Time / min	Yield ¹⁾ / %
1	30	55	210	143.2
2	30	5	210	89.2
3	30	25	210	150.2
4	30	40	210	159.3
5	7.5	55	210	83.0
6	15	55	210	83.5
7	30	55	60	158.5
8 ²⁾	30	55	210	153.3
9 ³⁾	30	55	210	155.1

¹⁾ Yields of vacuum-dried sodium salts of carboxymethylated materials.²⁾ CM-Weeping lovegrass, and ³⁾ CM-Canada goldenrod.

material. Based on these facts, 143% of yield is considered to be a proper value. Therefore, using direct CM reactions for TF, at most one aliphatic -OH in cellulose and C9-OH aliphatic -OH in lignocellulosics was reacted and converted into $-\text{COO}^- \text{Na}^+$. Interestingly, only a little decrease of yields has been observed through these processes. Although a part of hemicellulose was expected to be isolated from LC through this reaction as described in our purpose, almost all hemicellulose probably remained in TF-CM matrix. Therefore our first purpose of this reaction was quite broken. But, a resulting CM composite with almost whole components of lignocellulosics was obtained directly from wild grasses.

In order to determine adequate reaction conditions for synthesis of TF-CM materials, syntheses under different temperature (Run2-4), with different concentrations of NaOH (Run5-6) and with different reaction times (Run7) were carried out.

As shown in Table2 (run2), yield was down to 89.2% at 5 $^{\circ}\text{C}$ due to activation energy of CM reactions. But CM derivatives obtained at 25 $^{\circ}\text{C}$ (run3) and at 40 $^{\circ}\text{C}$ (run4) showed up to 150.2% and to 159.2% yield, respectively. That is, reaction temperature above 25 $^{\circ}\text{C}$ was required for synthesis of TF-CM. Remarkable influences were observed relatively low concentration of NaOH (7.5% and 15%) in Table2 (run5 and 6). Yields of TF-CM were only 83.0% and 83.5% under these conditions. Under these alkaline conditions, aliphatic -OH groups in both carbohydrates and lignin were not ionized sufficiently. But under these conditions, only phenolic -OH groups in lignins were changed to phenoxide ion forms for selective CM reactions of phenolic moieties in LC. In addition, a sufficient yield of TF-CM was obtained with reaction under the standard condition for 60 min (run7, Table2). Moreover, WLG (run8) and CG (run9) showed almost same yields as CM-TF materials. Interestingly, CG-TF which is *Asteraceae* with different plant tissues in stems showed almost same yield. This result implied that both *Gramineae* and *Asteraceae* have similar higher order structures of macromolecular matrix in cell walls.

As shown in Fig.2, there were remarkable changes in peaks around 1700 cm^{-1} which corresponded to both

Fig.2 FT-IR spectra for carboxymethylated Tall Fescue prepared under various conditions. (a) under the standard condition, 30% NaOH, 55 $^{\circ}\text{C}$, 3h, (b) 7.5% NaOH, (c) 15 % NaOH, (d) reaction for 1h, (e) 2 h, (f) 3.5 h, (g) reaction temperature at 5 $^{\circ}\text{C}$, (h) 25 $^{\circ}\text{C}$, (i) 40 $^{\circ}\text{C}$ and (j) carboxymethylated Canada Goldenrod prepared under the standard condition.

symmetric and asymmetric vibration modes of COO^- ions. In addition all spectra showed around 1100 cm^{-1}

(aliphatic ethers, stretching), 1500 cm^{-1} and 1600 cm^{-1} (aromatic ring, $\text{C}=\text{C}$ stretching). As derivatives of both carbohydrates and lignins were observed in these spectra, these results indicated grafting of CM groups on lignocellulosics were occurred. Though CM derivatives, which were prepared at 25 and 40°C , showed stable high yields (Table2, run 3 and run 4), only small peaks of COO^- were observed. Also, CM derivatives prepared with low concentrations of NaOH (Table2, run 5 and 6) showed low yields and only small COO^- peaks in FT-IR. Though WLG was expected to show same tendency as Tall fescue, FT-IR spectra implied insufficient reactions because Fig.2 (i) was similar to Fig.2 (b) and (c). In addition, Canada goldenrod showed similar spectrum to Fig.2 (d)-(f), sufficient CM reaction was expected to be occurred.

3.3. Measurements of viscosity

Although direct CM reactions for plants of the *Gramineae* into CM derivatives have been investigated for agricultural plants of the *Gramineae* materials [4, 8-10], dynamic mechanical properties were not investigated sufficiently. As shown in Table3, viscosities of 1% aqueous solution of CM derivatives prepared from wild grasses showed lower than a commercial CMC-Na and CM- α -cellulose of TF due to both lignin and lignocellulosic matrix. As shown in Table3, sufficient TF-CM which was prepared under $40\text{--}55^\circ\text{C}$, 30 % NaOH and 1-3 hrs reaction conditions showed good viscosities. Typical TF-CM showed around 7.0 mPa s of viscosity at 40°C , which value was similar to CM- α -cellulose of TF. Almost all CM materials also showed temperature dependences. Although there were only little differences in both yields and FT-IR spectra, both WLG-CM and CG-CM showed lower viscosity than TF-CM because of differences in structures of plant tissues. This result implied that varieties of herbal plants with different biological species showed slightly different properties in viscosity.

3.4. Charactersitics and properties of CG-CM

As mentioned above, CG-CM materials obtained with similar yield (155.1%) of TF-CM derivative (143.3%) with sufficient substitutions of carboxymethyl

Table3 Viscosity of 1% of aqueous dispersions of carboxymethylated Tall fescue and Canada goldenrod under different temperatures.

Run	Viscosity / mPa s		
	10°C	25°C	40°C
1	12.2	8.2	6.3
2	2.6	2.1	1.6
3	5.3	4.0	3.0
4	9.2	6.9	5.2
5	2.0	1.6	1.1
6	2.2	2.0	1.2
7	9.1	7.0	5.0
8	9.9	7.8	5.6
9 ¹⁾	----	6.8	6.4
10 ²⁾	5.7	3.8	2.8
11 ³⁾	12.0	8.0	6.1
12 ⁴⁾	37.0	23.6	19.2

1) Result of CM-Weeping lovegrass, 2) result of CM-Canada goldenrod materials, 3) CM-holocellulose of Tall fescue and 4) commercial CMC.

groups. In addition, degrees of substitution of both CG-CM and TF-CM were 0.08 and 0.11, respectively. Therefore similar properties of CG-CM and TF-CM were expected due to similarity on structural features. But both solubility to water and viscosity of aqueous dispersions were quite different (Table3). As ratio of viscosity at 5°C (TF/CG = 2.3) was slightly larger than at 40°C (TF/CG = 2.1), influences of inhibition on mobility was pointed out. These results indicated that CM reactions were mainly occurred on the surfaces of milled TF particles as Ren *et al* pointed out [5]. Based on these results, it was found that only information of chemical features was probably insufficient to be understood total properties of direct CM materials. Therefore mechanical properties such as both solubility and viscosity were also required to be understood these complicated composites. Moreover it was also important to distinguish species of wild plants for utilization of optimized applications.

4. CONCLUSION

CM reactions on weeds such as TF, CG and WLG have been succeeded directly without losing polymeric components. Although degrees of substitution of TF and CG were around 0.1, almost all components were dissolved or dispersed well in water. Therefore, these materials were able to be treated as hydrophilic macromolecular composites. Since viscosity of 1% aqueous solutions of CM derivatives showed dependences of both temperatures and pH, properties of these composites behaved as ionic and hydrophilic macromolecules. Moreover, there are differences in viscosity between TF and CG but with similar degree of substitutions. These results implied separation of mixtures of grass materials was required to be obtained particular property of each grass material.

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